

PHONON BOTTLENECK EFFECT AND PHOTON ABSORPTION IN SELF-ORDERED QUANTUM DOT INTERMEDIATE BAND SOLAR CELLS

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ABSTRACT: The purpose of this work is to study the so-called *phonon bottleneck effect*—the reduction in the efficiency of electron de-excitation via the emission of phonon(s)— and the *photon absorption fundamentals* in the quantum dot intermediate-band solar cell, which aims to exploit the absorption of sub-bandgap photons without degrading the cell voltage. This could be achieved by means of a self-ordered quantum dot superlattice that would create an electron intermediate band within the gap of the host material, which is sandwiched between two *n* and *p* conventional semiconductor emitters. When operating, the phonon bottleneck effect would keep the electron gasses in the conduction and intermediate bands completely separated and three electron gasses are allowed. The proper design of the QD superlattice aims to take advantage of the phonon bottleneck effect to become the radiative recombination dominant on the one hand, and to achieve strong photon absorption on the other.

Keywords: Fundamentals, High-Efficiency, PV Materials.

1 INTRODUCTION

Since quantum dots (QDs) mimic atoms, we have proposed them [1, 2, 3, 4, 5, 6] as a feasible way of putting the “intermediate band solar cell” (IBSC) concept [7, 8, 9, 10, 11, 12, 13, 14, 15, 16] into practise. A QD superlattice plays the role of the unusual light absorbing material shown in Figure 1(c): in addition to the absorption of higher-bandgap photons ($E > E_G$) such as that labelled (3), the two-step absorption of sub-bandgap photons (1) and (2) —via the “intermediate band” (IB) located within the semiconductor gap— generates extra electron-hole pairs. The enhanced photocurrent is extracted at the voltage corresponding to the separation between the quasi-Fermi levels for majority carriers in the *n* and *p* emitters that sandwich the array [9, 10]. What makes the operation of this cell different from the others is that it supports *three* electron gasses—that corresponding to the conduction band (CB), the IB, and the valence band (VB)—, which are described by their own quasi-Fermi levels, E_{FC} , E_{FI} , E_{FV} . In fact, keeping E_{FC} and E_{FI} separated is a very challenging goal. The so-called “phonon bottleneck effect” could assist us in this aim: by properly designing the QD size it is possible, in principle, to reduce the electron de-excitation severely via the emission of phonon(s) from the conduction to the intermediate band. This could make the radiative recombination between them become potentially dominant. In this work we explore both the phonon bottleneck effect and the photon absorption within the quantum dots.

2 PRELIMINARY CONCEPTS

As qualitatively shown in Figure 1 (a), one of these quantum dots is a nanostructure made up of a tiny island (typically ranging 10-20 nm in diameter) of a semiconductor material (called “dot material”) embedded in another semiconductor with a wider band-gap (“barrier material”). The variation in the conduction and valence bands between the dot and barrier materials produces *three-dimensional* confinement energy potentials (CP), U_e and U_h , for electrons and holes respectively, in all three directions in the space [17]. The dot size is so small

that carriers are almost completely *localised* within the dot [Figure 2] and *discrete* levels are formed. This is just one of the reasons that compels us to propose the use of quantum dots: the ability to create an intermediate level within the forbidden gap of the barrier semiconductor and control its energy value E_I [1–6]. Since the *density of states* (DOS) of carriers confined in a QD is ideally a delta function [see Figure 1 (b)], the intermediate state in the dot is separated from the CB and from the VB by means of sub-gaps (E_L and E_H , respectively) of *zero* density of states. The IB would ideally derive from the intermediate electron bound state in the ordered superlattice of dots [3] as illustrated in Figure 1 (c). By doping the QD superlattice at a rate of one donor impurity per QD, the IB may potentially be half filled with electrons [3], allowing both (1) and (2) transitions.

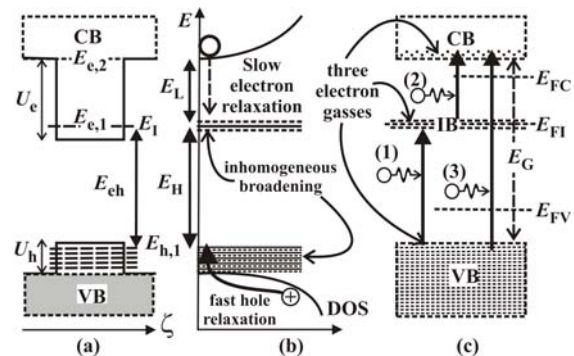


Figure 1. Band structure of a single QD along a line ζ crossing its centre. (b) Density of states (DOS) of the QD/barrier system, illustrating the slowed down electron relaxation. (c) As a result, three electron quasi-Fermi levels (E_{FC} , E_{FI} , E_{FV}) are expected to be had.

How can this proposed QD superlattice be manufactured? Self-assembled quantum dots (SAQDs) appear *spontaneously*, almost *without defects* during the *crystal growth* by means of metalorganic chemical vapour deposition (MOCVD) or molecular beam epitaxy (MBE) [18]. By using the proper growth conditions [17, 18] in the Stransky-Krastanow mode, it is possible to

create arrays and stacks of tiny dots (≈ 10 nm), *self-ordered*, with both high areal density ($>10^{11}$ cm $^{-2}$) and optical quality. *Self-ordered* quantum dot (SOQD) techniques are able to create a *three-dimensional quasi-crystal* made up of a high density of defect-free quantum dots where radiative recombination is dominant.

3 THE PHONON BOTTLENECK EFFECT

We have seen that a QD superlattice would create an IB energetically separated from the valence and conduction bands through sub-gap with zero DOS, this being one of the topics that the IB cell is based on. The other feature required is to have the three electron gasses shown in Figure 1, which will assist us in explaining this topic. In this regard, we are going to centre on the transition of one electron from an excited state in the CB-CP to the ground state (GS) of energy $E_{e,1}$. This is indeed an “intra-band” transition in the sense that it occurs between two states arising from a confinement potential in the same band, in this case, the CB. Figure 2 illustrates this particular, often confusing, terminology. This is the reason for which literature, mainly in the fields of QD laser and QD infrared photo-detectors, refers to it as a “relaxation process”, although, using our picture, this process can be considered as a “recombination” process between two completely separate energy bands.

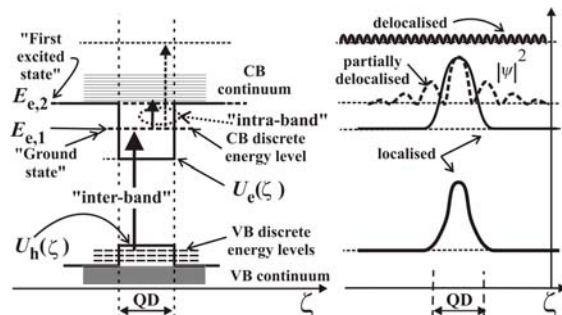


Figure 2. Sketch of electron transitions and the envelope wave functions involved within a QD.

If we look at one of the dots, the energy separation between the first excited and the ground levels, $E_{e,2} - E_{e,1}$, will be called “inter-sub-level separation”. As previously mentioned, the DOS in these levels is ideally a delta function. In this respect, the discrete nature of electron DOS in a QD could assist us in reaching the goal of reducing the electron “relaxation”. This is because this discrete character could greatly modify the carrier-phonon interaction when compared to that of the bulk material or even to that of quantum wells. It is worth mentioning that:

i) The emission of an LO phonon via Fröhlich interaction [18] is the dominant relaxation process in bulk semiconductors, quantum wells and quantum wires. Nevertheless it is forbidden in QDs unless the electron inter-sub-level separation in the QD matches the LO phonon energy $\hbar\omega_{LO}$, i.e., only if $E_{e,2} - E_{e,1} = \hbar\omega_{LO}$.

ii) Electron de-excitation through the emission of longitudinal-acoustic (LA) phonons in bulk material is weak when compared to that of the LO phonon

interaction and becomes even weaker with a decreasing dot size [18].

iii) Those electron relaxation processes involving more than one phonon, “multi-phonon” processes, are rather ineffectual [19]. In this reference, H. Jiang and J.Singh say that the electron relaxation via the emission of two LO phonons is inefficient as the inter-sub-level separation is

$$E_{e,2} - E_{e,1} > 3 \hbar\omega_{LO} \quad (1)$$

Relaxation processes that involve two LO phonons and one LA phonon give times larger than 1 ns. Other multi-phonon processes are even more suppressed [19].

Therefore, for InAs/GaAs QDs, the electron inter-sub-level de-excitation via the emission of phonon(s) is rather unlikely. This is because, by designing the dot size, $E_{e,2} - E_{e,1}$ may range 100-200 meV while $\hbar\omega_{LO} \approx 29.9$ meV (in bulk InAs) and 32.1 meV (in strained InAs QDs [20]).

This phenomenon, in which the electron relaxation/cooling dynamics in QDs is slowed down, is commonly known as the “phonon bottleneck” effect. There is, nevertheless, a certain controversy about whether this effect exists or not. One element of confusion is that, while some of the publications report on relatively long electron relaxation times (tens of ps) compared to that observed in bulk semiconductors, the results are reported as not being indicative of a phonon bottleneck because the relaxation times are not excessively long. However, as A.J. Nozik considers [21], the phonon bottleneck occurs if the relaxation time is longer than 10 ps, i.e. about one order of magnitude greater than that of bulk semiconductors (1 ps). The main aspects of the controversy are summarised below.

On the one hand, T. Inoshita suggests [22] that two-phonon processes, including LO and LA phonons, could be a mechanism for de-exciting electrons via the emission of phonons. A possible electron Auger de-excitation has also been reported [23] if the conduction band has a very high electron concentration.

But on the other hand, there are a number of works that suggest that the phonon bottleneck effect *does* exist. In a series of papers, M. Sugawara and K. Mukay [24, 25, 26, 27] have reported on a slow electron relaxation in self-assembled InGaAs QDs on GaAs substrates. They have reported relaxation times ranging 10 ps to 1 ns. This large electron lifetimes in the excited level indicates that the relaxation through phonon interaction has been greatly reduced or even suppressed. If the QD size is designed with a large inter-sub-level separation (say, for instance, larger than ≈ 100 -200 meV), it is potentially possible to de-couple the electron-phonon system, and thus the LO phonon relaxation mechanism can be suppressed. The reduced probability of electron relaxation via LA-phonon emission increases the relative importance of the competing relaxation mechanism via the emission of infrared photons, and causes this to become dominant.

4 PHOTON ABSORPTION WITHIN THE DOTS

The modelling of photon absorption in a conventional semiconductor, for instance GaAs, can be found in a number of references [28]. This absorption coefficient, that rules electron transitions between the VB

continuum and CB continuum, is well know. To model the other two kinds of absorptions, it is necessary to bring into play the most fundamental point of view explained in [28]. The system is divided into two sub-systems: first, the photon system, and second, the electron system that consists of a set of quantum states and their corresponding eigenvalues.

Let us first focus on the two electron gasses described respectively through the quasi-Fermi levels E_{F1} and E_{FV} . $|i\rangle$ represents an initial state of energy E_i in the valence band confinement potential (VB-CP), while $|f\rangle$ is the final state of energy E_f in the conduction band confinement potential (CB-CP). The corresponding absorption coefficient is

$$\alpha_{IV}^{QD}(E) = \frac{\hat{n}}{c} \sum_{i,f} \left\{ \frac{2\pi}{\hbar} \left| \langle f | H_{e-pt} | i \rangle_{inter} \right|^2 \delta[E - (E_f - E_i)] [f_V - f_I] \right\} \quad (2)$$

where \hat{n} is the refractive index, c the speed of light in vacuum, $\langle f | H_{e-pt} | i \rangle_{inter}$ is the matrix element of the transition, and

$$f_X = \frac{1}{1 + \exp\left(\frac{E - E_{FX}}{kT_C}\right)} \quad (3)$$

is, according to the Fermi-Dirac statistic, the probability of a state of energy E being occupied. E_{FX} represents the quasi-Fermi levels of the corresponding electron gas, and T_C the cell temperature.

Expression (2) physically means that α_{IV}^{QD} at a given photon energy, E , is created by collecting the individual contributions of all dots whose carrier spectrum fulfils $E_f - E_i = E$. Linking all quantum states in (2) to those created by the QD ensemble is not evident at first glance. For convenience, the states in (2) will be indexed by using the corresponding density of states (DOS), that is, the number of states per unit of volume and energy range, its units being [$eV^{-1} cm^{-3}$]. In this respect, for the sake of clarity, let us first imagine that only one quantum dot exists in the array and that it contains only one electron level and only one hole level. The separation between them will be labelled $E_f - E_i = E_{e1} - E_{h1} \equiv E_{eh}$ (see Figure 1(a)). Therefore, the corresponding electron density of states would be

$$g_{1QD}(E) = \frac{2}{U} \delta(E - E_{eh}), \quad (4)$$

U being the volume of the device in which the array of dots will be grown. We have included the factor 2 because, taking spin degeneracy into account, two quantum states are allowed for a given energy E .

If we now increase the complexity of the problem by growing a collection of N quantum dots inside the volume U , the density of states becomes

$$g_{QD-array}(E - E_{eh}) = 2 N_{QD} B_{in homo}(E - E_{eh}), \quad (5)$$

where $N_{QD} = N/U$ is the dot density, and

$$B_{in homo}(E - E_{eh}) = \frac{1}{\sqrt{2\pi\sigma_{in homo}^2}} \exp\left[-\frac{(E - E_{eh})^2}{2\sigma_{in homo}^2}\right] \quad (6)$$

is a Gaussian distribution [17, 18] whose expectation is E_{eh} and its variance $\sigma_{in homo}^2$.

By considering this DOS for the SAQD array, the

absorption coefficient in (2) can be expressed as

$$\alpha_{IV}^{QD}(E) = \frac{n}{c} \int_E \left\{ \frac{2\pi}{\hbar} \left| \langle f | H_{e-pt} | i \rangle_{inter} \right|^2 \times g_{QD-array}(\varepsilon - E_{eh}) [f_V(\varepsilon) - f_I(\varepsilon)] B_{homo}(E - \varepsilon) \right\} d\varepsilon \quad (7)$$

where the homogeneous broadening [17, 18], B_{homo} , has also been considered. This equation means that α_{IV}^{QD} at a given photon energy, E , is created by collecting the individual contributions of all dots within the homogeneous broadening around that energy. As the homogeneous broadening is very narrow, it can be approximated by a delta distribution [17] and hence

$$B_{homo}(E - \varepsilon) \rightarrow \delta(E - \varepsilon) \quad (8)$$

By inserting (8) into (7) and considering the transition matrix element between the CB and the VB edge states [24], then α_{IV}^{QD} becomes

$$\alpha_{IV}^{QD}(E) = \frac{2\pi e^2 \hbar N_{QD}}{c \hat{n} \varepsilon_0 m_0^2} \frac{\left| \langle u_C | \hat{e} \cdot \mathbf{P} | u_V \rangle \right|^2 \left| \langle \psi_e | \psi_h \rangle \right|^2}{E_{eh}} \frac{1}{\sqrt{2\pi\sigma_{in homo}^2}} \exp\left[-\frac{(E - E_{eh})^2}{2\sigma_{in homo}^2}\right] [f_V - f_I] \quad (9)$$

where ψ_e and ψ_h are the corresponding envelope function, m_0 the electron mass, and u_C and u_V the periodic part of the Bloch functions at the band edges.

Figure 3 represents Expression (9) (making use of the data collected in Table I. Its great value ($\approx 1.2 \times 10^5 cm^{-1}$) is because of: a) the high density of states at $E = E_{eh}$, and b) the matrix element $\langle \psi_e | \psi_h \rangle \approx 1$ since the electron and hole are very localised within the dot [Figure 2].

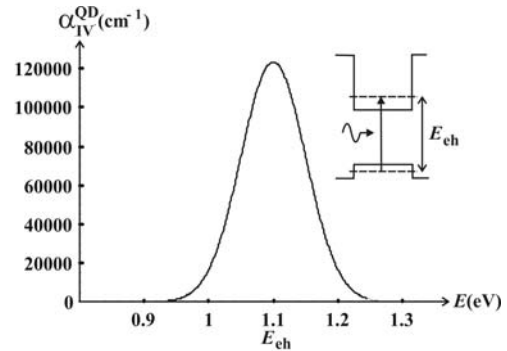


Figure 3. Absorption coefficient ruling transitions from the VB to the IB. A superlattice of InAs QDs embedded in a matrix of GaAs has been assumed. The inset shows a single QD and the corresponding transition. E_{eh} is the separation between the electron and hole confined within the QD. The numerical values used in this calculation have been listed in Table I.

As previously mentioned, the second absorption process in the QD-IBSC consists of the inter-sub-level transitions from the electron ground state (GS) up to a CB state in the continuum or in the quasi-continuum. In this respect, let us consider the electron gasses in the IB and in the CB, these gasses being described by the quasi-Fermi levels E_{F1} and E_{FC} , respectively. Now $|i\rangle$

represents the initial electron GS of energy E_{e1} , and $|f\rangle$ is the final state of energy E_{e2} (in the dot or in the quasi-continuum). Following similar considerations as α_{IV}^{QD} , the corresponding absorption coefficient is given by

$$\alpha_{Cl}^{QD}(E) = \frac{2\pi e^2 \hbar N_{QD}}{c \hat{n} \epsilon_0 m_0^2} \frac{|\langle \psi_{e,2} | \hat{e} \cdot \mathbf{P} | \psi_{e,1} \rangle|^2 |\langle u_C | u_C \rangle|^2}{E_{21}} \frac{1}{\sqrt{2\pi} \sigma_{inhomo}} \exp\left[-\frac{(E - E_{2,1})^2}{2\sigma_{inhomo}^2}\right] [f_1(E) - f_C(E)] \quad (10)$$

Table I. Parameters used in Figure 3.

<p>Roosbroek-Schockley-like relationships [5]:</p> $\frac{1}{\tau} \equiv \frac{1}{p_0} \frac{8\pi}{h^3 c^2} \int \alpha_{IV}^{QD}(E) E^2 \exp\left(-\frac{E}{kT_C}\right) dE$
<p>$\sigma_{inhomo} = 50$ meV; $\tau = 100$ ps; $N_{QD} = 10^{18}$ cm$^{-3}$; $E_{eh} = 1.1$ eV; $T_C = 300$ K</p>

5 SUMMARY

Phonon bottleneck effect may assist in the challenging goal of separating E_{FC} and E_{FI} effectively. By properly designing the QD size it is possible, in principle, to reduce the electron de-excitation severely via the emission of phonon(s) from the CB to the IB. Therefore, although difficult to achieve, we expect the IB to be sufficiently separated from the CB to make the radiative recombination between them become potentially dominant, and to keep the two electron gases completely separated. The recombination between electrons and holes confined to a quantum dot can be predominately radiative due to their high wave function overlap integral once selection rules allow it. The absorption coefficients involving states in the IB have also been modelled.

ACKNOWLEDGEMENTS

This work has been supported by the European Commission through the funding of the project FULLSPECTRUM (Ref. N: SES6-CT-2003-502620). L. Cuadra and N. Lopez are indebted to Comunidad de Madrid and Universidad Polit cnica de Madrid for their financial support.

REFERENCES

- [1] A. Mart , L. Cuadra and A. Luque, *Proc. of the 28th Photovoltaics Specialist Conference*, IEEE New York, pp. 940–943, 2000.
- [2] A. Mart , L. Cuadra and A. Luque, *IEEE Transactions on Electron Devices*, vol. 48, no. 10, pp. 2394–2399, 2001.
- [3] A. Mart , L. Cuadra and A. Luque, in *Photovoltaics for the 21st Century, Proc of the 199th Electrochemical Society Meeting*, The Electrochemical Society, Pennington, 2001, pp. 46–60.
- [4] A. Mart , L. Cuadra and A. Luque, *PHYSICA E*, vol. 14, pp. 150–157, 2002.
- [5] A. Mart , L. Cuadra and A. Luque, *IEEE Transactions on Electron Devices*, Vol. 49, No. 9, pp. 1632–1639, 2002.

- [6] L. Cuadra, A. Mart , A. Luque, C. R. Stanley, Andrew McKee, *Proc. of the 17th European Photovoltaic Solar Energy Conference*, Munich, James&James, London, pp. 98–101, 2001.

- [7] A. Luque and A. Mart , *Physical Review Letters*, vol. 78, no. 26, pp. 5014–5017, 1997.

- [8] L. Cuadra, A. Mart , A. Luque, *Proceedings of the 16th European Photovoltaic Solar Energy Conference and Exhibition*, Glasgow, pp. 15–21, 2000.

- [9] A. Luque, A. Mart , L. Cuadra, *Proc. of the 16th European Photovoltaic Solar Energy Conference and Exhibition*, Glasgow, 2000, pp. 59–62.

- [10] A. Luque and A. Mart , *Progress in Photovoltaics: Research and Applications*, vol. 9, no. 2, pp. 73–86, 2001.

- [11] A. Luque, A. Mart  and L. Cuadra, *IEEE Transactions on Electron Devices*, vol. 48, no. 9, pp. 2118–2124, 2001.

- [12] A. Luque, A. Mart  and L. Cuadra, *PHYSICA E*, vol. 14, no. 1–2, pp. 107–114, 2002.

- [13] A. Luque, A. Mart  and L. Cuadra, *IEEE Transactions on Electron Devices*, vol. 50, no.2, pp. 447–454, February 2003.

- [14] A. Luque, A. Mart , C. Stanley, N.L pez, L. Cuadra, D. Zhou, J. L. Pearson, A. McKee, To be published in *Journal of Applied Physics*.

- [15] L. Cuadra, A. Mart , N. L pez and A. Luque, *3rd World Conference on Photovoltaic Energy Conversion*, 2003, Osaka (Japan), (To be published).

- [16] L. Cuadra, A. Mart  and A. Luque, to be published in *IEEE Transactions on Electron Devices*, June 2004.

- [17] M. Sugawara (Editor), *Self-Assembled InGaAs/GaAs Quantum Dots*, Semiconductor and Semimetals, vol. 60, Academic Press, 1999.

- [18] D. Bimberg, M. Grundmann, N.N. Ledentsov, “Quantum Dot Heterostructures”, Ed. John Wiley & Sons, London, 1999.

- [19] H. Jiang and J. Singh, *IEEE Journal of Quantum Electronics*, vol. 34, no. 7, pp. 1188–1196, 1998.

- [20] M. Grundmann, O. Stier, and D. Bimberg, *Phys. Rev. B*, vol. 52, no. 16, pp. 11969–11981, 1995.

- [21] A.J. Nozik, in A. Mart  and A. Luque (Eds.), *Next Generation Photovoltaics: High Efficiency through Full Spectrum Utilization*, ISBN: 0750309059, Institute of Physics Publishing, 2003, pp. 196–222.

- [22] T. Inoshita and H. Sakaki, *Phys. Rev. B*, no. 46, pp. 7260.

- [23] U. Boklemann, W. Heller, A. Filoramo, and P. Roussignol, *Phys. Rev. B*, vol.55, pp. 4456, 1997.

- [24] M. Sugawara, K. Mukay, N. Ohtsuka, H. Shoji, and, *Applied Physics Letters*, **68**, 3013, 1996.

- [25] K. Mukay, N. Ohtsuka, H. Shoji, and M. Sugawara, *Applied Physics Letters*, **71**, 2791, 1997.

- [26] K. Mukay and M. Sugawara, *Japanese Journal of Applied Physics*, **37**, 5451, 1998.

- [27] K. Mukai and M. Sugawara, Chap 5 in *SELF-ASSEMBLED InGaAs/GaAs QUANTUM DOTS*, M. Sugawara. (Editor), Semiconductors and Semimetals **60**, Academic Press, San Diego, 1999.

- [28] S. Datta, *QUANTUM PHENOMENA*, Addison Wesley, 1989.