DEMONSTRATION AND ANALYSIS OF THE PHOTOCURRENT PRODUCED BY ABSORPTION OF TWO SUB-BANDGAP PHOTONS IN A QUANTUM DOT INTERMEDIATE BAND SOLAR CELL

E. Antolín*, A. Martí, P. G. Linares, E. Cánovas, D. Fuertes Marrón and A. Luque
Instituto de Energía Solar – ETSIT, Universidad Politécnica de Madrid, Ciudad Universitaria sn, 28040 Madrid, Spain
*Phone: +34 914533549, FAX: +34 915446341, email: elisa@ies-def.upm.es

C. D. Farmer and C. R. Stanley
Department of Electronics and Electrical Engineering, University of Glasgow, Glasgow G12 8QQ, U.K.

ABSTRACT: In order to surpass the efficiency limit of single gap solar cells, intermediate band solar cells (IBSC) have to fulfill two requirements: the production of extra photocurrent by absorption of sub-bandgap photons in electronic transitions involving the intermediate band (IB) and the preservation of a high output voltage, not limited by the existence of this band. This work presents experimental evidence of the production of two different sub-bandgap photons in IBSC prototypes fabricated with InAs/GaAs QD material. The experiments were carried out at low temperatures using a specifically designed modulated photocurrent measurement set-up with two light beams. The results are analysed with the help of a simple equivalent circuit model. This analysis is also used to highlight the relevance of the two-photon mechanism demonstrated in the experiment. It is discussed that, although the absorption of sub-bandgap photons in one of the IB transitions and subsequent thermal escape of carriers is a sufficient mechanism to obtain a photocurrent enhancement, the absorption of sub-bandgap photons in both transitions involving the IB is a requisite for the voltage preservation in IBSCs.

Keywords: High Efficiency; Intermediate Band; Quantum Dots.

1 INTRODUCTION

It is well-known that the efficiency achievable by conventional solar cells is fundamentally limited by the impossibility of fully converting through a single bandgap transition the energy distributed in a continuous photon spectrum. Detailed balance calculations set 40.7% as the fundamental efficiency limit for single gap conversion, where photons of higher energy than the bandgap are not efficiently used and those with energy lower than that threshold are wasted. This limit can be surpassed by a photovoltaic device which combines different absorption thresholds, such as multi-junction solar cells, which are presently showing a rapid increase in efficiency records. The intermediate band solar cell (IBSC) constitutes an alternative concept for combining different absorption thresholds in one photovoltaic device, with an efficiency limit (63.2%) similar to that of a three-junction cell, but in a more compact design [1].

The high efficiency limit of the IBSC relies on the production of extra photocurrent by the simultaneous absorption of sub-bandgap photons in two different electronic transitions allowed by the existence of an intermediate band (IB). These two transitions constitute the two lower absorption thresholds that, added to the fundamental bandgap of the semiconductor, make the potential of this system equivalent to that of a three-junction cell. But in principle it is also possible to obtain extra photocurrent in an IBSC device using only one of the two low energy transitions. One of the objectives of this paper will be to analyze the consequences on the global performance of the IBSC of using only one sub-bandgap transition.

The design of an IBSC, as well as its implementation by means of quantum dot (QD) materials, have been described in previous works (see for instance [1, 2]). For that reason, here we will focus on the characteristics of state-of-the-art QD-IBSC prototypes in comparison to the IBSC theoretical model, rather than extending on the details of the model itself.

The IBSC design is based on the use of an IB material, characterized by the existence of an isolated electronic band between the conduction and valence bands (CB and VB, respectively). In the QD-IBSC used in this work, the IB is formed by the confined states introduced by an array of InAs QDs embedded in a GaAs matrix. The IB divides the main semiconductor bandgap \( E_a \) (in our case that of GaAs, 1.4 eV at room temperature) in two sub-bands, referred to as \( E_{Fe} \) (the smallest one, in our case that between IB and CB) and \( E_{FIB} \) (the complementary of the later, in our case between VB and IB). Thus, we have three possible optical transitions in the IB material, that we label \( T_{IC} \), \( T_{VB} \) and \( T_{CB} \) (transitions in which an electron is promoted from the VB to the CB, from the VB to the IB and from the IB to the CB, respectively). Through modulated doping of the QDs we semi-fill the IB with electrons, in order to enable the simultaneous occurrence of both \( T_{IC} \) and \( T_{CB} \). In other words, we locate the Fermi level under equilibrium conditions at the energy position of the IB.

In an IBSC the IB material is sandwiched between two emitters of conventional semiconductor of opposite doping, which in our cells are also made of GaAs. They act as selective contacts, pinning the quasi-Fermi levels of electrons \( (E_{Fe}) \) and holes \( (E_{Fh}) \) when the cell is in operation. Consequently, the output voltage of the cell, given by the separation between both quasi-Fermi levels, is preserved, i.e. it is only limited by \( E_a \). On the other hand, the IB is isolated from the contacts. While absorption of high energy photons in \( T_{VC} \) contributes directly to the photocurrent flow that takes place in the CB and VB, sub-bandgap photons contribute through a two-step mechanism: an electron-hole pair is created when two sub-bandgap photons are absorbed, one in \( T_{IC} \) and the other in \( T_{CB} \). The electronic population of the IB is described by a third quasi-Fermi level \( (E_{FIB}) \). At this point it must be remarked that the 'absorption of two photons' that will be discussed throughout the paper does not refer to the simultaneous absorption of two photons by a single electron in the IB, a rather unlikely three
particle collision mechanism. Thanks to the existence of
the three bands and the associated three quasi-Fermi
levels, the interchange of carriers between bands is
governed by analogous statistical laws as in a two-band
semiconductor.

![Diagram of IBSC](image)

**Fig. 1**: Two possible band diagrams for an IBSC when it
is short-circuited and illuminated only with sub-bandgap
photons. Light generation (g), thermal generation (g_th)
and recombination (r) processes are represented, as well
as the position of the quasi-Fermi
levels. In (a) the two light generation rates are equal, and
in (b) the light generation rate between VB and IB is
much higher than that between IB and CB.

The relative strength of the three transitions within
the IB material is a sensitive aspect of the IBSC design
that needs to be discussed in some detail. It is quite
intuitive that the efficiency of the device would sink if
part of the energy of the photons gets lost because they
are absorbed in a transition of energy lower than possible
(for instance, if photons with energy enough to be
absorbed in T_VC are absorbed in T_IC). The most certain
way to achieve optimal performance in an IBSC would
be then to ensure the selectivity of the absorption
coefficients (\(\alpha_{VC}, \alpha_{V} \) and \(\alpha_{C} \)) associated respectively to
T_VC, T_IC and T_VC. This implies that \(\alpha_{VC}\) should be zero in the
range where \(\alpha_{V}\) is non-zero (photo energies \(\geq E_{V} \)) and \(\alpha_{V}\)
should behave analogously with respect to \(\alpha_{VC}\).

It seems difficult to achieve such a complete selectivity
in a real IB material. A more feasible approach is to engineer an IB material with \(\alpha_{VC} \ll \alpha_{V} \ll \alpha_{C} \). It has been proven that this configuration would also
lead to optimal efficiencies [3], in particular when
assisted by light confinement techniques for the weaker
transitions [4]. In the QDs, the optical transition rates
depend on the dipole matrix and thereby on the
overlapping of the initial and final states involved [5].

This means that the confined-to-confined excitonic
transition \(T_{VC}\) is stronger than the confined-to-continuum
transition \(T_{IC}\). Therefore, the QD material fits well in the
\(\alpha_{VC} \ll \alpha_{V} \) model. The transition \(T_{VC}\) associated to the
fundamental bandgap is far less problematic in this
context. It is reasonably expected to be stronger than the
sub-bandgap ones because it is present in the barrier
material of the QD stack and also in the emitters, which
are much thicker in QD-IBSCs than the IB material.

Let us then forget for the moment the band-to-band
transition \(T_{VC}\) and focus on the transitions involving the
IB. Fig. 1 (a) and (b) show two possible resulting
situations when the cell is short-circuited and
illuminated only with sub-bandgap photons. In Fig. 1 (a)
the generation rates in \(T_{VC}\) and \(T_{VC}\) are equal, what can be
regarded as an optimal situation. Fig. 1 (b) represents the
case in which the generation rate associated to \(T_{VC}\) is
higher than that of \(T_{IC}\). This will be generally the case if the
IB is implemented with QDs and no light trapping
techniques are used. Fig. 1 (b) represents hence the state-
of-the-art situation in QD-IBSC prototypes. In this
situation \(E_{FB}\) can be higher than \(E_{CB}\). We have neglected a
possible split between \(E_{FB}\) and \(E_{FB}\), due to finite
mobility which is irrelevant for our discussion and would
be small in short-circuit.

The inverted position of \(E_{FB}\) and \(E_{FB}\) that we see in
Fig. 1 (b) will necessarily cause a reaction of the system
in order to re-establish the population equilibrium. In the
same way that in any solar cell a positive \(E_{FB} - E_{FB}\) split
implies the occurrence of recombination, here the
negative split between \(E_{FB}\) and \(E_{FB}\) will release thermal
generation between the corresponding bands, or as it is
commonly said when referring to QDs, thermal escape of
carriers from the dots to the CB will be induced.

2 QUANTUM EFFICIENCY EXPERIMENTAL
RESULTS AND EQUIVALENT CIRCUIT MODEL

The previous discussion on Fig. 1 (b) will help us to
understand the experimental results obtained to the date
in QD-IBSC prototypes. The structure and fabrication
details of all samples used in this study are very similar
to those described in recent works (see for instance [6]).
The IV' characteristics of QD-IBSC prototypes under
illumination have been also presented elsewhere [7].
Comparing these to those of GaAs reference samples
(samples grown under the same conditions and with the
same structure except for not containing the QD layers)
we find that they QD-IBSC do not produce significantly
more current than their GaAs counterparts.

The \(I_{SC}\) produced by different QD-IBSC prototypes
depends on the technological details of the QDs growth.
The general tendency is that, when very large dots are
grown (in order to lower the energy of the confined states
and obtain a wider \(E_{L} \)) the strain accumulation causes a
poor material quality in the emitter grown on top of the
QD stack. For this reason, the \(I_{SC}\) of those prototypes is
reduced, whereas QD-IBSC prototypes containing stacks of
moderate QDs achieve the same current levels of
GaAs cells. But in any case, the accumulation of strain in
the material always limits the number of QDs layers that
can be epitaxially grown. For instance, the samples used in this work contain 10 layers of dots. Thus, the incapability of present QD-IBSC samples to produce significantly more \( I_{SC} \) than single gap counterparts is not surprising. To analyze the contribution of the QDs to the photocurrent, more sensitive methods have to be applied. Fig. 2 shows a quantum efficiency (QE) measurement of the QD-IBSCs and here it can be clearly seen that the QDs do produce photocurrent from sub-bandgap photons. From the two absorption thresholds on the graph we can deduce that \( E_L \) has in our samples a value around 1 eV and \( E_C \), the complementary value of about 0.4 eV (actually closer to 0.3, or even 0.2 eV, if we take into account an undetermined VB offset inherent to InAs/GaAs QDs and/or the states introduced by the wetting layer).

**Fig. 2:** Room temperature QE of a QD-IBSC prototype and a GaAs reference cell.

We see a sub-bandgap photocurrent in Fig. 2, but from this experiment alone we cannot know its nature. To explain its occurrence, we could consider that the monochromatic photons are being absorbed in both IB transitions according to the IBSC model, but it may also be possible that this photocurrent is better described by the situation of Fig. 1 (b). In fact, it is also possible that through an impact ionization process the absorption of two photons causing transitions from the VB to the IB would lead also to the net generation of an electron-hole pair [10]. In this paper we will focus our discussion on the possibilities that base on light generation processes only, which are expected to be dominant in our system. It might be of interest to study in future works if impact ionization mechanisms make also a significant contribution to the sub-bandgap photocurrent in QD-IBSC prototypes.

Considering the photon energy involved, absorption in \( T_{VC} \) implies the transition from a confined state to a continuum state deep in the CB. As it was already mentioned, this kind of transition is far less probable than absorption in \( T_{VL} \), where both final and initial states are localized. Hence, we will assume that the great majority of the photons in this energy range are mainly absorbed in \( T_{VL} \) and that the photocurrent is produced through thermal escape from the IB to the CB.

The equivalent circuits represented in Fig. 3 can help us to analyze the QE results. Fig. 3 (a) shows the simplified equivalent circuit of an IBSC under general working conditions. To keep the argumentation straightforward, only simple generation and recombination mechanisms have been taken into account, disregarding Auger processes, shunt resistance, etc (a more complete circuit model can be found in [8]). The current generators labeled \( J_{L,X,Y} \) represent the photogeneration between bands \( X \) and \( Y \), while the diodes \( J_{OV} \) represent the recombination between the same bands. Starting from this circuit we can draw the equivalent circuit for our QE measurement in the sub-bandgap range. This is shown in Fig. 3 (b), where it has been assumed that the sub-bandgap photocurrent measured has no contribution of \( J_{VC} \). Since in a QE measurement the cell is short-circuited, \( J_{VC} \) is not conducting and can be neglected. Regarding the other two recombination diodes, their voltage biases have to compensate each other. This means that when we extract a photocurrent \( J_R \), \( J_{OV} \) is forward biased and \( J_{VC} \) is reverse biased with the same absolute voltage (\( V_{BE} = -V_C \)).

The analogy between the circuit model of Fig. 3 (b) and the band diagram of Fig. 1 (b) is straightforward: the negative quasi-Fermi split \( (E_{BM} - E_{B}) \) is represented in the model by the reverse bias of \( J_{VC} \) and the thermal generation between IB and CB corresponds to the inverse saturation current of that diode. Given the low value of \( E_L \), the saturation current can be very high at room temperature, not limiting our extraction of \( J_R \) for practical values of \( J_{VL} \) [9]. The split \( (E_{BM} - E_{B}) \), which determines the recombination rate between IB and VB,
has its circuit counterpart on the forward bias of $J_{0V}$.

If the short-circuit condition is removed, the extraction of sub-bandgap photocurrent through $J_{SCL}$, profiting from thermal escape, implies a voltage loss. From the previous argumentation we realize that it is possible to increase the photocurrent of the cell by means of thermal escape, but voltage preservation requires that the absorption of a second photon is feasible to promote electrons from the IB to the CB.

3 TWO-PHOTON ABSORPTION MEASUREMENT

Motivated by the preceding argumentation, we have developed an experimental set-up to test that absorption in $T_{e}$ does actually take place in QD-IBSCs even if its effect is not strong enough in present prototypes to boost the efficiency. To distinguish the contribution of $T_{o}$ and $T_{e}$ to the photocurrent, in our set-up the QD-IBSC is excited simultaneously with two light beams, one of them chopped. A hydrogen lamp coupled to a monochromator constitutes the primary light source. It provides a monochromatic photon flux that is used to pump electrons from the VB to the IB. The secondary beam comes from a resistive filament that produces light mainly in the IR range. It is filtered by a 350 μm thick GaSb wafer to ensure that no photons from that source with energy over ~0.7 eV reach the sample. This implies that the secondary source can only contribute to the $T_{e}$ transition.

The secondary beam is mechanically chopped at a low frequency and the QD-IBSC is connected to a low noise transresistance preamplifier. The preamplifier has two purposes: it biases the cell at 0 V and converts its photocurrent into a voltage signal. Finally, a lock-in amplifier locked at the chopping frequency measures the ac voltage signal induced by the secondary source. The response to the primary source is a dc photocurrent, analogous to the one measured in a QE experiment (Fig. 2) and it is not recorded by the lock-in.

When we apply this experimental procedure to our QD-IBSC prototypes, we do not extract ac signal at room temperature. But this does not necessarily imply that there is no absorption in the $T_{e}$ transition. This will become clear again with the help of the circuit model.

The photocurrent showed in Fig. 4 is a direct proof of the existence of non-zero $I_{SCL}$, which is directly associated to the generation of current due to transitions from the IB to the CB as we wanted to demonstrate. Let us now analyze, continuing with the circuit model, how the temperature decrease has enabled its extraction. The measured signal can be written as

$$I_x = \frac{J_{SCL}}{1 + \frac{g_{SCL}}{g_{AB}}}$$

(1)

Let us assume, to simplify the discussion, that $J_{SCL}$ and $J_{AB}$ can be modelled as ideal diodes and that the variation of the respective bandgaps with the temperature is negligible. In the low-frequency regime the conductances are independent of the frequency and take the form [11]

$$g_{SCL} = J_{SCL}^0 \frac{q}{kT} \exp(qV_{STM}/kT)$$

(2)

where $q$ and $k$ stand as usual for electron charge and Boltzmann constant, and $J_{SCL}^0$ represents the reverse saturation current of diode $J_{SCL}$. The reverse saturation current of an ideal diode is proportional to $(n_i)^2$, being $n_i$ the intrinsic concentration at that temperature. The proportionality factor is determined by the electrical properties of the carrier that contributes more to the current flow (in a p'n junction, for instance, it would be the holes). In $g_{SCL}$ this factor is determined by the properties of CB electrons, and in $g_{AB}$ by those of VB holes. As the dependence of these factors on the temperature, as well as the dependence of the effective densities of states, is not significantly different for both diodes, we can write

$$g_{SCL} \propto n_i^2 \exp \left( \frac{qE_g}{kT} \right) \exp \left( \frac{(E_g - E_L) - 2qV_{STM}}{kT} \right)$$

(3)

The first term in (3) comes from the saturation...
measured when the photon energy of the primary source is 1.6 eV). Although $J_L$ is very large over $E_g$, the majority of the photons are absorbed in $T_{CV}$ and the contribution to $J_{LV}$ is small. As the energy of those photons decreases, the possibility of not being absorbed in the emitter and reaching the dots is higher. It must be remembered though that even very energetic photons, which are completely absorbed near the surface of the device, can reach the dots and be reabsorbed by them through photon recycling.

The measurements showed in Figs. 5 and 6 agree with the circuit model of the QD-IBSC exposed. There is no signal $J_R$ if there is no absorption in $T_{LV}$ (the diodes are at 0V and $g_{OC}$ is much higher than $g_{IV}$ for any $T$). In the range of Fig. 5 where $J_{LV}$ is higher, the signal has already saturated at 40K, whereas in the range of lower $J_{LV}$ it has not (the 80K curve shows a different behaviour, but this is due to the low signal to noise ratio at that temperature, as it can be seen by comparison to the noise level curve). Regarding Fig. 6, comparison between curve (2) and (3) shows that $J_R$ is proportional to $J_{LV}$ for any value of $J_{LV}$, as predicted by eq. (1). When the intensity of the primary source is low, the induced

![Fig. 5: Dependence of the two-photon photocurrent on the primary source photon energy for different temperatures.](image)

![Fig. 6: Dependence of the two-photon photocurrent on the primary source photon energy for different primary and secondary light intensities. All measurement taken at 6K.](image)
$J_{LIV}$ and $V_{LIV}$ are small, and $J_R$ is very sensitive to their changes. That is the case of curve (5). But when $J_{LIV}$ is much higher, expression (3) becomes $\approx 1$ and $J_R$ almost saturates, as showed by curves (2) and (3).

5 CONCLUSIONS AND FUTURE PROSPECTS

The absorption of sub-bandgap photons in the transition between the IB and CB in QD-IBSC prototypes and subsequent production of photocurrent has been experimentally proven. Comparison with an equivalent circuit model shows that the experimental results are in agreement with the theoretical principles of the IBSC. It is concluded from this analysis that the addition of this transition between VB and IB produces photocurrent, but this photocurrent cannot be measured at room temperature for two reasons: first, the absorption between IB and CB is very small in present devices, and second, the escape of carriers from the IB to the CB is too high. Lowering the temperature of the device has removed the second impediment and enabled the extraction of this photocurrent.

Once it has been demonstrated that absorption in both sub-bandgap transitions and subsequent production of photocurrent does actually take place in QD-IBSCs, technological improvements have to be undertaken to promote this effect. From the results obtained to date, the main short-term goals seem to be: (a) to enhance the absorption in the sub-bandgap range (growing more QD layers and/or implementing IR light trapping techniques), (b) to optimize the dot size, in order to increase the bandgap between IB and CB and reduce the thermal escape and recombination between these bands, and (c) to improve the overall material quality, included the emitter grown on top of the dots. From a technological point of view, the achievement of these objectives is much related to the capability of controlling strain accumulation. At this respect, notable improvements have been recently attained. Hubbard et al. [12] have grown QD-IBSCs of excellent material quality through insertion of GaP strain-relief layers between QD layers. Using another strain-relief strategy, the substitution of GaAs by InP (substrate) and InGaAlAs (barrier material), Oshima et al. have grown stacks of 100 QD layers of high uniformity [13]. The goal would be then to apply such strategies to obtain QD-IBSCs with thicker stacks and dots of optimized size.

To optimize the dot size it must be taken into account that there is a trade-off between the position of the IB and the number of extra confined levels. If large dots are grown, the ground state is low, but a high number of levels would be introduced between IB and CB, adding new recombination paths and consequently lowering the efficiency. From the theoretical model it is expected that at high illumination intensities these recombination paths saturate and the direct transitions between bands dominate [14]. This means that at high light concentrations the effect of extra levels is minimized and the efficiencies expected for the IBSC of three isolated bands are recovered. The higher the concentration ratio, the higher the number of extra levels that can be tolerated. So, if a compromise between dot size and practical concentration ratios is found, it is expected that the strategy described before, together with the use of light concentration, lead to the improvement of QD-IBSC performances.

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7 REFERENCES