Three-Bandgap Absolute Quantum Efficiency in GaSb/GaAs Quantum Dot Intermediate Band Solar Cells

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Abstract — In this work we study type-II GaSb/GaAs quantum-dot intermediate band solar cells (IBSCs) by means of quantum efficiency (QE) measurements. We are able, for the first time, to measure an absolute QE which clearly reveals the three characteristic bandgaps of an IBSC: \( E_\text{H}, E_\text{L} \) and \( E_\text{D} \), for which we found the values 1.52, 1.02 and 0.49 eV, respectively, at 9 K. Under monochromatic illumination, QE at the energies \( E_\text{H} \) and \( E_\text{L} \) is \( 10^{-4} \) and \( 10^{-5} \), respectively. These low values are explained by the lack of efficient mechanisms of completing the second sub-bandgap transition when only monochromatic illumination is used. The addition of a secondary light source (\( E = 1.32 \) eV) during the measurements produces an increase in the measured QE at \( E_\text{L} \) of almost three orders of magnitude.

I. INTRODUCTION AND BACKGROUND

Intermediate band solar cells (IBSCs) are conceived to exceed the conversion efficiency of conventional solar cells by efficiently harvesting sub-bandgap photons [1]. As of yet, however, the increase in short-circuit current, \( J_{\text{SC}} \), in the fabricated prototypes is too small for the intended purpose and, in general, it is accompanied by a degradation of the open-circuit voltage, \( V_{\text{OC}} \), of the solar cell. In order to characterize the sub-bandgap absorption and its contribution to the photocurrent, spectral photocurrent (PC) or quantum efficiency (QE) measurements have been extensively carried out [2]. Both techniques are useful to reveal the absorption thresholds present in intermediate band (IB) materials (see Fig. 1a), and the occurrence of subsequent carrier extraction in IBSCs. However, while PC measurements are qualitative, in the sense that they merely indicate the capability of producing photocurrent, QE measurements are quantitative: they express the ratio of collected electrons per incident photon. This information is essential to evaluate the absorption properties of IB materials and to provide feedback on the design parameters of IBSCs.

IB materials exhibit two sub-bandgaps, \( E_{\text{H}} \) and \( E_{\text{L}} \), in addition to the fundamental bandgap \( E_{\text{G}} \), as depicted in Fig. 1a. During the past decade, the larger of the two sub-bandgaps (\( E_{\text{H}} \)) has been widely characterized on different QD materials by QE measurements [2-6]. Also, two-photon photocurrent measurements have revealed absorption for energies lower than \( E_{\text{H}} \) in different QD systems, although without revealing the value of \( E_{\text{L}} \) [7-10]. Only recently, the smaller sub-bandgap (\( E_{\text{L}} \)) has been revealed by PC or ΔQE measurements in IBSC prototypes using the InAs/AlGaAs [11], InGaAs/GaAs [12] and InAs/InGaP [13] QD systems as IB material. Also recently, QE measurements extending to energies below \( E_{\text{H}} \) have been reported for the GaSb/GaAs system [14]. However, the latter result did not extend enough to reveal the value of \( E_{\text{L}} \). Moreover, a second, supra-bandgap (\( E > E_{\text{L}} \)) light beam was needed in order for the QE to be measured. In this work we show and discuss absolute QE measurements of type-II GaSb/GaAs QD-IBSC prototypes, which reveal the three absorption bandgaps. We also demonstrate that the extremely low value of the QE for the valence band (VB)→IB transition (labeled 3 in Fig. 1b) is not due to a small absorption coefficient of the QD material but rather to the absence of an efficient mechanism of completing the IB→conduction band (CB) transition under monochromatic illumination.

![Diagram](image)

Fig. 1. Simplified band diagram of: a) a generic IB material; b) a type-II GaSb/GaAs QD. The three existing bandgaps (\( E_{\text{H}}, E_{\text{L}}, \) and \( E_{\text{D}} \)) are indicated in each case. The three possible electronic transitions (1, 2 and 3) between each pair of bands are indicated in b.

II. SAMPLE INFORMATION AND EXPERIMENTAL METHODS

We have fabricated GaAs-based QD-IBSC prototypes containing 10 layers of n-doped GaSb QDs. The samples were grown by molecular beam epitaxy (MBE) on heavily n-doped GaAs (100) substrates. GaSb QDs were grown via the Stranski-Krastanov growth mode with 2.3 ML nominal thickness of a GaSb layer on an Sb-terminated (2x8) surface reconstruction. The QD areal density is in the order of \( 10^{10} \) cm\(^{-2} \). All QD layers were immediately capped by a 30 nm GaAs layer, leading to a QD volumetric density of...
approximately $3 \cdot 10^{15}$ cm$^{-3}$ in the QD stack. Fig. 2a sketches the layer structure of the samples, in which the QD-stack is sandwiched between p and n GaAs emitters. The QD-stack is has n-graded (10$^{15}$–10$^{17}$ cm$^{-3}$) doping, similarly to previous reported devices [15]. The p-n junctions were fabricated into square solar cells of area 6.84 mm$^2$. All devices were mesa isolated, with ohmic metal contacts provided by Pd/Zn/Pd/Au and Ni/Ge/Au/Ti/Au for p-type and n-type GaAs, respectively, followed by rapid thermal annealing at 400°C. An anti-reflection coating of ZnS and MgF$_2$ was deposited on the top surface.

Fig 2b shows two cross-sectional TEM images of our samples. Fig 2b (top) shows the QD-stack region. Fig 2b (bottom) shows GaSb QDs of two consecutive layers. In Fig. 2b, zones rich in Sb appear darker than zones rich in As. A high density of closely spaced QDs is deduced from the image. Details of the structural properties of GaSb/GaAs QDs grown under these conditions are described in [16], where GaSb islands imaged by TEM are found to form ring-like clusters.

![TEM images](image)

**Fig. 2.** Sample information. a) Layer structure. b) TEM images showing the QD stack (top) and QDs in two consecutive layers (bottom).

For the external quantum efficiency (EQE) measurements of Fig. 3, light from a 100 W tungsten lamp was diffracted by a 1/4 m monochromator and directed onto the sample under test. Order sorting filters are set at the output of the monochromator to avoid undesired secondary diffracted orders to reach the sample. The sample is mounted in a closed-cycle helium cryostat. Conventional lock-in techniques were used to measure the current response to the incident light. For convenience in the next paragraphs we will refer to this experimental setup as “QE setup #1”.

For the EQE measurements of Fig. 5, the two-photon experimental setup sketched in Ref. [17] was used. For the two photon photocurrent (TPPC) measurements, samples were mounted on a closed-cycle He-cryostat. Two light sources could illuminate simultaneously the samples. The primary source, a 140 W SiC lamp, was chopped and directed into a three-grating 1/4 m monochromator. A set of IR long-pass optical filters was placed at the exit of the monochromator to minimise the impact of residual broadband and second-order light on the measurements. The secondary light source (which could be turned ON or OFF) was a 1.32-eV laser diode. Samples were connected to a low-noise transimpedance amplifier. This amplifier also served as the voltage source to bias the sample. The final signal detection was made using a lock-in amplifier to measure at the chopping frequency (23 Hz). All measurements were performed at zero voltage bias.

For converting the measured TPPC into two-photon quantum efficiency, $QE_{2\text{ph}}$, the spectral power density (SPD) of the primary beam impinging onto the sample, $SPD_{1\text{ph}}$, must be measured. For this, the following procedure was carried out: (1) Measure the QE of the samples, $QE_{\text{sample}}$, at 9 K in the range of detection of our calibrated Ge detector ($E > 0.7$ eV) using the QE setup #1. This step is standard in solar cell and photodetector laboratories and will not be detailed here. (2) From $QE_{\text{sample}}$ and $SPD_{1\text{ph}}$ is directly obtained through the TPPC measurements for the case of single-photon illumination (secondary light in OFF mode), $TPPC_{1\text{ph}}$. As it well known and used in conventional QE measurements, $SPD_{1\text{ph}}(E) \propto PPC_{1\text{ph}}(E)/QE_{\text{sample}}(E)$, valid for $E > 0.7$ eV. (3) Model the SiC lamp as a grey body. For this, we measured the temperature of the SiC lamp under working conditions, $T_{\text{SiC}}$, with a thermocouple. The emissivity of the SiC, $\varepsilon_{\text{SiC}}$, was measured by the lamp manufacturer and matches reasonable well with the values reported in Ref. [18]. (4) The spectrum emitted by the lamp, $S_{\text{SiC}}$, was modelled as a grey body at $T_{\text{SiC}}$ with emissivity $\varepsilon_{\text{SiC}}$. (5) The spectrum distribution reaching the sample, $S_{\text{sample}}$ is obtained by correcting $S_{\text{SiC}}$ with the combined optical efficiency of all the optical elements placed in between the SiC lamp and the sample (monochromator, filters, mirrors and lenses), $\eta_{\text{opt}}$: $S_{\text{sample}}(E) = S_{\text{SiC}}(E) * \eta_{\text{opt}}(E)$. The optical efficiencies were either measured or provided by the manufacturer. In the particular case of the monochromator, the efficiency of the diffraction gratings was provided by the manufacturer and, as for the reflection of the internal mirrors, the tabulated reflectivity of the appropriate metals was used. (6) The SPD reaching the sample, $SPD_{\text{sample}}$ can be directly obtained by scaling $S_{\text{sample}}$ to the measured $SPD_{\text{1ph}}$: $SPD_{\text{sample}}(E) = S_{\text{sample}}(E) * sf$, where $sf$ is the scaling factor. $SPD_{\text{sample}}$ is valid for the whole TPPC measurement energy range. Note that $SPD_{\text{sample}}$ should closely match $SPD_{1\text{ph}}$ for the energy range where $SPD_{\text{1ph}}$ is defined. This step is crucial and will determine if the modelling was successful. (7) Once the goodness of the modelling has been verified, the measured TPPC and $SPD_{\text{sample}}$ allow obtaining the QE in the whole measurement energy range, $QE_{\text{final}}$. (8) For each measurement, for the one-photon-only and the two-photon cases, $QE_{1\text{ph}} = QE_{\text{final}}$ and $QE_{2\text{ph}} = QE_{\text{final}}$, respectively.
The secondary light flux values plotted in the inset of Fig. 6 were measured using our samples as photodetector, since the QE$_{\text{sample}}$ at the energy of the secondary light source is known (step 1 of the previous procedure).

III. RESULTS AND DISCUSSION

Fig. 3 shows the EQE of our samples at different temperatures, ranging from room temperature (RT) to 20 K. Two absorption edges are identified, which correspond to $E_0$ and $E_\text{h}$ as defined in Fig. 1a. At 20 K, $E_0$ is found to be 1.52 eV, which corresponds to the GaAs bandgap. The sub-bandgap ($E < E_0$) EQE is attributed to the promotion of electrons from the potential well of the QDs to the CB of the GaAs barriers (transition 2 in Fig. 1b). As described in Fig. 1b, in our samples $E_\text{h}$ is the energy difference between the most confined electronic state in the potential well of the QD (the IB) and the minimum of the CB of the barrier. Resulting, probably, from inhomogeneity in the QD size and the presence of multiple hole confined states in the potential well, the sub-bandgap signature is broad and does not show an abrupt edge. Electroluminescence measurements, showed in Fig. 4, allow determining $E_\text{h} \approx 1.02$ eV at 9 K. The measured $E_\text{h}$ is within the range of prior reports (1.0–1.3 eV) [19-23], though in the low energy range.

![Fig. 3. EQE at different temperatures of the GaSb/GaAs samples. The inset illustrates the production of e-h pairs by photon absorption and thermal escape (red arrow) processes. The solid vertical line indicates the energy of the second photon used in the two-photon measurements showed in Fig. 5.](image)

At RT the supra-bandgap EQE is close to one, while the sub-bandgap EQE is much lower. In particular, close to $E_\text{h}$ $QE \approx 10^{-3}$. At low temperatures, the sub-bandgap EQE is reduced by approximately one order of magnitude. The dependence of the sub-bandgap EQE with temperature is illustrated in the inset of Fig. 3. In order for photocurrent to be produced in the device, holes confined in the QDs after the optical IB$\rightarrow$CB excitation of electrons must escape the potential well. At RT the thermal activation of the required carrier escape is efficient and, therefore, the IB$\rightarrow$CB photogeneration is detected as photocurrent. This thermal process is hindered at very low temperatures. The fact that sub-bandgap EQE can still be detected at 20 K suggests the existence of other escape mechanisms, such as tunneling, and/or of a quasi-continuum of levels in the QD well or WL which allows efficient thermal escape even at such low temperatures [24].

Fig. 4 shows electroluminescence measurements at 9 K of our solar cells. The excitation current was approximately 0.2 A/cm$^2$. Measured points are represented by open circles. Two emission peaks are found at 1.02 and 1.15 eV, as resulted from Gaussian fitting (green dotted curves). The total fitted emission is represented by a black solid line. Emission at 1.02 eV is attributed to electron relaxation from the CB to the IB; therefore, it represents $E_\text{h}$. It must be noted that emission energy of GaSb/GaAs QDs is expected to increase with the third root of the of the excitation intensity [19-21]. Therefore, the measured $E_\text{h}$ in the electroluminescence measurements sets an upper limit for the value at the lower intensities used in the photocurrent measurements, where $E_\text{h}$ may be somewhat smaller. The emission at 1.15 eV, labelled $E_1$, cannot yet clearly be assigned to a particular transition. Similar values for $E_\text{h}$ and $E_1$ are reported in [20]. We believe that $E_1$ is too low to be assigned to transition in the thin wetting layer. In [16], multiple peaks in the photoluminescence spectrum of GaSb/GaAs QDs were attributed to different families of dots.

![Fig. 4. Electroluminescence of our GaSb/GaAs devices. Measured points are represented by open circles. The total fitted emission is represented by a black solid line. Two emission peaks are found at 1.02 and 1.15 eV, as resulted from Gaussian fitting (green dotted curves).](image)

Fig. 5 shows EQE measurements of our samples for longer wavelengths (smaller energies). Two types of measurements were performed, as described in Section II: the solid line shows EQE measurement under monochromatic illumination, EQE$_{\text{1ph}}$, while the discontinuous lines show two-photon EQE...
measurements, EQE_{2ph}. All the measurements were performed at 9 K. The measurements reveal two absorption thresholds, corresponding to $E_{L1}$ and $E_{L2}$. The EQE at energies lower than $E_{H}$ is attributed to transitions of holes confined in the potential well to the VB of the host material (labeled 3 in Fig. 1b). $E_{L}$ is, then, defined as the confining energy of the ground state for holes. We have measured $E_{L} \approx 0.49$ eV (see below and Fig. 6). This value of $E_{L}$ is somewhat higher than values reported in the literature [25, 26], with one exception [27]. The high value of $E_{L}$ is in agreement with the low value of $E_{H}$. Note that, as expected for our type-II QDs, which exhibit null CB offset [20, 21, 28, 29] (see Fig. 1b), $E_{L} + E_{H} \approx 1.51 \pm 0.01$ eV $\approx E_{G}$. To our knowledge, this is the first time that $E_{L}$ is identified in GaSb/GaAs QDs by means of photocurrent experiments. Our measurements reveal photon absorption extended from 0.4 μm to almost 3.5 μm.

For energies higher than $E_{H}$, the monochromatic and two-photon EQE results are very close. Although not noticeable in the logarithmic scale of Fig. 5, a subtle decrease in the two-photon EQE is found for high intensities of the secondary light. Let us now analyze the low-energy part of the graphs. Under monochromatic primary illumination only, holes are excited out of the potential well. However, for photocurrent to be produced, the new electron in the QD must promote to the CB, thus completing a new electron-hole (e-h) pair. Therefore, a second mechanism (whether it is of thermal, tunnel or impact ionization nature) must take place concurrently with the absorption of monochromatic photons. This phenomenon has been analyzed in [30] on the basis of a circuitual model. The IB$\rightarrow$CB escape mechanism is illustrated by a dashed blue arrow in the bottom-left inset of Fig. 5.

![Fig. 5. EQE of the GaSb/GaAs samples at T = 9 K. The solid line corresponds to monochromatic illumination. The discontinuous lines show two-photon measurements. The e-h pair generation is illustrated in the bottom-left (monochromatic) and top-right (two-photon) insets. The blue dashed arrow represents non-optical IB$\rightarrow$CB excitation of electrons.](image-url)

Note that, although nominally n-doped $10^{16}$ cm$^{-3}$ (see Fig. 2a), the electron population in the QD layers closer to the p-n junction is actually smaller. This is due to the fact that these layers are placed at the edge of the space charge region (SCR) of the junction. In fact, since the 150 nm lightly doped n-GaAs layer placed between the p-emitter and the QD stack does not completely accommodates the electrostatic potential drop at the junction, the SCR extends into the QD region depleting it of electrons. The lower electron concentration in the first QD layers allows for the presence of holes in the IB, which explains the absorption of low-energy photons causing IB$\rightarrow$VB hole excitation and the consequent finite EQE_{1ph}.

When the secondary light source ($E_{S} < E_{L}$ or $E_{G}$, see Fig. 3) is added, the EQE greatly increases. At this point we want to remind that only response to the chopped primary beam is detected by the lock-in amplifier. We explain the results as follows. The second photon beam on the one hand, pumps electrons from the IB to the CB thus completing the generation of an e-h pair, which enables the extraction of photocurrent. On the other hand, it increases the hole population in the IB, which results in an increased absorption of low-energy photons. The two-photon absorption process is illustrated in the top-right inset of Fig. 5.

This result has important implications: (1) It confirms the production of two-sub-bandgap-photon photocurrent in type-II QDs (previously demonstrated in [10]). (2) It shows that the low $E_{QE_{1ph}}$ at $E_{L}$ ($\approx 10^4$) under monochromatic illumination should not be interpreted only in terms of low absorption coefficient but rather as the absence of an efficient mechanism of completing the IB$\rightarrow$CB transition. Note that the fact that sub-bandgap QE requires a second photon is in perfect agreement with the ideal model of an IBSC, since this model states: (1) that photocurrent can be produced by absorption of two-sub-bandgap-energy photons, and (2) that electronic transitions between bands be of radiative nature only, so that energy conversion be maximized.

Fig. 6 shows the gain in QE ($G_{QE}$), calculated as $EQE_{2ph}/EQE_{1ph}$ as a function of the primary-light photon energy, for a particular intensity of the secondary-light beam. The curve is well described by a Gaussian function (red solid line). The curve indicates the energies at which the QE increases more with the secondary beam (IB$\rightarrow$CB electron transition), hence, revealing the absorption spectrum of the IB$\rightarrow$VB hole transition. By fitting $G_{QE}$ at different secondary-beam intensities, the value $E_{L} = 490 \pm 8$ meV is obtained. The peak of the fitted $G_{QE}$ indicates the QE increase at $E_{L}$. For the highest employed secondary-light intensity we have measured $G_{QE} \approx 700$ (see the inset in Fig. 6), for an $EQE_{2ph} \approx 10^5$.

The measured bandgap distribution at 9K of our IB material ($E_{G} = 1.52$ eV, $E_{G} = 1.02$ eV, $E_{L} = 0.49$ eV), albeit not optimal, is very appropriate for harvesting solar radiation in an IBSC. In fact, it can potentially achieve conversion efficiencies of approximately 60% [1]. Type-I QDs – which present a straddled band lineup – suffer from voltage losses due to the
existence of a finite VB offset [31]. Moreover, In(Ga)As/GaAs QDs – the most employed QD system in IBSCs – exhibit inappropriate bandgap distributions with undesirably low $E_1$ [32-34]. The type-II GaSb/GaAs QD system overcomes both problems. However, one big pending issue for realizing practical IBSCs, the low sub-bandgap absorptivity of IB materials [2], is not solved in these devices. Actually, the type-II transition in our QDs is predicted to have reduced absorption strength, since it is spatially indirect. Regardless, we observe very reasonable QE for this transition even at very low temperatures, at which thermal carrier escape should be hindered. A combination of increasing the number of QDs and light trapping has been suggested [35] to overcome the problem of low sub-bandgap absorptivity.

Fig.6. $G_{QB} (E_{QB}/E_{QB})$ at $T=9$ K. The red line is a Gaussian fitting. The inset shows the dependence of $G_{QB}$ at $E_k$ with the secondary-light intensity. The arrow in the inset indicates the point that corresponds to the displayed fitting.

IV. CONCLUSIONS
We have measured the first absolute QE which unambiguously reveals the three absorption bandgaps of an IBSC. In our GaSb/GaAs QD-IBSCs we have measured $E_0=1.52$ eV, $E_{II}=1.02$ eV and $E_L=0.49$ eV at 9 K. Under monochromatic illumination, $EQE$ is $10^4$ and $10^3$, at $E_{II}$ and $E_L$, respectively. We have shown that the low values of QE cannot be directly ascribed to low absorptivity. Regarding $E_0$, QE is enhanced by IB$\rightarrow$VB thermal escape of holes, which is reduced at low temperatures. Regarding $E_L$, the addition of a second photon ($E_{II} < E < E_L$) to the QE measurement produces an increase by up to a factor 700 in the measured QE, proving that the absorption strength of the IB$\rightarrow$VB hole transition is much greater than it is deduced from one-photon measurements.

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