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# Voltage limitation analysis in strain-balanced InAs/GaAsN quantum dot solar cells applied to the intermediate band concept



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## **ABSTRACT**

Several attempts have been carried out to manufacture intermediate band solar cells (IBSC) by means of quantum dot (QD) superlattices. This novel photovoltaic concept allows the collection of a wider range of the sunlight spectrum in order to provide higher cell photocurrent while maintaining the open-circuit voltage ( $V_{\text{OC}}$ ) of the cell. In this work, we analyze InAs/GaAsN QD-IBSCs. In these cells, the dilute nitrogen in the barrier plays an important role for the strain-balance (SB) of the QD layer region that would otherwise create dislocations under the effect of the accumulated strain. The introduction of GaAsN SB layers allows increasing the light absorption in the QD region by multi-stacking more than 100 QD layers. The photo-generated current density  $(J_L)$  versus  $V_{OC}$  was measured under varied concentrated light intensity and temperature. We found that the  $V_{OC}$  of the cell at 20 K is limited by the bandgap of the GaAsN barriers, which has important consequences regarding IBSC bandgap engineering that are also discussed in this work.

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## 1. Introduction

The intermediate band solar cell (IBSC) concept has been proposed as a means to achieve high efficiency photovoltaics [\[1,2\].](#page--1-0) The idea behind the concept relies on the use of an engineered material, known as intermediate band (IB) material, which hosts a collection of energy levels (the so-called IB) within the bandgap, i.e. between the valence band (VB) and the conduction band (CB). In an IBSC, the IB material has to be embedded between p- and nemitters in order to isolate the IB levels from the contacts. A sketch of the energy band diagram of such IBSC is shown in [Fig. 1.](#page-1-0) With respect to its operation, the IBSC has to fulfill two essential requirements: on the one hand, the generation of an extra current by means of the exploitation of sub-bandgap photons in a twostep absorption processes through the IB and, on the other hand, the preservation of the output voltage with respect to the material without IB. This second requirement can also be regarded as if the solar cell  $V_{\text{OC}}$  is exclusively limited by its fundamental bandgap  $(E_G)$  and not by any of the two sub-bandgaps, neither  $E_H$  nor  $E_L$ (see [Fig. 1\)](#page-1-0). Not fulfilling this voltage preservation would imply that the Shockley–Queisser efficiency limit cannot be surpassed

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<http://dx.doi.org/10.1016/j.solmat.2014.08.041> 0927-0248/© 2014 Elsevier B.V. All rights reserved. and such material should be rejected as IB material candidate. Both requirements have already been experimentally verified in quantum dots (QD) IBSCs. In this respect, sub-bandgap photocurrent  $(I_L)$  originated by two-step photon absorption has been reported in  $[3,4]$  while open-circuit voltage ( $V_{\text{OC}}$ ) not limited by any of the IB material sub-bandgaps has been reported in [5–[7\]](#page--1-0) at low temperature. In order to accomplish these principles, the IBSC concept demands some requirements such as, for example, that the IB is partially filled with electrons during operation but their discussion is out of the scope of this work [\[8,9\].](#page--1-0)

### 2. InAs/GaAsN quantum dot (QD) strain balance solar cells

One method for making IB materials is by stacking QD layers. QDs confine electrons in the three spatial directions causing the appearance of discrete energy levels that act as IB. InAs/GaAs QD technology has been widely used to implement IBSCs and has been the first one that has allowed verifying the two aforementioned operation principles. However, these self-assembled QDs provide weak sub-bandgap absorption and, subsequently low additional  $I_I$ . Several strategies have been proposed to counteract this lack of absorption, such as reducing the size of the dots [\[10\],](#page--1-0) using high-index substrates to order and pack the in-plane dots [\[11\]](#page--1-0) or employing metal nanoparticles [\[12\]](#page--1-0) or diffraction grid

<span id="page-1-0"></span>patterns [\[13\]](#page--1-0) as light trapping techniques. However, these techniques are still challenging to implement.

A straightforward approach to boost light absorption is to increase the number of QD layers. However, the practical implementation of multiple InAs/GaAs QD layers faces problems derived from the accumulation of strain. This strain is primarily caused by the large difference in lattice constant  $(a<sub>lc</sub>)$  between the barrier material, GaAs, and the QD material, InAs. Strain is transmitted vertically in the growth direction so that it increases throughout the successive QD layers until it is inelastically relaxed causing the formation of dislocations in the crystal structure [\[14\].](#page--1-0) Therefore, the maximum number of stacked QD layers that can be grown becomes limited unless strain balance (SB) is used. This consists of the use of a tensile-strained barrier material, characterized by a lattice constant  $a_{1c}$  smaller than that of the substrate. These tensile-strained barriers compensate the compressive strain of the QD layers leading to a zero overall in-plane stress [\[15,16\]](#page--1-0). The successive compressive-tensile strain components lead to a strain symmetrization where no strain is vertically accumulated. A simplified sketch explaining the SB technique applied to a InAs/ GaAs QD stack is shown in Fig. 2. Horizontal arrows indicate the compressive and tensile strains exerted in each layer. GaN and GaP are suitable strain-balancing materials for the InAs/GaAs QD system since in both cases their lattice constant is smaller than that of the GaAs. Therefore, both  $GaAs_{1-x}N_x$  or  $GaAs_{1-x}P_x$  alloys can be chosen as barrier materials for strain balancing. The first of them is studied in this work.



Fig. 1. Band diagram of an IBSC where the IB material is shown hosting a threeband system. The three existing sub-bandgaps are labeled as  $E_G$ ,  $E_H$  and  $E_L$  and the associated electronic transitions are indicated with arrows.

### 3. Experiments

InAs/GaAs<sub>1-x</sub>N<sub>x</sub> QD cells were fabricated at the University of Tokyo with  $x=0.01$  following the typical layer structure of an IBSC, i.e. sandwiching the stacked QD layers between p- and n-bulk emitters in order to isolate the intermediate levels from the contacts. Up to 25 InAs QD layers were grown using 20 nm thick intrinsic  $GaAs<sub>0.99</sub>N<sub>0.01</sub>$  spacers as SB material. Doping of the barrier or directly in the dots is commonly carried out in order to half-fill the IB with electrons [\[2,4\]](#page--1-0) and maximize below bandgap two photon absorption. However, in order to progress step by step with the study of this system and proceed with the study of voltage preservation first, QDs were intentionally undoped since doping is expected to have no impact on voltage preservation and the structure is simplified.

A GaAs control cell where the QD layers and the GaAsN spacers have been substituted by an intrinsic GaAs region was also prepared. Both QD and reference cells were grown on top of 001  $n<sup>+</sup>$  GaAs substrates, including a 1000 nm thick *n*-base, a 250 nm thick p-emitter, a 30 nm thick AlGaAs window layer and a highly doped contact layer. Neither anti-reflecting coating (ARC) nor back surface field (BSF) layers were included for simplicity. Both solar cells were metalized with a dense metal grid pattern that should allow low series resistance  $(r_s)$  for high current transport at low power loss. A sketch of the layer structure of the QD cell is represented in [Fig. 3](#page--1-0).

As stated by the band anticrossing (BAC) model [\[17,18\]](#page--1-0), some nitride dilute alloys abruptly split their CB in two bands as small amounts of nitrogen are incorporated. The energy edge of these bands,  $E_+(k)$ , is described by

$$
E_{\pm}(k) = 1/2 \left\{ \left[ E^{C}(k) + E^{N} \right] \pm \sqrt{[E^{C}(k) + E^{N}]^{2}} + 4V_{int}^{2} \lambda \right\}
$$
 (1)

[\[17\]](#page--1-0), where  $E^N$  is the position of the isoelectronic impurity  $(N)$ ] within the host compound,  $V_{int}$  is the interaction potential between the two bands,  $x$  is the variable representing the nitrogen content and  $E^{C}(k)$  is the CB dispersion of the non-nitrogen semiconductor. In our case,  $x=0.01$  implies a shrinkage of the GaAs<sub>1-x</sub>N<sub>x</sub> bandgap, when compared to GaAs, of  $\sim$ 200 meV. In fact, also the IBSC structure proposed in Ref. [\[19\]](#page--1-0) relies on the BAC effect splitting the CB of the host material in two  $(E_{-}$  and  $E_{+}$  with  $E_{\perp}$  playing the role of the CB). This split is believed to create a three-band configuration in GaAsN that allows collecting subbandgap energy photons through the VB $\rightarrow$ E<sub>-</sub> (E<sub>H</sub>) and E<sub>-</sub> $\rightarrow$ E<sub>+</sub>  $(E<sub>L</sub>)$  transitions. The viability of this IBSC structure will be later discussed in connection to the results obtained in this work.



Fig. 2. Sketch of the stacked InAs QD layers on GaAs substrate with (right) and without (left) strain compensation in the barrier. A bar on the right of each structure indicates the strain accumulated throughout the vertical axis.

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