APPLIED PHYSICS LETTERS **104**, 223903 (2014)

Analyzing carrier escape mechanisms in InAs/GaAs quantum dot p-*i*-n junction photovoltaic cells

D. G. Sellers,[1] S. Polly,[2] S. M. Hubbard,[2] and M. F. Doty[1]
[1]*Department of Materials Science and Engineering, University of Delaware, Newark, Delaware 19716, USA*
[2]*NanoPower Research Laboratory, Rochester Institute of Technology, Rochester, New York 14623, USA*

(Received 11 April 2014; accepted 21 May 2014; published online 2 June 2014)

Intermediate band solar cells (IBSCs) are third-generation photovoltaic (PV) devices that can harvest sub-bandgap photons normally not absorbed in a single-junction solar cell. Despite the large increase in total solar energy conversion efficiency predicted for IBSC devices, substantial challenges remain to realizing these efficiency gains in practical devices. We evaluate carrier escape mechanisms in an InAs/GaAs quantum dot intermediate band p-i-n junction PV device using photocurrent measurements under sub-bandgap illumination. We show that sub-bandgap photons generate photocurrent through a two-photon absorption process, but that carrier trapping and retrapping limit the overall photocurrent. The results identify a key obstacle that must be overcome in order to realize intermediate band devices that outperform single junction photovoltaic cells. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4881181]

Conventional single-junction photovoltaic devices are limited to harvesting no more than 31% of incident solar energy, as described by Shockley and Queisser.[1] In 1997, Luque and Marti proposed that an intermediate band solar cell (IBSC) could exceed the Shockley-Queisser limit by harvesting photons below the bandgap of the host single-junction solar cell.[2] In the ideal IBSC device, high-energy photons are harvested in the host cell while low-energy photons are harvested in an intermediate band region through a two step process. A first low-energy photon promotes a carrier from the bulk valence band (VB) to an intermediate state; a second low-energy photon promotes the carrier from the intermediate state to the bulk conduction band (CB). The additional carriers generated by these low-energy photons contribute additional current while allowing carriers to be extracted at the relatively large open circuit voltage of the host cell.

Numerous methods for implementing an IBSC device design have been proposed. The most common approach is based on InAs quantum dots (QDs) embedded in a III–V material platform, which provides extensive opportunity to tailor energy levels, strain profiles, and QD spacing to optimize device performance.[3,4] Despite the exciting potential, realization of IBSC devices that exceed the Shockley-Queisser limit has proven to be extremely challenging. Only recently was the absolute efficiency of an InAs/GaAs QD IBSC shown to outperform that of control devices.[5] Among the most significant challenges are the rapid relaxation of carriers into the intermediate states, which prohibits maintenance of a high open circuit voltage, and losses associated with carrier recombination in the QD.[5,6] Overcoming these challenges requires the design of materials and devices that suppress carrier loss and efficiently utilize solar energy to promote carriers into and out of intermediate states. In presently available devices under normal operating conditions, thermal escape and tunneling are believed to be the dominant pathways for carrier escape from intermediate states.[7–9] Understanding the competition between thermal, tunneling, and optically driven escape mechanisms is essential for the development of new devices that suppress loss pathways and improve device efficiency.

In this work, we investigate the escape of carriers from intermediate states in an InAs/GaAs IBSC device. The intermediate states arise from InAs QDs embedded in a GaAs p-i-n junction cell grown by metal-organic vapor phase epitaxy (MOVPE) using the Stranski-Krastanov (SK) growth mode. The band diagram for the InAs/GaAs p-i-n junction structure is schematically shown in Figure 1(a). A GaP strain balancing layer is included between each of the 10 InAs QD layers to offset the compressive stress introduced during SK growth of InAs QDs.[10] A more detailed explanation of sample growth and growth parameters is given in the supplementary material and prior publications.[11] Figure 1(b) shows the steady-state photoluminescence (PL) spectrum of the device measured at room temperature and under illumination by photons of 2.4 eV. The PL peak centered at 1.42 eV is attributed to recombination across the GaAs bandgap, and the peak centered at 1.35 eV is attributed to the InAs wetting layer. The lower-energy PL peaks (1.19 eV, 1.24 eV, and 1.29 eV) correspond to emission from excited states of the InAs QDs. The PL from the lowest-energy confined state of the InAs QDs has a FWHM of 0.062 eV (based on a Gaussian fit), suggesting that the QD states are localized to individual QDs and do not form a delocalized band.[6]

To selectively populate InAs QD states and isolate optically driven carrier escape mechanisms, we measure the device photocurrent under illumination with photons having energy below the GaAs bandgap. A diagram of our experimental setup is shown in Figure S1 of the supplementary material. A continuous wave diode laser at 1.17 eV was used to selectively excite the lowest-energy excitonic transition of the InAs QDs, creating a carrier population only within the QDs. Illumination with 0.80 eV photons was used to selectively promote carriers from the InAs states to higher-energy InAs QD or GaAs CB and VB states. We note that 0.80 eV photons do not have sufficient energy to excite carriers across the GaAs or InAs QD bandgaps and thus cannot change the number of carriers excited into intermediate states. Fluences for both excitation lasers (1.17 and 0.8 eV) ranged from 5 mW/cm^2 to 1.13 W/cm^2. These extremely

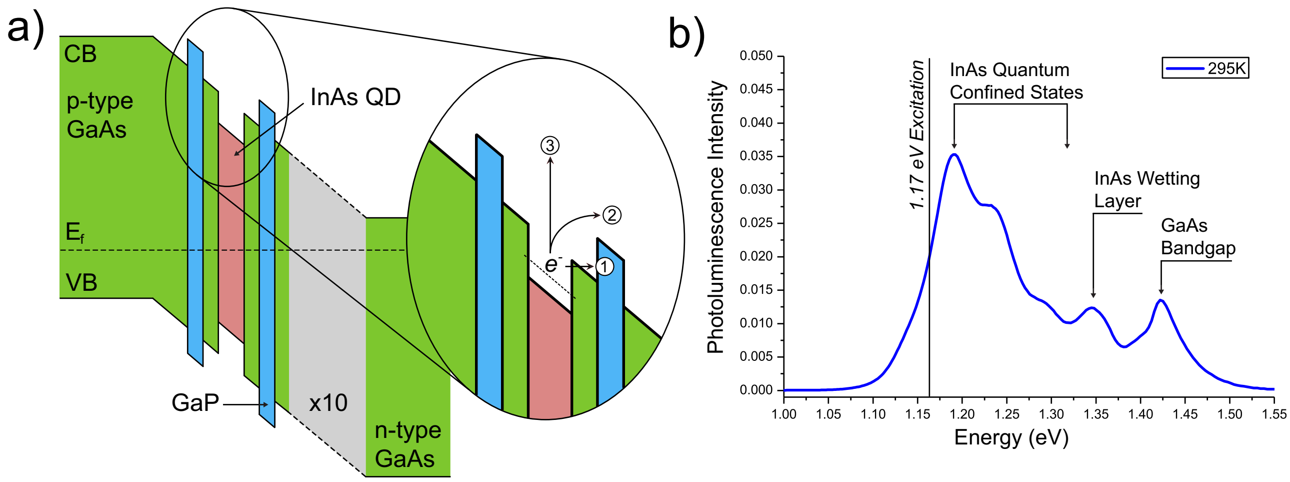

FIG. 1. (a) Schematic of the InAs/GaAs p-i-n junction solar cell device band gap structure. Inset: Shows the carrier escape pathways following InAs QD excitation (pathway 1 = tunneling escape, pathway 2 = thermal escape, and pathway 3 = optically driven escape). (b) Steady-state photoluminescence spectrum of the InAs/GaAs p-i-n junction solar cells (excitation wavelength = 2.4 eV, intensity = 37 W/cm^2).

high fluences are achieved by illuminating a small spot, approximately 2 mm in diameter, and thus the absolute photocurrent measured is quite low.

The inset to Figure 1(a) depicts the three competing mechanisms for carrier extraction from intermediate states: tunneling (pathway 1), thermal (pathway 2), and optically driven (pathway 3). The efficiency of carrier escape in InAs QD IBSC devices is typically quantified by measuring the device photocurrent with current-voltage (I-V) scans.[12–15] We have performed such scans, as described in the supplementary material. Under the high laser fluences used here sample heating leads to changes in the rate of thermal escape of carriers from the intermediates states, leading to photocurrent values that are dependent on illumination (heating) time. Our quantification of these effects is described in the supplementary material. We isolate the optically driven contributions to carrier escape by taking single-shot current readings under short-circuit conditions immediately upon exposure to the sub-bandgap illumination. We further enhance the optically driven contributions by using high excitation fluences; the maximum fluence used corresponds to approximately 80x AM1.5 solar concentration.[16] The measurement approach is described fully in the supplementary material.[17]

We first analyze the device photocurrent as a function of the fluence of the 1.17 eV photon source. Illumination with photons at this energy can generate carriers only in the QD region of the device. The carriers generated within the QDs can escape to produce photocurrent via any of the three pathways described above. Optically driven escape from the QD states would require the sequential absorption of two 1.17 eV photons. If this optically driven escape mechanism contributed significantly to the total photocurrent, we would expect to see a super-linear dependence of the photocurrent on the fluence of the 1.17 eV source. Figure 2 displays the device photocurrent as a function of the fluence of the 1.17 eV photon source (black symbols), obtained with single-shot photocurrent ($I_{1.17\,eV}$) measurements taken under short circuit conditions. The photocurrent increases linearly with laser fluence over the range of fluences studied. The linear increase suggests that thermal and tunneling escape mechanisms dominate any carrier escape driven optically by 1.17 eV photons. The data of Figure 2 establish that the total photocurrent is linearly proportional to the number of carriers excited into the QD states, which is in turn proportional to the fluence of the 1.17 eV source.

We selectively probe the optical escape pathway by adding illumination from a 0.8 eV photon source. Photons of energy 0.8 eV cannot excite carriers across the bandgap of the host material or the QDs, but they can excite carriers from the QDs states to the bulk conduction band. The red data points in Figure 2 show single-shot photocurrent measurements ($I_{1.17\,eV+0.80\,eV}$) taken as a function of 1.17 eV photon source fluence in the presence of 600 mW/cm^2 of 0.80 eV illumination. The addition of 0.8 eV photons results in an increase in photocurrent, shown most clearly in the inset. We use Δ_{opt} to describe the increased photocurrent due to the addition of 0.8 eV light. We note that sample illumination with only 0.8 eV photons resulted in no photocurrent, irrespective of illumination intensity.

To isolate the photophysics of the processes driven by 0.8 eV photons, we focus on the Δ_{opt} value. Figure 3 shows

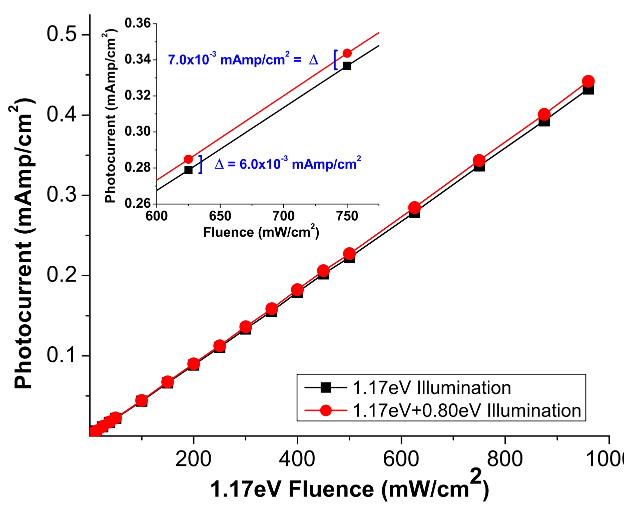

FIG. 2. Photocurrent as a function of 1.17 eV illumination fluence with and without the addition of 600 mW/cm^2 0.80 eV light. Inset: Expanded region displaying the change in photocurrent (Δ_{opt}) with the addition of 600 mW/cm^2 of 0.80 eV light.

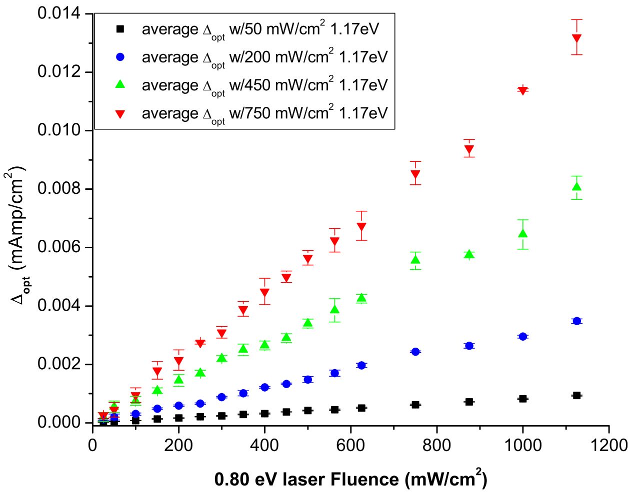

FIG. 3. Change in photocurrent with addition of 0.80 eV light to 1.17 eV illumination, Δ_{opt}, as a function of 0.80 eV intensity for fixed 1.17 eV intensities of 50 mW/cm^2, 200 mW/cm^2, 450 mW/cm^2, and 750 mW/cm^2.

Δ_{opt} as a function of 0.8 eV photon source fluence at four fixed fluences of 1.17 eV illumination. Because only 1.17 eV photons can generate carriers within the QDs, the 1.17 eV illumination fluence is proportional to the carrier population optically generated within the QDs. For each fixed fluence of 1.17 eV, the Δ_{opt} value increases linearly with increasing 0.80 eV fluence. We note that the Δ_{opt} also increases linearly as a function of fluence of the 1.17 eV source under constant 0.8 eV photon fluence (data not shown).

The linear dependence of Δ_{opt} on the fluence of both 1.17 eV and 0.8 eV photons is surprising. We hypothesize that carriers excited out of QD states can be easily trapped in subsequent QDs or at the shallow triangular well (TW) formed by the interface with the strain compensation layer. In the absence of 0.8 eV photons, thermal and tunneling escape mechanisms depopulate these traps and allow the current to flow. The addition of 0.8 eV photons creates an additional optically driven escape pathway and thus increases the photocurrent. There are three pieces of evidence that support this hypothesis: the absence of photocurrent saturation for low fluences of 1.17 eV photons, the low fractional contribution of optically driven escape for low fluences of 1.17 eV photons, and the linear dependence of Δ_{opt} on both 1.17 eV and 0.8 eV photon fluence.

Because only 1.17 eV photons can generate carriers in the QD, low 1.17 eV photon fluences (e.g., 50 mW/cm^2) must result in a small number of carriers generated in the QDs. Indeed, we observe a small total photocurrent under these conditions (e.g., Figure 2) If the photocurrent was limited solely by the generation of carriers within the QDs, we would expect Δ_{opt} to saturate for high fluences of 0.8 eV photons. Physically, this saturation point would correspond to the fluence of 0.8 eV photons at which every carrier generated by a 1.17 eV photon was immediately optically driven out of the QD. However, we observe no such saturation, only a linear increase in Δ_{opt}. The absence of saturation under these conditions suggests that there is an infinite supply of carriers that can be optically excited by 0.8 eV photons. Carrier re-trapping would continually supply carriers to the QD or TW, preventing saturation of Δ_{opt} as a function of 0.8 eV photon fluence. This is consistent with our experimental measurements (Figure 3).

The fractional contribution of optically driven carrier escape to the total photocurrent ($\Delta_{opt}/I_{1.17\ eV+0.80\ eV}$) provides additional support for our hypothesis. For high fluence of 0.8 eV photons, $\Delta_{opt}/I_{1.17\ eV+0.80eV}$ is independent of the fluence of 1.17 eV photons, contributing 3.73($\pm$0.05)% of the total photocurrent for the lowest fluence of 1.17 eV photons and 3.6($\pm$0.2)% of the photocurrent for the highest fluence of 1.17 eV photons. The observation that the fractional contribution to the total photocurrent depends only on the fluence of 0.8 eV photons indicates that there is an effectively infinite supply of carriers eligible for optically driven carrier escape, consistent with our carrier re-trapping hypothesis.

The linear dependence of Δ_{opt} on both 0.8 eV and 1.17 eV photon fluence, discussed above and presented in Figure 3, is consistent with the existence of two quasi-independent contributions to photocurrent as described in our hypothesis. Δ_{opt} depends linearly on the fluence of 1.17 eV photons, because the total number of charge carriers increases. Δ_{opt} depends linearly on the fluence of 0.8 eV photons, because the addition of an optical escape pathway reduces the mean time carriers spend in traps and therefore increases the conductivity even for a fixed number of carriers.

The results presented here demonstrate that 0.8 eV photons, below the bandgap of either the host GaAs or the InAs QDs, can improve the photocurrent harvested from an IBSC device. However, tunneling and thermal excitation remain the dominant carrier escape mechanisms even under photon fluences far beyond the range of solar concentrations that might be practical. The linear dependence of both total photocurrent and Δ_{opt} on the fluence of 1.17 eV and 0.8 eV photons is consistent with the existence of a carrier re-trapping mechanism in which free carriers repeatedly relax into QD or TW trap states. The results thus suggest that further efforts to realize the promise of high-efficiency solar energy harvesting with IBSC devices must focus on mitigating carrier relaxation and enhancing carrier transport efficiency.

This project was supported by the U.S. Department of Energy through an Office of Energy Efficiency and Renewable Energy (EERE) Postdoctoral Research Award under the SunShot Solar Energy Technologies Program. S.M.H. would like to acknowledge financial support from the National Science Foundation (No. DMR-0955752).

[1]W. Shockley and H. J. Queisser, J. Appl. Phys. **32**, 510 (1961).
[2]A. Luque and A. Marti, Phys. Rev. Lett. **78**, 5014 (1997).
[3]A. Luque and A. Martí, Prog. Photovoltaics: Res. Appl. **9**, 73 (2001).
[4]A. Martí, L. Cuadra, and A. Luque, Physica E **14**, 150 (2002).
[5]C. G. Bailey, S. Member, D. V. Forbes, S. J. Polly, Z. S. Bittner, Y. Dai, C. Mackos, R. P. Raffaelle, S. M. Hubbard, A. Ten, and I. Gaas, in *37th IEEE Photovoltaic Specialists Conference 2011 (PVSC)* (2012), Vol. 2, p. 269.
[6]W. M. Reid, T. Driscoll, and M. F. Doty, J. Appl. Phys. **111**, 056102 (2012).
[7]O. Rubel, P. Dawson, S. D. Baranovskii, K. Pierz, P. Thomas, and E. O. Göbel, Phys. Status Solidi C **3**, 2397 (2006).
[8]E. Antolin, A. Marti, C. D. Farmer, P. G. Linares, E. Hernandez, A. M. Sanchez, T. Ben, S. I. Molina, C. R. Stanley, and A. Luque, J. Appl. Phys. **108**, 064513 (2010).
[9]Y. Dai, C. G. Baile, C. Kerestesl, D. V. Forbesl, and S. M. Hubbardl, in *38th IEEE Photovoltaic Specialists Conference 2012 (PVSC)* (2011), p. 39.

[10]S. M. Hubbard, C. D. Cress, C. G. Bailey, R. P. Raffaelle, S. G. Bailey, and D. M. Wilt, Appl. Phys. Lett. **92**, 123512 (2008).
[11]S. M. Hubbard, A. Podell, C. Mackos, S. Polly, C. G. Bailey, and D. V. Forbes, Sol. Energy Mater. Sol. Cells **108**, 256 (2013).
[12]A. Martí, E. Antolín, C. R. Stanley, C. D. Farmer, N. López, P. Díaz, E. Cánovas, P. G. Linares, and A. Luque, Phys. Rev. Lett. **97**, 247701 (2006).
[13]D. Guimard, R. Morihara, D. Bordel, K. Tanabe, Y. Wakayama, M. Nishioka, and Y. Arakawa, Appl. Phys. Lett. **96**, 203507 (2010).
[14]Y. Okada, T. Morioka, K. Yoshida, R. Oshima, Y. Shoji, T. Inoue, and T. Kita, J. Appl. Phys. **109**, 024301 (2011).
[15]D. M. Tex, I. Kamiya, and Y. Kanemitsu, Phys. Rev. B **87**, 245305 (2013).
[16]Solar concentration values were estimated by comparing the number of 1.17 eV (0.8 eV) photons/m^2/s incident on the sample under laser excitation to the integrated number of photons/m^2/s in the portion of the AM1.5 solar spectrum that excites carriers to the confined states of the InAs QDs (out of the InAs QDs).
[17]See supplementary material at http://dx.doi.org/10.1063/1.4881181 for a more detailed explanation of sample growth parameters and sample heating experiments.