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Semiconductor nanostructure quantum ratchet for high efficiency solar cells

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Conventional solar cell efficiencies are capped by the ~31% Shockley–Queisser limit because, even with an optimally chosen bandgap, some red photons will go unabsorbed and the excess energy of the blue photons is wasted as heat. Here we demonstrate a “quantum ratchet” device that avoids this limitation by inserting a pair of linked states that form a metastable photoelectron trap in the bandgap. It is designed both to reduce non-radiative recombination, and to break the Shockley–Queisser limit by introducing an additional “sequential two photon absorption” (STPA) excitation channel across the bandgap. We realise the quantum ratchet concept with a semiconductor nanostructure. It raises the electron lifetime in the metastable trap by ~10^4, and gives a STPA channel that increases the photocurrent by a factor of ~50%. This result illustrates a new paradigm for designing ultra-efficient photovoltaic devices.
Interband (IB) cells\textsuperscript{1,2} have recently been studied as a way of beating the \textasciitilde31\% Shockley-Queisser (SQ) limit\textsuperscript{3}. They work by placing an IB level in the bandgap that introduces a parallel excitation channel, allowing the sequential-two-photon-absorption (STPA) of sub-bandgap energy photons. A number of practical implementations based on well-established semiconductor nanostructure fabrication technologies, including quantum dots\textsuperscript{4}, and superlattices\textsuperscript{5} have been reported. However, the short IB lifetime\textsuperscript{6} means they also induce high levels of Shockley-Read-Hall interband recombination\textsuperscript{7} that lower the cell voltage. The theoretical "quantum ratchet" (QR) concept\textsuperscript{8} has been proposed to circumvent this problem.

This QR approach (Fig. 1) introduces two states\textsuperscript{6,9} lying in the bandgap. The upper one (intermediate band, IB) is optically coupled only to the valence band (VB) and the lower one (Ratchet band, R) is optically coupled only to the conduction band (CB). A rapid irreversible scattering process links the two, so their carrier populations are characterised by the same quasi-Fermi level. In spite of the energy, $\Delta E$, lost in the IB $\Rightarrow$ RB transition, idealised global optimisation models\textsuperscript{8} predict limiting QR device efficiencies of $>46\%$ ($\Delta E \approx 270$ meV) at one sun and $>63\%$ at full concentration ($\Delta E = 0$). Both are significantly better than the corresponding SQ limits.

Our implementation (Fig. 1b) uses a quantum well (QW) interband transition for the VB $\Rightarrow$ IB stage, transport through a QW superlattice for the IB $\Rightarrow$ RB ratchet stage, followed by an intraband bound-to-continuum intersubband (ISBT) transition between two electron states for the RB $\Rightarrow$ CB stage. A test device was designed in order to isolate the photocurrent contribution of the STPA channel experimentally. The bandgap corresponding to the VB $\Rightarrow$ IB transition (taking place in the 25 nm thick In$_{0.05}$Ga$_{0.95}$As layer adjacent to the QW’s), was designed to be the lowest energy interband transition in the multilayer, so that it could be driven without generating photocarriers anywhere else. In order to optimise the fraction of IB electrons being scattered into the metastable RB state, rapid IB $\Rightarrow$ RB scattering was facilitated by designing the QW superlattice so that neighbouring wells had confined state energies separated by an optical phonon energy\textsuperscript{9}. The device was packaged in a bevelled configuration to allow the RB $\Rightarrow$ CB transition to be driven with p-polarised light, as is required by the dipole selection rules for ISBT\textsuperscript{9,10}.

Using high speed, time resolved STPA photocurrent measurements, we find here that the QR design increases the electron lifetime in the RB state by $\sim 10^4$ to $\sim 10\mu$s. It introduces an STPA channel that increases the photocurrent by a factor of $\sim 50\%$.

### Results

**STPA photocurrent spectral characteristics.** The 100 µm diameter device was cooled to $\sim 14$ K and illuminated with two independently tuneable laser pulse trains at a 100 kHz repetition rate. The VB $\Rightarrow$ IB transition was resonantly driven with a $\lambda = 850$ nm, $\sim 150$ ps pulse filtered out from an optical fibre supercontinuum source, with a bandwidth of 2.5 nm and a pulse power/energy up to 2.5 W/0.4 nJ. The RB $\Rightarrow$ CB transition was driven with a bank of tuneable quantum cascade laser (QCL) diodes, giving 6 µm $< \lambda < 10$ µm pulses $\sim 100$ ns long and $\sim 800$ µW CW power. This corresponded to a mean pulse power/energy of up to approximately 80 mW/8 nJ.

The two pulse trains could be mechanically chopped (at $\sim 465$ Hz for the VB $\Rightarrow$ IB supercontinuum beam and $\sim 535$ Hz for the RB $\Rightarrow$ CB QCL beam) to measure their single photon contribution to the photocurrent with independent lock-in amplifiers. The QCL beam generated no detectable single photon photocurrent, whereas the supercontinuum beam generated a photo current I$-V$ curve with a pronounced low-current plateau in the 0.4--0.8 V bias range, indicative of the QR action (Supplementary Note 1).

In common with IB cell devices based on semiconductor heterostructures the electronic transport in our device is temperature sensitive and so the STPA measurements must be done in a way that avoids artefacts due to sample heating. STPA experiments presented in the literature have used either CW sources\textsuperscript{4,5,11}, or ones that are chopped at a low fixed frequency, and thermal effects have been shown to give changes in photocurrent at the 10\% level (see ref.\textsuperscript{12} and supplementary material therein). These thermal artefacts are avoidable by modulating the illumination sources at rates that are fast compared with the systems’ thermal time constant. The fact that this has been achieved can be checked by verifying that the STPA signal is independent of the modulation frequencies. One of the unique aspects of the present work is that we used a frequency mixing circuit to drive a third lock-in amplifier at a frequency corresponding to the difference between the modulation frequencies of the two laser beams. This is done in order to isolate the fast contribution to the photocurrent that originates from the STPA excitation process.

In the lower-noise, mechanically chopped experimental configuration, the frequency mixing was achieved with a custom
made digital electronic circuit. However, we also checked that the signal was unchanged when we took the experiment to the highest frequency available. This was achieved by mixing the (fixed) 100 kHz modulation frequency of the supercontinuum source with an 80 kHz pulse train from electronically triggered QCL’s in an analogue diode mixer, and lock-in detecting at the ~20 kHz difference frequency. This gave a STPA signal that was the same to within experimental error as the much slower mechanically chopped experiment. However, for technical reasons the mechanically chopped setup gave a better signal-to-noise ratio and was used for all the data presented here. At all times, the STPA signal disappeared when either laser was blocked, and no STPA signals were found with a control device that was grown with a large bandgap layer inserted into the QW superlattice in a way that was designed to block the IB → RB transport.

The 14 K photocurrent I–V curve (Fig. 2) shows an almost zero-current plateau on the 0.4–0.8 V bias range, consistent with efficient charge-trapping in the RB state, (Supplementary Note 1). Only samples showing this plateau gave an STPA photocurrent signal and it was only ever non-zero within this bias range. At lower forward biases the field is enough to extract electrons from the RB state into the CB one (as signified by a pronounced increase in the VB → IB single photon photocurrent at this bias, see Supplementary Note 1). At higher forward biases, the IB → RB ratchet is too shallow to scatter the IB electrons quickly enough into the RB state to collect a significant fraction of them before they recombine back into the VB state.

Tuning the QCL’s revealed a peaked spectral response (Fig. 2b) in the STPA photocurrent, centred at λ ~ 6.5 µm, with a wavelength full-width-half-maximum of Δλ ~ 1 µm. Rotating the polarisation plane of the QCL revealed the transition to be p-polarised at a level of more than 28:1 (limited by measurement noise), and its energy corresponded well with the λ ~ 6.4 µm modelled transition energy of the RB → CB transition.

**Fig. 2** STPA photocurrent. a Filled squares: 14 K photo current–voltage curve for the quantum ratchet device, showing the 0.4–0.8 V current plateau where carriers are effectively trapped in the RB state. Circles, bias dependence of the STPA photocurrent, peaking at ~0.62 V. At lower biases the field in the QW superlattice is insufficient to separate the photocarriers into the RB state, and at higher biases the carriers can tunnel out of the RB state without two photon excitation. b Spectral dependence of the 14 K STPA signal on mid-IR wavelength when pumped with a fixed a λ = 850 nm interband excitation beam. Error bars correspond to the standard error of the mean of 10 consecutive measurements.

**Intensity dependence of the STPA photocurrent.** The STPA photocurrent was linear in RB → CB QCL intensity over the accessible range (Fig. 3), but it saturated readily, and even decreased with ~30% of the laser intensity that was available for the VB → IB excitation. Order of magnitude estimates (Supplementary Note 2) indicate that at this stage electron space charge accumulation in the RB state would start to generate enough field to flatten the IB → RB ratchet potential. This would reduce its ability to quickly separate electron-hole pairs generated by the VB → IB laser before they have time to recombine.

**Time resolved measurements of the RB level lifetime.** Time resolved studies were initially done with an optical delay line capable of generating a delay of up to 2 ns between the pulse trains, but no time dependence in the signals could be detected on these timescales. All the results reported here were obtained by electronically varying the delay between the pulse trains on a much longer timescale, one that was limited by the 10 µs pulse repetition rate.

The lifetime measurements (Fig. 4) showed a decay time that was comparable with the 10 µs laser repetition rate, i.e., a ~10^4 fold enhancement over the approximately nanosecond values typical of interband recombination in direct-gap QW materials. Its bias (Fig. 4a) and temperature (Fig. 4b) dependencies both showed an approximately reciprocal relationship with those of the STPA photocurrent, furthering the argument that the lifetime enhancement in the RB state is key to achieving effective two-photon absorption. As the device temperature is raised from 14 to 50 K, (by which time the RB lifetime reduces from ~10 to ~0.8 µs), the time averaged STPA photocurrent has dropped by a factor of ~3 before becoming lost in the measurement noise. The thermally activated lifetime reduction correlated with the disappearance of the current plateau in the I–V curves.

**Discussion**

The modelled 10^{-9}–10^{-10} quantum mechanical overlap factor between the IB and RB wave functions is approximately six decades less than the inverse of the measured ~10^4 lifetime enhancement factor. This suggests that the measured lifetimes are limited by a thermally activated process. Estimates of the effects of carrier screening, and band filling (Supplementary Note 2) suggest that the former flattens out the ratchet potential at carrier densities roughly a decade lower than those when the Fermi energy starts to rise significantly in the RB, so we surmise screening is the dominant contribution to the saturation effect in Fig. 3a. When the saturation sets in (at ~0.25 nJ/pulse) we estimate a RB occupancy ~1.3 x 10^{11} cm^{-2}, which compares
The present design uses a materials system chosen because of its mature growth technology, and it operates with transition energies which are lower that would be needed to beat the SQ limit in practice. Future experiments, with wider bandgap semiconductor materials\(^5\) would be needed to match the transition energies on the ratchet device to the spectral content of the solar spectrum. At the same time, this would increase the trapping energy for the RB level, to give higher temperature operation.

In conclusion, we believe that this proof-of-principle result, and the dramatic \((\times 10^6)\) lifetime enhancements achieved, argue the case for the quantum ratchet concept having an important role in a new family of ultra-efficient PV devices.

**Methods**

**Device design and fabrication.** The device was grown by Molecular Beam Epitaxy on an undoped GaAs substrate (Fig. 5), chosen to be transparent to the QCL laser beam. The QR portion (Table 1, layers 4–15) consists of an Al\(_x\)(Ga\(_{1-x}\))As/GaAs QW superlattice structure embedded in a p–n junction. It is capped with a 25 nm layer of In\(_{0.05}\)Ga\(_{0.95}\)As, which has the lowest bandgap in the whole structure (appearing as the \(\lambda \sim 850\) nm eV PL peak in Supplementary Figure 1(b)), so that a suitably infrared detectors (QWIP’s), both of these can be increased towards unity. A variety of surface patterning techniques have been demonstrated\(^4\) that couple normally incident mid-IR light with efficiencies up to \(~90\%\) to the vertically polarised ISBT. The escape probability has been shown to be exponentially dependent on field\(^3\), and QWIPs routinely achieve values close to \(100\%\) by utilising fields that are \(~40\) times higher than the \(\sim 4 \times 10^5\) \(\text{V/m}\) present in the RB region of this test device.

With the \(\sim 6 \times 10^{11}\) \(\text{cm}^{-2}\) needed to completely screen out the ratchet potential (Supplementary Note 2).

At the optimum bias (0.63 V) the STPA channel increases the time-averaged photocurrent by 0.5% of the single photon current generated by the interband pumping alone, (Supplementary Note 3). However, ISBT lifetimes lie typically in the sub-ps range\(^3\), so it is likely that all the STPA photocurrent occurs within the \(~100\) ns QCL pulse; correcting for the 100:1 duty cycle in the QCL pulse train implies an actual STPA photocurrent that is \(~50\%) of the single photon value.

A quantitative analysis (Supplementary Note 3) implies a reasonable IB-RB scattering efficiency of \(~57\%). The low overall power conversion rates are predominantly due to combination of a low \((7.4 \times 10^{-5})\) optical coupling factor to the RB-CB transition in the present experimental geometry, and to a low escape probability into the CB \((3.9 \times 10^{-5})\) for electrons excited into the upper level of the RB QW. Based on the literature on QW

![Fig. 3](image1.png) **Fig. 3** Intensity dependence of the STPA photocurrent. a STPA contribution to the photocurrent as a function of \(\lambda = 850\) nm interband beam intensity, and b STPA contribution to the photocurrent \(\lambda = 6.5\) \(\mu\)m intraband beam intensity. For each curve the intensity of the other beam was fixed at the value corresponding to the maximum STPA response. The saturation effect in (a) corresponds to approximate estimates of the excitation rate needed to generate a 2D electron space charge density in the RB that is high enough to screen out the potential drop along the ratchet scattering channel. Error bars correspond to the standard error of the mean of 10 consecutive measurements

![Fig. 4](image2.png) **Fig. 4** Measured decay time of the STPA signal. a As a function of sample bias at 14 K, b As a function of temperature, at a sample bias of 0.62 V. The solid lines are guides to the eye, and the curves have been normalised to the zero time delay value. Error bars correspond to the standard error of the mean of 10 consecutive measurements.
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The cascade scattering rate is maximised by designing each confined electron state to be separated from its neighbour by an optical phonon energy. Towards the end of the cascade, the Aluminium fraction in the barriers is increased to 0.7 to increase the electron trapping in the RB state and thereby increase the likelihood of photodetection.

Quantum mechanical selection rules for excitation of the 2-dimensional intraband transition require a component of the beam with its electric field polarisation normal to the QW planes, so they cannot be driven in a simple normal incidence illumination geometry. For this reason, the wafer was cleaved along a line close to 45° through the substrate and impinging on the QW’s in the device at this

current. The threshold energy for this transition was designed at 0.195 eV so as to be attainable with the available quantum cascade laser sources. This corresponds closely to the $\lambda = 6.7 \mu m$ peak of the measured spectral response of the STPA signal seen in the inset of Fig. 2.

The cascade was optimised for efficient electron transport using an annealing genetic optimisation algorithm, as described in ref. 9. A control sample was also grown, with the GaAs in one of the wells (layer 9 in Table 1) replaced with Al$_0.3$Ga$_0.7$As so as to create a 7 nm thick layer to block the QR operation. No STPA photo-current could be detected with this sample.

The grown wafer was processed into devices for opto-electronic characterisation and for the spectroscopy experiments. In order to be transparent to the mid-IR radiation, both the buffer layer and substrate were nominally undoped GaAs. Both the p- and n-contacts had to be formed on the top of the devices, by exposing the n-type layers for metallisation (In–Ge, 20 nm/Au 200 nm) with a partial etch of the wafer. For the p-type metallisations (Au 5 nm/Zn 10 nm/Au 200 nm) we chose to use a series of ring-shaped Ohmic contacts ranging in diameter from 50–400 μm (Fig. 6a). The centres of each of the circular mesa were positioned to align with the centre of the mid-IR beam after it had been refracted by the bevelled substrate. A mesa etch was performed to isolate individual devices and bond pads for both the p-contacts, an insulating layer of 200 nm silicon nitride was deposited first to prevent shorting of the device (Fig. 6b).

Finally, the GaAs contacting layer (layer number 1 in Table 1) was removed from the optical window of each mesa with another etch.
angle. Provided the incident mid-IR is p-polarised, then it can couple to the intraband excitations in this geometry. A standard TO8 header was modified by drilling a hole through its centre. The devices were mounted and wire bonded with the wedge overhanging the hole in a way that allowed optical access to its rear.

STPA spectroscopy experimental details. Two independently tunable pulsed laser sources were used for the experiment (Fig. 7). Interband excitation was provided by a supercontinuum fibre laser (Fianium SC450-8-PP). It had a variable repetition rate of 100 kHz to 1 MHz. It had a typical maximum pulse energy of 0.4 nJ, a temporal width of 150 ps and bandwidth of 2.5 nm FWHM. A mid-IR quantum cascade laser (QCL) (Block Engineering "$\lambda\text{range}^\text{TM}$\$) was used to excite the ISBT transitions. It could be tuned over the wavelength range 6–10 µm, and its repetition rate could be varied in the range 0–100 kHz. The QCL pulse was ~100 ns in duration and had a maximum energy of 8 nJ.

Both beams were focused down using 25 mm, f/6 lenses, which generated a spot size which just over-fills the 100 µm device.

The transimpedance amplifier used was a Femto DHPCA-100. It gave a current gain of $10^7$ V/A, and had a bandwidth of 1.8 MHz (~3 dB) and rise time of 0.2 µs (10–90%).

The digital mixing circuit was built around a logical AND gate that multiplies the digital values in the square-wave digital frequency reference waveforms that would isolate the STPA photocurrent component.

Data availability. Data for this report is available from dataenquiryExSS@imperial.ac.uk.

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Author contributions
N.E.D., N.H., M.F., A.P., C.C.P., A.V.S. and M.Y. contributed to the design of the experiments; N.H., M.F., C.C.P., A.V.S., T.W. and M.Y. contributed to the spectroscopy; O.C., N.H., A.P. and M.Y. to sample modelling; O.C., N.E.D., N.H., A.P., C.C.P. and M.Y. to sample design; E.C. to sample growth; K.K. to device fabrication; N.E.D., O.H. and C.C.P. to project conception and management. All authors participated in the preparation of the manuscript.

Additional information
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