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<th>Control of hot-carrier relaxation for realizing ideal quantum-dot intermediate-band solar cells.</th>
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For intermediate-band solar cells, the broad absorption spectrum of quantum dots (QDs) offers a favorable conversion efficiency, and photocurrent generation via efficient two-step two-photon-absorption (TS-TPA) in QDs is essential for realizing high-performance solar cells. In the last decade, many works were dedicated to improve the TS-TPA efficiency by modifying the QD itself, however, the obtained results are far from the requirements for practical applications. To reveal the mechanisms behind the low TS-TPA efficiency in QDs, we report here on two- and three-beam photocurrent measurements of InAs quantum structures embedded in AlGaAs. Comparison of two- and three-beam photocurrent spectra obtained by subbandgap excitation reveals that the QD TS-TPA efficiency is improved significantly by suppressing the relaxation of hot TS-TPA carriers to unoccupied shallow InAs quantum structure states.
Results

Single- and two-beam experiments. The sample structure used in this work is shown in Fig. 1 (see Methods for details). Growing InAs on GaAs or AlGaAs with MBE leads to the formation of pyramidal QDs and flat disk-like QWIs. Because the InAs quantum structures have different heights, the QWI states are situated at high energies, whereas the QD states are found at low energies. The PC is generated upon wavelength selective excitation of different structures and extracted via an applied bias. PC data at room temperature are shown in Figs. 2a,b. Figure 2a shows the PC intensity \( I(\lambda_{B1}) \) for single-beam excitation with a variable wavelength \( \lambda_{B1} \) in red and PC intensity \( I(\lambda_{B1}, \lambda_{IR}) \) for two-beam excitation with a variable \( \lambda_{B1} \) and fixed \( \lambda_{IR} \) ~ 1550 nm in blue obtained with excitation powers of \( P_{B1} = 8 \) mW and \( P_{IR} = 1.5 \) mW, corresponding to excitation power densities of approximately 8 and 1.5 W/cm\(^2\), respectively. Details of the optical setup are given in the Methods, Measurement system section. Peaks in the PC spectra were assigned to carrier generation in the QWIs and QDs\(^{16}\). Single-beam experiments on QWIs\(^{16}\) and QDs\(^{15}\) have revealed that the major upconversion mechanisms are Auger\(^{14}\) and thermal processes, respectively.

By using a two-beam configuration with sufficiently high excitation power, the TS-TPA contribution can be revealed. In the present experimental setup we require more than about 1 W/cm\(^2\) average excitation power (\( \sqrt{P_{B1} \times P_{IR}} \)) to obtain clear TS-TPA signals from all quantum structures. The difference between the two- and single-beam room-temperature data (Fig. 2b) gives a measure of the TS-TPA efficiency, since \( \lambda_{IR} = 1550 \) nm photons cannot create new carriers but only excite carriers above the barrier. No significant TS-TPA contribution from \( \lambda_{IR} = 1550 \) nm photons is observed in the InAs region at room temperature, and a contribution is observed at temperatures below 100 K, as shown in Figs. 2c and d. Note that the shape of the single wavelength data (red curve) in Fig. 2c has been discussed in our previous work\(^{16}\). On additional excitation with \( \lambda_{IR} \), we see that the PC increases at several energy levels. We assigned, in accordance with the PL spectra, the peaks in Fig. 2d to PC generation via TS-TPA processes in GaAs (\( \lambda < 820 \) nm), 2-ML-thick QWIs (\( \lambda \approx 850 \) nm), 3-ML-thick QWIs (\( \lambda \approx 900 \) nm), and QDs (\( \lambda > 960 \) nm). Because shallow QWIs have the highest PC generation efficiency, from this point, "QWI" is used to refer only to QWIs with emission and absorption at about 850 nm. The TS-TPA signatures arise for excitation of well-defined quantum structures, which are formed for a wide range of growth conditions. A quantitative analysis of this TS-TPA contribution is required.

Detailed temperature dependence. Figure 3 shows the temperature dependence of the PC generated by the excitation of QWIs and QDs. At each temperature, \( \lambda_{B1} \) was tuned to the QWI and QD energy levels. The measured total PC \( I(\lambda_{B1}) \) (large dots) consists of contributions from TS-TPA processes in both quantum structures as well Auger processes in the QWIs\(^{16}\) and thermal upconversion in the QDs\(^{15}\). To estimate the TS-TPA contribution, the PC \( I(\lambda_{B1}, \lambda_{IR}) \)
for excitation with beam 1 (B1) and an additional IR beam was measured. The PC difference between the two- and single-beam excitation, \( I(\lambda_{B1}, \lambda_{IR}) - I(\lambda_{B1}) \), is the TS-TPA contribution due to IR excitation. This TS-TPA contribution was evaluated at each temperature, and subtracted from the total measured PC (large dots), resulting in an evaluated PC without TS-TPA contribution (small dots). The differences between the broken and solid curves visualize the contribution of TS-TPA to the PC (colored area). The figure shows qualitatively that the TS-TPA processes in both QWIs and QDs are much weaker than the Auger process observed in QWIs. The PC due to TS-TPA is only observed at low temperatures, and TS-TPA has no significant contribution to PC at room temperature. We note that at low temperatures, the TS-TPA efficiency for QD excitation is about an order weaker than for QWI excitation.

**Two- and three-beam maps.** Two- and three-beam experiments were carried out to clarify the limiting factor of PC generation via TS-TPA in QDs using the experimental setup, shown in Fig. 4. Total and evaluated PC contributions obtained from single-, two-, and three-beam experiments are compared in Fig. 5. The maps are plotted as functions of the excitation wavelengths \( \lambda_{B1} \) and \( \lambda_{IR} \), and the two-beam map is obtained by scanning both \( \lambda_{B1} \) and \( \lambda_{IR} \) from short to long wavelengths. The PC intensity map \( I(\lambda_{B1}, \lambda_{IR}) \) in Fig. 5a is for simultaneous excitation with both beams, while Fig. 5b shows the sum \( I(\lambda_{B1}) + I(\lambda_{B2}) \) of two PC wavelength scans, measured by single excitations with \( \lambda_{B1} \) and \( \lambda_{B2} \). The latter single-beam PC map does not contain effects due to simultaneous two-beam excitation. The differences between these two PC maps is the two beam effect, shown in Fig. 5c.

Further, the TS-TPA effect due to an additional IR beam at 1550 nm is plotted in Fig. 5d. Note that the term “TS-TPA effect” is used to refer to the additional PC induced by means of TS-TPA transitions (no new carriers are created). The TS-TPA effect can be negative when carriers that have already been created in the QDs are excited to trap states, which is a process that does not contribute to the PC. A strong positive TS-TPA effect obviously means a high TS-TPA efficiency. The TS-TPA effect is calculated by subtracting the PC contribution of two-beams \( I(\lambda_{B1}, \lambda_{IR}) \) from the three-beam PC data \( I(\lambda_{B1}, \lambda_{B2}, \lambda_{IR}) \) (if the two-beam effect is written as \( B_1 \cap B_2 - B_1 - B_2 \) and the IR effect \( B_1 \cap IR - B_1 \), we obtain by substitution the definition of \( I = I(\lambda_{B1}, \lambda_{IR}) + I(\lambda_{B2}, \lambda_{IR}) - I(\lambda_{B1}) - I(\lambda_{B2}) \)). This data will be discussed later. There are many features in the PC maps that deserve attention; however, we focus here on those features that have a bearing on the TS-TPA in the QDs.

The regions A and B in Fig. 5c correspond to excitation conditions in which one beam resonantly excites the shallow QWI states (\( \lambda_{QWI} = 850 – 880 \) nm, obtained from PL), and the second beam excites the lower lying states, e.g., QDs. In contrast, region C defines the case in which both beams excite the lower lying states, i.e., shallow QWI states are not excited, and we see that a weak two-beam effect appears in region C. This PC contribution becomes slightly smaller as \( \lambda_{IR} \) is increased, and decreases significantly below the QD energy level \( \lambda_{QD} \approx 1060 \) nm, obtained from PL. Since in region C only the QDs are excited, this PC contribution is assigned to PC via TS-TPA in the QDs. The 3-ML-thick QWIs are discarded for the origin of this PC.
because no sharp features are observed at ≈900 nm. The PC in region C is very weak and therefore insufficient for IB solar cells. We also observe in regions A and B that the PC enhancement is strongest for direct excitation of the shallow QWI states with one beam, with the second beam exciting the lower QD states. Regions A and B with pronounced PC are where enhanced TS-TPA occurs in the QWIs or QDs. Because the two-beam effect for simultaneous excitation of the QWIs with $\lambda_{B_1} = \lambda_{B_2} = 850$ nm is significantly smaller, the origin of the PC via TS-TPA is most likely to be the QD states. PC generation via TS-TPA, for the excitation of QWIs and QDs (regions A and B) is an order stronger than that via TS-TPA for the excitation of the QDs only (region C). This shows that additional excitation of the QWIs contributes to further PC generation. To apply TS-TPA in IB solar cells, it is important to understand the mechanisms for this exceptional enhancement.

To investigate the TS-TPA mechanisms in regions A and B in more detail, we measured the PC intensity $I(\lambda_{B_1}, \lambda_{B_2}, \lambda_{IR})$ in a three-beam experiment and calculated the absolute TS-TPA effect of the IR beam, as shown in Fig. 5d. The TS-TPA effect in region A is positive, while that in region B is negative. This asymmetry is an important indicator of the TS-TPA mechanism and arises because different excitation powers for $B_1$ and $B_2$ were used ($P_{B_1} = 1$ mW and $P_{B_2} = 140$ $\mu$W). The excitation power of the QWI state determines whether the TS-TPA effect is positive or negative, meaning that the carrier population in the QWI is a primary issue for realizing IB solar cells.

**Model.** The results of the previous section indicate that a significant PC enhancement via TS-TPA can only be obtained by simultaneous excitation of the QWIs and QDs (Fig. 5c; regions A and B). We propose that the remarkable TS-TPA enhancement is caused by thecarrier population of the higher lying QWI states. Figure 6a illustrates this behavior; when the shallow QWI is only weakly excited (corresponding to area B; $\lambda_{B_2} = 850$ nm with $P_{B_2} = 140$ $\mu$W), photocarriers generated via TS-TPA via the deep QD states can be trapped in the unoccupied QWI states. Recombination of the trapped carriers will lead to an overall loss of carriers because the IR beam cannot create new carriers, i.e., a negative TS-TPA effect can be observed. However, when the QWI state is strongly occupied (corresponding to area A; $\lambda_{B_1} = 850$ nm with $P_{B_1} = 1$ mW), the trapping effect is suppressed (Fig. 6b), and as shown in Fig. 6c, filling the QWI state results in a significant enhancement in the PC generation via TS-TPA in QDs.

**Verification with power dependence.** To verify that the TS-TPA efficiency is reduced by the capture of upconverted carriers in the high-energy QWI states, we investigated the power dependence of the TS-TPA map in Fig. 5d. A TS-TPA map for similar excitation conditions is shown in Fig. 7a. Region A shows a positive signal for the strong excitation of the QWIs (Fig. 7a, red vertical line; $\lambda_{B_1} = 850$ nm with $P_{B_1} = 1$ mW), and region B shows a negative signal for the weak excitation of the QWIs (Fig. 7a, blue horizontal line; $\lambda_{B_2} = 850$ nm with $P_{B_2} = 150$ $\mu$W). By gradually varying the B1 excitation power (a to f), the initial positive signal region begins to exhibit a negative signal (Fig. 6b), and as shown in Fig. 6c, filling the QWI state results in a significant enhancement in the PC generation via TS-TPA in QDs.

**Discussion**

The power dependence of the TS-TPA effect confirms that PC generation via the TS-TPA process occurs in QDs at low temperatures, and that the generation efficiency is significantly reduced by the fast recapture of photocarriers at trap states situated at higher energy levels (see Figs. 6a). This result is important for all structures containing InAs quantum structures, since the formation of such higher lying trap states cannot be prevented by using present growth techniques. The recapture of photocarriers is most likely responsible for several unexpected results reported previously. While improvement of the TS-TPA in QDs has been explored by increasing the the absorption coefficient by QD coupling or enhancing the deep IR absorption by doping of QDs, new phenomena have been observed. For example, a small additional PC due to illumination of doped QDs with low-energy photons (IR photons) was observed, but the additional PC also became stronger when the doped QD were excited with high-energy photons (visible photons)\(^2\). Increased intraband absorption from QD states to the continuum has also been observed.

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**Figure 6 | Reason for generally low TS-TPA efficiency.** (a,b) Band diagrams illustrating the mechanism responsible for the low TS-TPA efficiencies observed experimentally. (a) QD states (red) are excited, while QWI states (blue) are hardly occupied. Photocarriers created via TS-TPA from QDs by IR illumination are immediately captured by QWIs. (b) High QWI occupation condition: carriers created by TS-TPA are extracted efficiently. (c) Experimental enhancement of TS-TPA for QD and QWI excitation. The red curve shows the TS-TPA effect due to additional IR illumination in a single wavelength scan. The PC contribution at QD energies (≈1000 nm) is almost null. The blue curve shows the TS-TPA effect due to additional IR illumination in a two-beam experiment with a variable first beam and a fixed second beam at QWI energies. A significant enhancement in the TS-TPA efficiency from the QDs is observed.
under high-energy photon illumination, when compared to that obtained under low-energy photon excitation (155). In addition, positive as well as negative effect of doping on PC generation have been reported (15,21,30–32); changes in the PC spectra did not reflect a definitive increase of PC contribution by TS-TPA via QDs.

There have been no consistent explanations of the results mentioned above, since the influence of states other than the QD state on the TS-TPA efficiency was not considered. However, a consistent explanation is offered by considering the recapture of TS-TPA-generated photocarriers in InAs states with an energy above the QD state. Only when these trap states are already occupied (with additional excitation or doping) or the second photon in the TS-TPA process excites the carrier to an energy level much higher than the conduction band (via TS-TPA from QDs using visible photons), recapture is avoided and TS-TPA PC generation is enhanced.

To improve the IB solar-cell efficiency we must consider the following points: The QWs enable efficient PC generation via multi-carrier Auger processes, but have a narrower absorption band than QDs and also reduce the PC generation via TS-TPA in QDs. However, a high-efficiency IB solar cell requires the use of both quantum structures to obtain broad-band upconversion with the best efficiency. Hence, a structural design that enables the most efficient upconversion in each structure without disturbing the other must be identified. Further work is required to elucidate these prospects.

In summary, we have investigated the TS-TPA efficiency in InAs QWIs and QDs using two- and three-beam experiments. Performing these experiments with two tunable sources, provides critical information about upconversion and recombination dynamics and is thus an effective approach for determining the limiting mechanism of the TS-TPA process. It has been revealed that the PC generated via TS-TPA in QDs is actually limited by the relaxation to shallow states after the absorption of the second photon. To achieve a higher TS-TPA PC contribution in IB solar cells, considering structures consisting of both QWIs and QDs is essential.

**Methods**

**Growth.** The sample structure shown in Fig. 1 was prepared by molecular beam epitaxy (MBE) and consists of an InAs layer embedded in AlGaAs and GaAs. The self-assembly of the quantum structures occurs via the Stransky–Krastanov growth mode (a strain driven growth), using either by MBE or metalorganic chemical vapor deposition. The strain due to the lattice mismatch between InAs and AlGaAs leads to the formation of the QWIs and QDs on top of the single-ML thick wetting layer. The ultra-thin QWIs are sometimes also interpreted as monolayer fluctuations of a rough wetting layer, but for upconversion the electronic properties of this well-defined island-structure are important and thus exact terminology is required.

**Sample structure.** A nominally undoped sample structure was grown with MBE on top of a semi-insulating GaAs (001) substrate, followed by the growth of a GaAs buffer, an AlGaAs layer including a 2 ML InAs layer (forming QDs and QWIs), and a GaAs quantum well (QW) for reference. The top of the structure was capped by a GaAs layer including a 1.4 ML InAs layer (forming only QWIs). The two InAs layers assist in determining the barrier height dependence of different upconversion mechanisms (16). For the PC experiments, we used an Au contact on top and an In contact at the bottom of the structure. The applied bias voltage was below 1 V.

**Measurement system.** Three excitation sources (see Fig. 4) were employed: a continuous wave (cw) laser (B1) tunable from 800 to 1010 nm, a pulsed white light source in combination with a monochromator (B2) (λ_{BW} = 800 to 1350 nm), and a cw IR laser diode (IR) with λ_{IR} = 1550 nm. In general, different excitation powers were used for B1 and B2, which is important because the effect of the modulated carrier population in different energy levels needs to be probed. Owing to the difference in carrier distribution induced by pulsed and cw excitation, small asymmetries arise in the interchanged excitation powers. The effect of pulsed excitation was verified to be minor and mainly visible as a slight reduction in the TS-TPA PC for high excitation powers due to heating.

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Author contributions
D.M.T. designed and performed experiments, analysed data and wrote the paper. Y.K. conceived the project, and Y.K. and I.K. discussed the results and wrote the manuscript.

Additional information
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