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Experimental demonstration of energy-transfer ratchet intermediate-band solar cell

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A detailed balance calculation reveals an extremely high efficiency of 63.2% for intermediateband solar cells (IBSCs) under maximum sunlight concentration. However, an actual IBSC device with an efficiency larger than the Shockley-Queisser (SQ) limit has so far not been reported. The main difficulties lie in realizing an efficient sequential two-photon absorption (STPA) which requires a sufficiently long lifetime intermediate state or intermediate band. In this article, we propose the concept of a ratchet type IBSC, utilizing a long lifetime of rareearth ion luminescence centers in Erbium-doped GaAs. The temperature dependent differential external quantum efficiency reveals a significant STPA contribution originating from the Er^{3+} luminescence center. All the results were modeled and interpreted by integrating the ratchet effect with up-conversion along with a density functional theory (DFT) simulation. Our work demonstrates that the long lifetime energy-transfer mechanism in Er^{3+} centers contributes directly to the formation of a ratchet type IB. Check for updates

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nergy levels that are located within the bandgap of semiconductor materials enable absorption of photons with energies below the bandgap energy of the host semiconductor. It has been proposed that sequential excitation of an electron to the conduction band (CB) via such an intermediate energy level can improve solar cell conversion efficiencies¹. A detailed balance calculation reveals that the theoretical efficiency limit of an ideal solar cell that employs sequential two-photon absorption (STPA) and intermediate levels is 63.2% under maximum sunlight concentration^{1,2}, which is almost one and a half times higher than the Shockley-Queisser (SQ) limit of ≈42% for conventional single-junction solar cells under the same condition^{3,4}. This high efficiency limit has attracted considerable attention and has encouraged many scientists to develop and realize such high-efficiency intermediate-band solar cells (IBSCs). However, an actual IBSC device with an efficiency larger than the SQ limit has so far not been reported. The issue that is regarded as most difficult in realizing feasible IBSCs is the realization of an intermediate state or intermediate band (IB) with an efficient STPA process, because this requires a reasonably long lifetime of the electrons in the IB. A long lifetime enhances the probability of optical excitation to the CB before the electron in the IB recombines with the hole in the valence band (VB). The formation of IBs itself has been investigated from the viewpoints of crystal growth and material engineering, and several structure candidates have been proposed. In particular, IBSC device structures based on quantum dot superlattices and the bulk-type IBSC employing band anti-crossing have received much attention^{5,6}. Despite significant research efforts, the realization of efficient STPA still remains challenging, because this topic involves more complex physics including carrier dynamics. As a matter of fact, all IBSCs, which have been widely studied with respect to the IB formation, are suffering from short carrier lifetimes in the IB⁵.

Recently, the quantum ratchet IBSC has been proposed that aims at circumventing the abovementioned problem by introducing another band below the IB^{7,8}. The term "ratchet" is taken to describe an energy band or state that accommodates the relaxed electrons from the IB. Here the conventional IB, which has both transitions from the VB to the IB and from the IB to the CB, is replaced by an IB that is only coupled to the VB, and simultaneously a non-emissive ratchet band that is only coupled to the CB is introduced at an energy ΔE below the IB (Fig. 1a). Given all these conditions along with the assumption that the ΔE dependent carrier-longitudinal optical phonon scattering rate between the ratchet band and IB is in the order of picoseconds^{9,10}, the lifetime of electrons in the ratchet state can be treated as being long enough to significantly enhance the STPA probability. Furthermore, if the energy relaxation from the IB to the ratchet state is sufficiently fast, most of the carriers excited to the IB will be transferred to ratchet band. This transfer can significantly suppress the recombination between the IB and the VB and thus can lead to a higher efficiency than that of an IBSC with a single IB only, especially at low or moderate light concentrations⁷.

Regarding the implementation of the ratchet IBSC concept, several approaches have been proposed and demonstrated^{8,10-12}, for example, a combination of a direct IB and a type-II indirect IB and a quantum ratchet based on a quantum-well superlattice. Unfortunately, the reported devices have not been able to provide clear evidence of the occurrence of decoupling between the ratchet band and the VB. In 2008, the concept of the moleculartype IB was proposed where the transition from the excited triplet state to the ground state singlet state is forbidden¹¹. Since a forbidden transition ensures the decoupling process, we consider an extension of this forbidden-transition concept to the rareearth-ion-doped materials. In these materials, a well-known energy-transfer mechanism exists and an originally forbidden dipole-dipole transition ${}^{4}I_{13/2} \leftrightarrow {}^{4}I_{15/2}$ of Er^{3+} plays the key role in the energy-transfer process¹³. A long lifetime on the order of milliseconds has been reported¹⁴. The widely accepted energytransfer model in rare-earth-ion-doped materials is depicted in Fig. 1b, which involves the following steps: (i) electrons relax from the CB and are trapped in an IB level that is induced by rare-earth ion doping; (ii) formation of an exciton due to Coulomb attraction between the electron in the IB and a hole in the VB; (iii) exciton recombination and transfer of the energy to the 4f shell of the rare-earth ion center [this creates an electron-hole pair at slightly lower energies that is responsible for the observed photoluminescence (PL)]; (iv) electron back transfer can occur at elevated temperatures. Rare-earth-ion-doped materials have been widely studied for their interesting features as luminescent light sources, and the erbium (Er) ions tend to form deep trap levels near the center of the bandgap^{15,16} and these may act as nonradiative recombination centers^{17,18}. Meanwhile, the two-photon up-conversion effect related to the energy transfer in rare-earthion-doped materials has been extensively studied in the fields of up-conversion lasers and bioimaging^{19,20}. Here, after the energy transfer, the electron in the excited rare-earth ion state (e.g., ${}^{4}I_{13/2}$) absorbs a sub-bandgap photon and reaches the CB where radiative recombination can lead to emission of a highenergy photon. Rare-earth-ion-doped materials have also been considered for use as spectrum converters in solar cells, because they provide an efficient two-photon up-conversion mechanism or impurity band, which improves overall light absorption^{21–26}. To the best of our knowledge, this has so far not been reported on



Fig. 1 Operation schemes of different types of intermediate-band solar cells (IBSCs) and the energy-transfer model. a Conventional ratchet IBSC involving carrier excitation, recombination, and sequential two-photon absorption (STPA) among the valence band (VB), intermediate band (IB), conduction band (CB), and ratchet band located at an energy ΔE below the IB, **b** energy-transfer and back transfer model, and **c** the energy-transfer-coupled ratchet IBSC along with proposed in this work, respectively.

an IBSC based on rare-earth-ion-doped materials, where the STPA process rather than the two-photon up-conversion^{15,16}, is the key to successful device operation.

In this work, we propose and demonstrate an implementation scheme of the ratchet IBSC concept, and the device is hereafter referred to as energy-transfer ratchet IBSC (ETR-IBSC). As explained in Fig. 1c, the STPA process employed to generate additional photocurrent from sub-bandgap photons is: (i) an electron is excited from the VB to the IB (formed due to rareearth ion doping) by absorbing a sub-bandgap photon, (ii) the energy-transfer process creates an electron at the rare-earth-ion center at slightly lower energies (in our case, the ${}^{4}I_{13/2}$ state), and (iii) instead of the back transfer process to the IB where recombination is likely, the electron in the ${}^{4}I_{13/2}$ state absorbs another sub-bandgap photon and reaches the CB of the host material. Thus two sub-bandgap photons were able to contribute to photocurrent generation. For proof of concept, we prepared Er-doped Er³⁺: GaAs compound solar cells and measured the differential external quantum efficiency (EQE) spectra. We show that the temperature-dependent STPA-induced current exhibits a feature at 1540 nm, which corresponds exactly to the energy transition between ${}^{4}I_{13/2} \leftrightarrow {}^{4}I_{15/2}$ of Er³⁺. This indicates that the observed current contribution via STPA processes is consistent with an energy-transfer process between states in the GaAs host material and the Er³⁺ luminescence center, thus implying occurrence of an ETR effect in this type of IBSC.

Results

Confirmation of energy transfer by using PL. All samples discussed here were grown by molecular beam epitaxy (MBE). First, we prepared samples for the PL measurements. The MBE system was equipped with an Er effusion source and the experimental details are provided in the "Methods" section. Table 1 shows the relation between the Er doping concentration and the Er cell temperature $T_{\rm Er}$. The Er luminescence properties were studied as a function of the growth temperature and the Er doping concentration by temperature-dependent PL measurements. The second harmonic of an Nd:YAG laser was used to excite the Erdoped samples at 532 nm, which is significantly above the GaAs bandgap, with a power density of 1 mW cm^{-2} (spot size $\approx 100 \,\mu\text{m}$). We found that the PL intensity increases as T_{Er} increases from 973 to 1073 K, and for $T_{\rm Er}$ > 1073 K, the PL intensity decreases. Figure 2a shows the temperature dependence of the PL spectra in the temperature range from 20 to 295 K for the sample grown at $T_{\rm Er} = 1173$ K. A magnified and smoothed set of the data is shown in Fig. 2b. It can be clearly seen that there is no energy shift of the main peak (≈1540 nm) within the resolution limit of the experiments. This observation is consistent with the previously reported PL results, which have been attributed to the fact that the filled outer 5s and 5p electron shells of Er effectively screen the intra-4f transitions from the host material¹³.

Characterization of the ETR-IBSC devices. To verify the proposed operating principle of the ETR-IBSC, five solar cell devices

Table 1 Relation between the dopant concentration and Ercell temperature calibrated using secondary ion massspectroscopy (SIMS).

Er cell temperature (°C)	Dopant concentration (cm ⁻³)
1000	1.85 × 10 ²⁰
900	1.86 × 10 ¹⁹
800	8.21 × 10 ¹⁷
700	2.14 × 10 ¹⁶

were prepared as explained in the "Methods" section. Figure 3a shows the device structure of the fabricated devices. All samples employed the same growth procedure except for the Er concentration controlled by the Er cell temperature: four samples with Er doping (referred to as Er700, Er800, Er900, and Er1000 corresponding to Er cell temperatures of 973, 1073, 1173, and 1273 K, respectively) and, for reference, a control GaAs solar cell with the same device structure and doping profiles but without Er. The performances of the solar cell devices were characterized by current-voltage (I-V) curves obtained under 1 sun illumination with an AM1.5 spectrum and EQE spectra at room temperature. The ratchet effect (that is, decoupling of carriers in intermediate levels from the VB by aid of the ratchet band) was verified by STPA measurements: bias-voltage-dependent EQE measurements and temperature-dependent differential EQE measurements.

Figure 3b shows the J-V characteristics of the four Er-doped GaAs solar cells and the GaAs control cell. Compared to the GaAs control cell, the Er-doped samples exhibit a reduction in both open-circuit voltage ($V_{\rm oc}$) and short-circuit current ($I_{\rm sc}$). This reduction is assigned to the introduction of defects by Er doping in the intrinsic region; the Er ions tend to form deep trap levels near the center of the bandgap^{15,16} and these may act as nonradiative recombination centers, which reduce the carrier density and the carrier collection efficiency. Hence, they can lead to the observed reduction of $I_{\rm sc}$ and $V_{\rm oc}$. Since the degradation is mainly due to material quality, the device performance of the Er-doped GaAs solar cells may be improved by optimizing growth conditions.

In order to examine the optical response in the longwavelength region, we performed EQE measurements under reverse-bias conditions. The reverse-bias condition is used to maximize the carrier collection efficiency by increasing the electric field in the *i*-layer. For the Er-doped GaAs device, the reverse bias was applied in order to extract the carriers trapped at the non-radiative recombination centers (induced by Er doping), and thus the reverse-bias-dependent EQE provides direct information about the actual optical response of the Er^{3+} center. For this measurement, we employed a broadband white-light lamp source and a monochromator that changes the wavelength used to illuminate the sample. Figure 3c plots the EQE spectra of all five devices under a bias voltage of -5 V. In the wavelength range of 400-800 nm, the EQE decreases with Er³⁺ concentration as a result of an increasing density of non-radiative recombination centers induced by Er^{3+} . However, at wavelengths >900 nm, the Er900 and Er1000 samples exhibit a significant increase compared to the other samples, as shown in the inset. We attribute the increase of the EQE in this latter region to the thermal activation of carriers that have been excited to the Erinduced IB. In contrast, for Er700 and Er800, we consider that the doping densities were too low and no functional IB was formed and thus no effect appears in the spectral response.

To assess the amount of optical transitions of electrons from the ratchet state to the CB via infrared (IR) absorption, we conducted STPA measurements. Here we determined the differential EQE (Δ EQE) spectra where an IR light source (with wavelengths $\lambda > 1400$ nm corresponding to photon energies <0.86 eV) was used to create the differential signal. Since the IR photon energies are well below the bandgap energy of GaAs (1.42 eV), the illumination with photons from the IR source cannot excite electrons from the VB to the CB. Instead, they can only induce transitions from the IB or the ratchet state to the CB or from the VB to the IB. The Δ EQE spectra are obtained under modulated IR illumination at the short-circuit condition as well as other bias voltages using a lock-in technique (see "Methods"). The result of this measurement describes the differential signal



Fig. 2 Photoluminescence (PL) measurement results. a Temperature dependence of PL obtained from the device under excitation at 532 nm, and **b** magnified and fitted results shown in **a**, respectively. The curves were fitted with a Gaussian distribution by minimizing the chi-square χ^2 and the error bars here represent one standard deviation (1 s.d.) of the fitting errors.



Fig. 3 Schematic device structure and measured current density (*J*)-voltage (V) curves. a Energy-transfer ratchet IBSC (ETR-IBSC) structure based on Er-doped GaAs, b *J*-V curves obtained under 1 sun illumination with an AM1.5 spectrum, and c external quantum efficiency spectra of all five devices under a bias voltage of -5 V, respectively.

defined as $\Delta EQE = EQE_{IR_{on}} - EQE_{IR_{off}}$. A non-zero ΔEQE can only be caused by the absorption of IR photons. Note that this ΔEQE spectrum is not affected by signals that are only induced by the primary scanning beam (e.g., via thermal escape or twophoton up-conversion).

Figure 4a shows the ΔEQE spectra measured at room temperature at a bias of 0 V. We find that the Er900 sample shows the highest IR-enhanced current among the five samples. The ΔEQE of the reference cell is zero, because it has no functional IB states that can contribute to the spectral response. The Er800 sample also exhibits no noticeable increase within the whole wavelength range. Regarding the Er700 sample, there is a constant enhancement in the whole measurement range, probably caused by leak current or noise. Both Er900 and Er1000 exhibit an increased Δ EQE in the wavelength range from 450 to 900 nm, which is related to the carriers in the CB that have relaxed to the IB and are then re-excited to the CB by absorbing IR photons^{27,28}. This result is also consistent with the Δ EQE results of previously reported quantum-dot IBSCs⁶. It is important to note that this recovery of trapped carriers is a process that is not related to the ETR-IBSC operating principle. Instead, this process is partially overlapping with the conventional energy-transfer model described in Fig. 1b. It is actually an open question if the trapped carrier is directly re-excited to the CB by the IR bias light



Fig. 4 Sequential two-photon absorption (STPA) measurement results. a Differential external quantum efficiency (Δ EQE) spectra measured at room temperature at a bias of 0 V (short circuit), and **b** the bias-voltage dependence of Δ EQE spectra for the samples Er900 and Er1000, respectively.

or if it first participates in the energy-transfer process involving the Er^{3+} center and then is re-excited to the CB.

The bias-voltage dependences of the Δ EQE spectra for the samples Er900 and Er1000 are shown in Fig. 4b. Here the applied reverse-bias voltage leads to a suppression of the Δ EQE signal, which is opposite to the tendency found for the EQE signal shown in Fig. 3c. The trend in Fig. 4b is a result of the reduction of the carrier density in the IB. Regarding the wavelength region beyond 900 nm in Fig. 4, there is no significant STPA response in the Δ EQE. This is attributed to the effect of thermal escape of carriers in the IB. The thermal escape suppresses the contribution by the IR excitation, and consequently we were not able to detect the optical response of Er³⁺ at the wavelength region <900 nm, but here the carrier density is much higher and thus we were able to observe an IR-induced signal.

In order to investigate the IR response of the $Er^{3+} 4f$ transition, the temperature-dependent \triangle EQE measurement at short circuit condition was evaluated with two long-pass filters with cutoff wavelengths of 1340 and 1550 nm. The long-pass filters were inserted in the IR excitation path to control the IR photon energy range. Figure 5a plots the temperature dependences of the EQE obtained from the Er900 sample at temperatures ranging from 9 to 295 K. It is found that decreasing temperature suppresses carrier collection at the wavelength of 1350 nm and beyond. Figure 5b plots the temperature dependences of the ΔEQE obtained from the Er900 sample with the 1340-nm long-pass filter at temperatures ranging from 9 to 295 K and that of the Δ EQE obtained with the 1550-nm long-pass filter is shown in Fig. 5c. The temperature-dependent STPA measurement was conducted with a different experimental set-up, and therefore there exists a deviation between the absolute magnitudes of the Δ EQE spectra shown in Figs. 5b, c and 4. Figure 5b, c use the same scales for easy comparison of the two data sets. The ΔEQE spectra of the Er900 sample with the 1340-nm filter exhibit a peak centered at 1540 nm, and the magnification of the Er³⁺-induced Δ EQE signal around 1540 nm is shown in Fig. 5d. This figure verifies that the \triangle EQE signals at 1540 nm are strongest in the temperature range from 9 to 100 K, and the Δ EQE intensity decreases for temperatures >100 K. In the case of 1550-nm filter (Fig. 5c), no peaks are observed. Based on these results, it can be concluded that the \triangle EQE peak at 1540 nm is influenced by the additional absorption of IR photons with wavelengths between 1340 and 1550 nm. The carrier excitation process that is responsible for this behavior is explained in the "Discussion" section. The peak at 1540 nm is consistent with the well-known Er^{3+} energy-transfer transition ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ at 1540 nm²⁹ and is remarkably stable over a wide temperature range (9–100 K). The Er1000 sample exhibits a behavior (not shown here) that is similar to that of the Er900 sample but with a reduced ΔEQE intensity.

Discussion

Based on the experimental results described above, we consider that Er-induced multi-intermediate levels form inside the GaAs bandgap. Figure 6 shows the band structure of Er-doped GaAs calculated by density functional theory (DFT) simulations (for the computational details, see the "Methods" section). The local structure relaxation was evaluated prior to the DFT simulation by using a molecular dynamics (MD) simulation³⁰. Figure 6a shows the local structures before and after relaxation of a larger GaAs unit cell with an Er atom as a substitute for the central Ga atom. It can be seen that a significant distortion occurs around the Er atom. It looks like the Er atom "repels" the nearest-neighbor atoms, and thus it is seemingly isolated from the surrounding Ga and As atoms. This structural relaxation is the fundamental reason for the observed atomic-like optical properties of Er³⁺ and the stability of the PL peak energy with respect to temperature. For the calculation of the band structure shown in Fig. 6b, we considered three types of structure models, that is, the 2-atom GaAs basis model (blue line), the 12-atom Ga₅As₆Er basis model (green line), and the isolated Ga₁₂As₄Er nanocluster (pink line). Three bands corresponding to the VB, IB, and CB can be distinguished and are indicated on the right side of Fig. 6b. It should be mentioned here that the bandgap of GaAs:Er was determined using the conventional exchange-correlation of the local density approximation (LDA) or generalized gradient approximation (GGA)-based DFT simulation. The LDA approximation was used to determine the bandgap of the 2-atom GaAs basis model and the 12-atom Ga5As6Er basis model. The GGA was used to determine the bandgap of the isolated Ga₁₂As₄Er nanocluster. Therefore, the obtained bandgap is much smaller than the experimentally observed value. This theoretical issue can be improved by introducing the Hubbard U to correct the self-



Fig. 5 Temperature dependence of the external quantum efficiency (EQE) and differential external quantum efficiency (\DeltaEQE) spectra. a The temperature dependence of EQE, b the temperature dependence of Δ EQE obtained from the Er900 sample with a 1340-nm long-pass filter, **c** the temperature dependence of Δ EQE obtained from the Er900 sample with a 1550-nm long-pass filter, and **d** the magnification of Er³⁺-induced Δ EQE signal around 1540 nm under 1340-nm long-pass filter as of **b**, respectively.



Fig. 6 Density functional theory (DFT) simulation results. a Local structure relaxation around the Er atom and **b** calculated band structure of Er-doped GaAs, respectively. Three types of structure models were implemented: the 2-atom GaAs basis model (blue line), the 12-atom Ga₅As₆Er basis model (green line), and the isolated Ga₁₂As₄Er nanocluster (pink line), respectively. Here CB, VB, and IB stand for conduction band, valence band, and intermediate band, respectively.

interaction $(\text{LDA} + \text{U})^{31}$, but here we adopted a scaling method to match the theoretical bandgap to the experimental one. We determined a scaling factor $\alpha \approx 2.33$, which allows us to extract the following approximate information of the sub-band: $E_{VB^-IB} \approx$ 0.45 eV, $\Delta E_{IB} \approx 0.34 \text{ eV}$, and $E_{IB^-CB} \approx 0.63 \text{ eV}$. These values should be considered only as reference to clarify that the presently considered intermediate state or IB can exist in our sample and to clarify what range of energy levels we can expect.

Based on this band structure model, the experimental results can be explained by the STPA model as schematically shown in Fig. 7. This figure shows the Er-induced IB states with a width of about 0.34 eV on the left side and three states of the Er³⁺ luminescence center on the right side (${}^{4}I_{15/2}$, ${}^{4}I_{13/2}$, and ${}^{4}I_{9/2}$). The arrows that show to the left side indicate that the energy back transfer can be triggered by either thermal activation or optical excitation. The former is the thermal back transfer corresponding to the well-known thermal quenching of PL observed from Erdoped silicon materials or III–V compounds at the onset temperature near 150 K³². The latter is the optical back transfer, which corresponds to the optically induced large decrease of PL



Fig. 7 Operating principle of the Er:GaAs energy-transfer ratchet IBSC (ETR-IBSC) device. First, a sub-bandgap photon excites an electron from the valence band (VB) to the intermediate band (IB) induced by Er doping. The recombination of this carrier generates an electron at the $4I_{13/2}$ state via an energy transfer. This carrier may be transferred back to the IB via thermal activation or optical excitation. In the sequential two-photon absorption (STPA) process, which is required for the additional current generation in the ETR-IBSC, an additional sub-bandgap photon excites the electron at the $4I_{13/2}$ state to the conduction band (CB).

observed at the onset energy of about 145 meV³³. The optical back transfer is regarded as temperature independent and can occur even at temperatures as low as 4 K³³. A general picture of back transfer model also allows the carrier to escape to other states than the IB, and this is the key of the proposed concept; the carrier at the excited state of the Er³⁺ luminescence center (the ${}^{4}I_{13/2}$ state at about 0.8 eV above the VB) can be directly excited to the energy bands or states of the host semiconductor, thus leading to the reduction of the PL of the Er3+ luminescence center. Based on this general model, the STPA demonstrated in this work is considered as an extension of the optical back transfer where the carrier at the excited state ${}^{4}I_{13/2}$ is optically excited to the CB of GaAs by the light with appropriate energy. The carriers at the excited state of the Er³⁺ center are created through an energy transfer and possess a very long lifetime (~50 $(\mu s)^{14}$, which effectively decouples the carrier in the Er³⁺ center from the VB. This realizes the ratchet effect in our IBSC. Compared to the conventional energy-transfer model, another distinct feature of our proposed model is that the electrons in the IB are generated by direct excitation from the VB instead of relaxation from the CB of GaAs. Our experimental results verify this concept and demonstrate that IBSCs based on the ratchet effect can be implemented in actual devices.

The model in Fig. 7 is now used to describe how STPA is involved in the \triangle EQE results shown in Fig. 5. First, in the case of IR illumination using the 1340-nm long-pass filter, the IR light with wavelengths >1340 nm can excite electrons in the GaAs host material from the VB to the IB. These electrons in the IB states can participate in the energy-transfer process that creates electrons at the excited state of the Er^{3+} center. The long lifetime at ${}^{4}I_{13/2}$ ensures that the carriers can be easily excited to the CB by light from the monochromator. This excitation contributes to the enhanced \triangle EQE signal observed in Fig. 5b, d. Second, for the IR light source with the 1550-nm long-pass filter, IR light is not able to excite electrons from the VB to the IB. Thus the energy exchange between the IB states and Er³⁺ center cannot occur and no ΔEQE signal is observed in Fig. 5c. Third, Fig. 5b, d also reveals that the STPA-induced Δ EQE is temperature independent up to ~100 K, which is consistent with the reported optical back transfer results³³. Furthermore, when the temperature is elevated

above 150 K, a distinct drop of the Δ EQE (due to thermal escape of carriers) is clearly observed, which is consistent with the reported onset temperature for the thermal quench of PL of Erdoped silicon materials or III-V compounds. Finally, the profile of the STPA-induced \triangle EQE in Fig. 5d exhibits two resonant peaks. One is located at 1540 nm, which coincidences exactly with the ${}^{4}I_{13/2} \leftrightarrow {}^{4}I_{15/2}$ transition energy and the PL results shown in Fig. 2a. The other one is located at 1640 nm and has a broad profile, which can be attributed to the Stark splitting due to the crystal field induced by the distortion of Er-centered GaAs environment as shown in Fig. 6a¹⁵. These results suggest that the transition from the ratchet state ${}^{4}I_{13/2}$ to the CB of GaAs also indirectly affects the transition from the Er^{3+} ground state ${}^{4}I_{15/2}$ to the excited state ${}^{4}I_{13/2}$. This strongly suggests that the STPAinduced photocurrent generation involves the transition ${}^{4}I_{13/2} \leftrightarrow$ ${}^{4}I_{9/2}$, which has the same transition energy as ${}^{4}I_{15/2} \leftrightarrow {}^{4}I_{13/2}$. This is a typical feature of two-photon up-conversion observed in Erdoped solar cell materials (the ${}^{4}I_{9/2}$ state is shown in Fig. 7 as a resonant state inside the CB of GaAs)²⁵. In other words, the STPA reported in this work shares characteristics with the twophoton up-conversion solar cell.

In order to evaluate the effect of the ETR on the IBSC device performance, we calculated the enhancement of the short-circuit current density (ΔJ_{sc}) that occurs via STPA in our sample for the effective number of suns C as defined by the IR bias light. By using the ΔJ_{sc} obtained from our ΔEQE results, the ETR-IBSC figure of merit can be defined as $\zeta = \frac{\Delta J_{sc}}{C_1 C_2}$, where C_1 and C_2 represent the effective number of suns in the first step (from the VB to the IB) and the second step (from the IB to the CB), respectively. This figure of merit is similar to the one used in the two-photon up-conversion solar cells^{34,35}. A detailed explanation of the calculation of ζ is provided in the "Methods" section. Figure 8 shows the temperature dependence of ζ for the Er900 sample, as well as the best figure-of-merit results for an a-Si:H thin film, an organic solar cell, and a crystalline c-Si solar cell enhanced by the Er3+ lanthanoid up-conversion effect as reported in the literature^{35–37}. Our ETR-IBSC figure of merit ζ below 100 K exhibits values that are comparable to one of the state-ofthe-art up-conversion-enhanced c-Si solar cell. In the temperature region between 100 and 200 K, our sample's figure of merit is



Fig. 8 Figures of merit plotted for solar cells enhanced by additional absorption of sub-bandgap photons from the sun. The blue dots show the figure of merit for our Er900 sample, which uses the sequential two-photon absorption (STPA) process via the ratchet state. The results of the figures of merit for other integration widths are represented in the filled area by using the variance of the calculated ζ determined by the figure of merit at the maximum differential external quantum efficiency (Δ EQE_{max}) spectra. We also show the best results for a thin-film solar cell (α -Si:H), an organic solar cell, and a crystalline wafer-based solar cell (c-Si) enhanced by the Er³⁺ lanthanoid up-conversion effect reported in the literature³⁶⁻³⁸.

comparable to the one reported for the organic solar cell. It should be noted that the wavelength region used for integration was limited from 1500 to 1550 nm to enable a fair comparison with the figures of merit calculated in the literature. The results of the figures of merit for other integration widths are represented by using the variance of the calculated ζ determined by the figure of merit at the maximum Δ EQE (see filled area in Fig. 8).

For the sake of clarity, we briefly discuss the internal link between the ETR effect and the two-photon up-conversion effect. From the definition of the figure of merit, $\zeta = \frac{\Delta J_{sc}}{C_{r}C_{r}}$, the lanthanoid-based two-photon up-conversion solar cell can be interpreted as a special case of the ETR effect. In fact, in the case where $C_1 = C_2$, the figure of merit becomes $\zeta = \frac{\Delta J_{sc}}{C^2}$, which corresponds to the figure of merit used in up-conversion solar cells. The equality between C_1 and C_2 originates from the use of the same light source for the up-conversion process (the two photons contribute equally to the resonant two-photon absorption process). An ideal resonance or the "entanglement" of {1st photon \leftrightarrow electron \leftrightarrow 2nd photon} would ensure that the electron at the intermediate virtual state has zero probability for relaxation to any lower lying energy state, which is of course an ideal condition that cannot be reached. However, this entanglement-induced infinite lifetime has also a drawback, since it is well known that the entangled absorption process imposes tremendous difficulties in both understanding the physics of the virtual state and upconversion dynamics as well as manipulating the light absorption dynamics. From this point view, the ETR-IBSC disentangles the up-conversion process and allows a controllable two-step light absorption process, which might be considered as a more practical approach toward a solar cell that is enhanced with a nonlinear light absorption effect.

Although the current density improvement in our present ETR-IBSC has already a magnitude comparable to other twophoton up-conversion solar cells, the low quantum yield at room temperature is a major issue for applications. Various approaches are under consideration to solve this issue. The most straight-forward approach is to adopt the (GaAs:Er+2O) or (GaAs:Er³⁺ + Yb³⁺) co-doping techniques, which are well-established techniques used in rare-earth-ion-centered luminescent light sources to reach larger quantum yields at room temperature^{38,39}. Mean-while, it should be noted that the ETR effect reported here is not restricted to Er³⁺-doped GaAs devices. Other lanthanoid elements are also expected to exhibit the same or a similar behavior. We therefore expect multiple-rare-earth-ion-hybridized GaAs ETR-IBSCs to absorb a wide range of that part of the solar spectrum that has wavelengths beyond the GaAs absorption edge.

Conclusion. In this work, we performed an experimental investigation of the ratchet effect in Er-doped GaAs solar cells. The optical characterization of Er-doped GaAs grown by MBE showed that the energy level at 1540 nm exhibits an atomic-like PL signal whose peak energy is almost independent of the temperature. Four Er-doped GaAs solar cells were fabricated by varying the Er concentration in the *i*-layer of the junction. Temperature-dependent differential EQE experiments revealed that the Er900 sample (grown at an Er cell temperature of 1173 K) showed a current enhancement via STPA at a wavelength of 1540 nm. Based on the differential EQE spectra, we determined the ETR-IBSC figure of merit ζ and we found that it is comparable to the figures of merit of other up-conversion-enhanced solar cells up to 200 K. Finally, an IBSC model including the ratchet effect was proposed to explain the observed results based on the electronic structure calculated using DFT simulations. We note that the experimental results presented here are still at a preliminary stage in terms of the solar cell energy conversion efficiency. We also emphasize that, despite our experimental results rigorously demonstrating the proposed operation principle of STPA in ETR-IBSC device, it is by no means certain that we could completely rule out the possibility that there exists an alternative channel for the STPA not to occur via Er³⁺ but instead via IB directly. Furthermore, the fundamental STPA mechanism and dynamics of the Er-doped states have not yet been fully understood. With respect to experiments, deep-level transient spectroscopy or Fourier transform IR spectroscopy could reveal additional information regarding the dynamic behavior of the ETR effect. With respect to theory, modeling of the many-body physics involved in the energy transfer in STPA is considered necessary for device development.

Methods

Preparation of sample for PL measurements. After GaAs surface oxide desorption, a 250-nm-thick GaAs buffer layer was grown on a GaAs (001) substrate at 853 K (determined by an optical pyrometer) to obtain an atomically smooth surface. Then the Er-doped GaAs thin film was grown at a growth rate of 1 μ m h⁻¹. To identify suited growth conditions, the samples were grown using different growth temperatures and cell temperatures. The Er cell temperature was varied from 973 to 1273 K. The As beam equivalent pressure was kept constant at 2.4 × 10⁻⁵ Torr. The surface morphologies of the Er-doped GaAs layers were characterized by atomic force microscopy and reflection high-energy electron diffraction and will be reported elsewhere. Secondary ion mass spectroscopy was employed to determine the Er concentration (CAMECA IMS-7f, O₂⁺ at 3 keV with a raster size of 30 µm²).

Preparation of solar cell devices. After oxide removal of the *n*⁺-GaAs (001) substrate, a 200-nm-thick *n*-type GaAs buffer layer $(n = 1 \times 10^{18} \text{ cm}^{-3})$ and a 1-µm-thick *n*-type GaAs *n*-layer ($n = 1 \times 10^{17}$ cm⁻³) were grown at a growth rate of 1 µm/h. The growth of the p-i-n device structure, which contains the Er:GaAs ilayer, was followed by a growth of a p-Al_{0.3}Ga_{0.7}As window layer with a thickness of 250 nm. Finally, a heavily doped p^+ -GaAs contact layer ($p = 1 \times 10^{19} \text{ cm}^{-3}$) with a thickness of 50 nm was prepared. For the current-voltage measurements, we prepared AuZn/Au electrodes on the top (by vacuum evaporation under 2×10^{-6} Torr) and an In contact on the backside of the solar cell. To obtain a high-quality GaAs layer, we employed a growth temperature of 853 K for all layers of the solar cell. In order to study the effect of the Er-doping amount on the performance of ETR-IBSCs, four samples with different Er doping (referred to as Er700, Er800, Er900, and Er1000 corresponding to Er cell temperatures of 973, 1073, 1173, and 1273 K, respectively) were fabricated. As a reference, a control GaAs solar cell was also grown with the same device structure and doping profiles but without Er in the i-region.

STPA measurements. The data were recorded with a lock-in technique. Here the intensity of the IR illumination was modulated by a chopper and the light that has

passed the monochromator was continuously illuminating the sample at given wavelength. The current that is generated due to the continuous illumination (we consider generation processes like thermal excitation, up-conversion, or direct band-to-band excitation) constitutes the direct current baseline signal in the lock-in measurement and thus is not included in the final differential EQE spectrum. The in-phase alternating current signal was recorded by the lock-in amplifier to probe the transitions that are induced by the additional IR light. The monochromator is used to scan the excitation energy to measure the whole ΔEQE spectrum.

Figure-of-merit calculation. The enhancement of the short-circuit current density via STPA, ΔJ_{sc} is calculated from the Δ EQE spectrum at each temperature in order to evaluate the effect of the ETR on the IBSC device performance:

$$\Delta J_{\rm sc} = Ce \int I_{\rm AM1.5G}(\lambda) \Delta EQE \, d\lambda$$

Here *C* is the effective number of suns imposed by the IR bias light, and $I_{AM1.5G}$ is the solar irradiance of the AM1.5G reference solar spectrum in units of W m⁻¹ nm⁻¹ from the National Renewable Energy Laboratory. By using SI units for all the physical constants on the right-hand side of the equation, the current density in units of mA cm⁻² can be approximated in a discretized form as:

$$\Delta J_{\rm sc} = 8 \times 10^{-5} \cdot \Delta \lambda \sum_{i=1}^{N} I_{\rm AM1.5G}(\lambda_i) \Delta E Q E_i \lambda_i$$

We used the calibrated $J_{\rm sc}$ of a standard single-junction Si solar cell and an InGaP/GaAs/Ge triple-junction solar cell to tune the wavelength interval $\Delta\lambda$ to ensure the accuracy and reliability of the calculated results⁶. The ETR-IBSC figure of merit, ζ , is then calculated as follows:

$$\zeta = \frac{\Delta J_{\rm sc}}{C_1 \ C_2}$$

Here C_1 (1 sun) and C_2 (0.7 sun) represent the effective number of suns in the first step (from the VB to the IB) and the second step (from the ratchet state to the CB) of the STPA process in our device, respectively.

DFT and MD simulations. The electronic band structures for various GaAs:Er materials were performed by using the Kohn–Sham self-consistent DFT code SIESTA with a GGA (GGA-PBE) exchange–correlation functional and a double- ζ polarized atomic-orbital basis set. The cutoff energy was 100 Ry. The MD simulations were conducted by using the conjugate gradients (CG) method. During this calculation of the structural relaxation, the cell volume is kept constant in a variable-cell relaxation approach. The maximum force tolerance was set to 0.04 eV \dot{A}^{-1} and the maximum atomic displacement in the CG optimization was set to 0.04 Å. Meanwhile, Pulay mixing was used to accelerate the convergence in the following way: $p_{in}^{n+1} = \alpha \bar{\rho}_{out}^n + (1 - \alpha) \bar{\rho}_{in}^n$, where the $\bar{\rho}_{out}$ and $\bar{\rho}_{in}^n$ are input and output matrices constructed from the weighted sum of the previous self-consistent field (SCF) cycles. For the GaAs:Er structural relaxation, the number of Pulay SCF cycles was set to 10 and the mixing weight α was set to 0.1.

Data availability

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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Author contributions

T.S. and Y.O. planned and organized the experiment and analysis. C-Y.H. carried out the solar cell device fabrication and PL experiment. R.T. carried out the temperature-dependent STPA measurement. T.S. and S.T. carried out the theoretical simulation. K.Y. and N.E.-D. contributed to research design. T.S. and C-Y.H. wrote the manuscript. Y.O. supervised the project. All authors discussed the results and agreed on the final contents of the manuscript draft.

Competing interests

The authors declare no competing interests.

Additional information

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