Energy relaxation in optically excited Si and Ge nanocrystals

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CHAPTER 4

Optical extraction of hot-carrier energy

This chapter quantifies the efficiency of the Si nanocrystals-mediated PL from Er\(^{3+}\) ions embedded in SiO\(_2\) matrix. Quantum yield of this emission increases in a step-like manner with the excitation energy. By comparing differently prepared materials, it is explicitly demonstrated that the actual values of the threshold energies and the rate of the observed increase of the external quantum yield depend on sample characteristics. In that way detailed insights into the efficient excitation of Er\(^{3+}\) ions are obtained. In particular, the essential role of the hot-carrier mediated excitation route is established, and its possible application scheme for future photovoltaics is put forward.
4.1 Introduction

Efficient conversion of photon energy is at the heart of many optoelectronic applications and, prominently, detectors and solar cells. For that purpose new materials and also new physical processes are intensively explored and considerable progress is being made, especially the efficiency of solar cells steadily increasing over the last few decades. In these efforts, a major possibility for further improvement now lies in the (efficient) use of the excess energy of hot carriers. Such carriers are generated by photons whose energies considerably exceed the bandgap of the absorber and their excess energy is typically converted into heat. Harvesting this energy is highly challenging, since thermalization of hot carriers with the host typically takes place on a picosecond time scale or faster. In photovoltaics, heat dissipation by hot carriers constitutes a major loss channel responsible for the Shockley-Queisser efficiency limit [1]. Two currently explored strategies to resolve this problem involve: (i) CM [53-55], where the excess energy is converted into additional electron-hole pairs, and (ii) extraction of hot carriers at an energy higher than that determined by the absorber bandgap [56-60]. Both strategies have essential shortcomings since (i) CM is sufficiently efficient only in nanostructures where charge extraction becomes problematic, and (ii) making use of energy-selective contacts, hot-carrier solar cells are notoriously inefficient.

Here a different approach, in which the excess energy of hot carriers is converted into IR photons, and in this manner optically extracted, is considered. Therefore, the hurdles of the present ‘traditional’ strategies can be avoided, which makes this approach interesting for photovoltaics. This optical extraction of hot-carrier energy has been theoretically modelled and it is stated that this concept might attain an upper efficiency approaching that of the ideal conventional hot-carrier solar cells [61]. Figure 4.1 compares the presently considered solar-cell concepts for extraction of hot-carrier energy [60] – Fig. 4.1(a) – with the optical variant described in this study – Fig. 4.1(b). The proposed scheme, where absorption of a high-energy photon generates a hot carrier whose cooling results in emission of (multiple) IR photons is conceptually similar to ‘photon cutting’ with RE ions [62], but is potentially much more efficient.

The RE-doped materials are frequently investigated for the purpose of light transformation by means of photon down- and up-conversion. RE-based phosphors utilizing photon down-conversion [62-64] are commonly used in (white) lighting applications, converting UV photons into the visible range. Also up-conversion, i.e., emission of high-energy photons upon sequential excitation at a lower energy, has been demonstrated [65,66]. However, the common disadvantage of ‘spectral conversion’ with RE ions is their extremely low absorption cross-section, due to the only-marginally-allowed character of the
optical transitions within the 4f-electron shell.

Figure 4.1: (a) Three currently considered hot-carrier solar cell strategies: a direct extraction of hot carriers through energy-selective contacts, application of an intermediate band-assisted absorber, and multiple exciton generation, when a hot carrier induces additional excitations across the bandgap. (b) The concept of optical extraction: a hot carrier transfers its excess energy to nearby Er$^{3+}$ ions, which subsequently emit IR photons.

Our approach makes use of thin films of Er-doped solid-state dispersions of Si NCs in SiO$_2$. As described in the previous chapter, the detailed TR spectroscopy of Si NC-mediated PL of Er$^{3+}$ ions revealed two major energy transfer mechanisms leading to the 0.8 eV (1.5 μm) emission, distinguishable by their dynamics: a slow one (microseconds), due to non-radiative recombination of an exciton, and a fast one, due to intraband transitions of hot carriers (sub-nanosecond range) [32,43]. The hot-carrier mediated excitation requires the sufficiently large excess energy, and therefore appears only at sufficiently high excitation energies, or at sufficiently high fluxes of low-energy photons, as Auger recombination of multiple excitons generated in the same NCs also produces hot carriers. The present study confirms this initial result by showing that at low flux pumping, the initial fast component in dynamics of Er-related PL appears only upon high energy excitation. In order to investigate the potential of the Si NC-mediated emission from Er$^{3+}$ ions for UV-to-IR spectral conversion, the EQY (defined as the ratio between the numbers of emitted and absorbed photons) of Er-related PL is determined. It is demonstrated that the EQY increases above a certain threshold of excitation energy, as the excitation channel by hot carriers is activated. The effects of material characteristics (size of Si NCs, concentration of Si NC and Er$^{3+}$ ions) on the EQY of Er-related PL are discussed. This provides detailed insights on the excitation and energy
Optical extraction of hot-carrier energy

transfer processes taking place in this material. Finally, a possible practical application of the NC-sensitized Er-related PL for development of ‘solar shapers’ for the next generation photovoltaics is given.

4.2 External quantum yield
4.2.1 EQY of Si NCs and Er-related PL
Figure 4.2 presents a comparison of EQY of Si NC- and Er-related emission bands in Er-doped and Er-free samples as function of excitation photon energy. Both samples have identical average diameter and concentration of Si NCs, \(d_{NC} = 4\) nm and \([NC] = 2.1 \times 10^{18}\) cm\(^{-3}\), respectively. The NC-related PL in the undoped sample has a constant EQY of \(\sim 6.5\%\) for excitation energies below \(\sim 2.5\) eV, and increases in a step-like manner above this threshold. This behavior has been observed in the past for similar material and assigned to a specific CM process, which increases the number of excitons generated by absorption of a single photon with a sufficiently high energy [33,36].

![Figure 4.2: The external quantum yield (EQY) of Si NC- (blue) and Er-related (red) PL from undoped (open circles) and Er-doped (solid circles) samples. Both samples have the similar average Si NC diameter and concentration of \(d_{NC} = 4\) nm and \([NC] = 2.1 \times 10^{18}\) cm\(^{-3}\), respectively.](image)

Upon doping with Er\(^{3+}\) ions, the EQY of NC-related PL is overall reduced, indicating that though the relevant CM process is still active, the PL efficiency of NCs is quenched. This is readily understood, since in the doped sample, a part of the NCs transfer their energy to the neighboring Er\(^{3+}\) ions and therefore do not
emit. Further, the EQY of the Er-related PL also shows a threshold-governed increase, but with the threshold energy significantly lower than that for CM. The increase of EQY from the initial value of ~ 0.5% appears due to the onset of the hot-carrier mediated Er\textsuperscript{3+} ion excitation process, which operates at higher pump energies, in addition to the slow exciton energy transfer [33]. The threshold for the activation of the hot-carrier mediated excitation is given by the sum of the bandgap energy of Si NCs and the 0.8 eV energy of 1\textsuperscript{st} excited state of Er\textsuperscript{3+} ion, and for this particular material appears at $E_1 = 2.0-2.1$ eV. For the highest investigated pump photon energy of 4.25 eV the EQY of Er-related PL reaches ~ 4.5 %, representing a ~ 9-fold enhancement.

### 4.2.2 EQY dependence on Si NCs sizes

Figure 4.3 compares the EQY of Er-related PL as a function of excitation energy for two samples which have identical concentrations of Si NCs and Er\textsuperscript{3+} ions, of \([\text{NC}] = 2.1 \times 10^{18} \text{ cm}^{-3}\) and \([\text{Er}^{3+}] = 2.7 \times 10^{19} \text{ cm}^{-3}\), respectively, but a different size of Si NCs - with average diameters of $d_{\text{NC}} = 4 \text{ nm}$ (a) and $d_{\text{NC}} = 3 \text{ nm}$ (b).

![Figure 4.3: EQY of Er-related PL from the samples with Si NC diameter of $d_{\text{NC}} = 4 \text{ nm}$ (a) and $d_{\text{NC}} = 3 \text{ nm}$ (b). Both samples have the same concentrations of Si NCs ([NC] $= 2.1 \times 10^{18} \text{ cm}^{-3}$) and Er\textsuperscript{3+} ions ([Er\textsuperscript{3+}] $= 2.7 \times 10^{19} \text{ cm}^{-3}$). Insets show the excitonic PL spectra recorded for both samples.](image)

As can be seen, for both materials EQY is characterized by a constant value for low excitation energies up to a certain threshold, after which it increases. For 4
nm sized Si NCs the onset is \( E_{\text{th4}} \approx 2.0 \text{ eV} \), while for smaller Si NCs of 3 nm this onset is somewhat higher, at \( E_{\text{th3}} \approx 2.2 \text{ eV} \). The inset of both figures shows the Si NCs emission spectra for the investigated samples, with the emission bands peaking at \( E_{\text{PL4}} \approx 1.37 \text{ eV} \) and \( E_{\text{PL3}} \approx 1.55 \text{ eV} \) for Si NC diameters of \( d_{\text{NC}} = 4 \text{ nm} \) and \( d_{\text{NC}} = 3 \text{ nm} \), respectively. It is clear that the shifts of the emission peak \( E_{\text{PL}} \) and the EQY threshold energy \( E_{\text{th}} \) are mutually correlated. Other than different thresholds, the absolute values as well as the enhancement rate of EQY at higher excitation energies are also sample-dependent. For the material with \( d_{\text{NC}} = 4 \text{ nm} \), EQY of Er-related PL rises within the investigated range from \( \sim 0.5\% \) to \( \sim 4.5\% \), showing at an excitation energy of 4.25 eV the relative increase of 9 times. For the sample with \( d_{\text{NC}} = 3 \text{ nm} \), the absolute EQY is higher, – rising from \( \sim 1\% \) to \( \sim 6.5\% \), while the relative enhancement is lower, reaching \( \sim 6.5\text{-fold} \) at 4.25 eV. In addition, we also note that for the sample with the smaller linewidth of the emission band \( (E_{\text{PL}} \approx 1.55 \text{ eV}, d_{\text{NC}} = 3 \text{ nm}) \) the EQY dependence has a step-like character; we recall that such a step-like behavior has previously been observed for carbon nanotubes [67] and Si NCs [36], and also has been modelled theoretically for the MEG in semiconductor NCs [68].

### 4.2.3 EQY dependence on Er contents

The EQY of 0.8 eV Er-related PL for three samples with identical size \( (d_{\text{NC}} = 3 \text{ nm}) \) and concentration \( ([\text{NC}] = 4.1 \times 10^{18} \text{ cm}^{-3}) \) of Si NCs, but different Er content of \( [\text{Er}^{3+}] = 0.5, 1.1 \text{ and } 2.8 \times 10^{19} \text{ cm}^{-3} \) is compared in Fig. 4.4.

![Figure 4.4: Comparison of the EQY of the Si NC-mediated Er-related PL from three samples having different Er\(^{3+}\) ion concentrations but with a similar Si NC size and concentration: the enhancement of the EQY at higher excitation energies increases with the Er concentration.](image-url)

\[ \text{EQY} \]
With increasing Er\(^{3+}\) ion concentration the mutual Er-to-NC ratio is increasing (from 1.2 to 7), and one can anticipate that the NC-to-Er energy transfer might be enhanced. As can be seen, a similar threshold-governed increase in EQY is observed for all the three samples, with the same initial value of the EQY of < 1% and the threshold energy of \(E_{\text{th}} \approx 2.2 \text{ eV}\). The subsequent enhancement of EQY for higher energies, however, is clearly different, increasing with the Er\(^{3+}\) ion concentration.

### 4.2.4 EQY dependence on Si NC concentration

EQY of 0.8 eV Er-related PL for two samples with an identical Si NCs size (\(d_{\text{NC}} = 3 \text{ nm}\)) and concentration of Er\(^{3+}\) ions ([Er\(^{3+}\)] = 2.8\times10^{19} \text{ cm}^{-3}\)), but different Si NCs concentration are compared in Fig. 4.5. A step-like behavior is observed for both samples, with the similar threshold energy of \(E_{\text{th}} \approx 2.2 \text{ eV}\), but with the subsequent enhancement being clearly higher for the material with the lower concentration of Si NCs. The microscopic origin of this change is unclear, but it can be speculated that it might be related to a reduction of the energy transfer among Si NCs, or to a better crystalline quality/lower defect level of the layer with a lower concentration of Si NCs.

![Figure 4.5: The comparison of the EQY of two samples having same Er\(^{3+}\) ion concentration and Si NCs size but different Si NC concentrations. The enhancement of the EQY is lower in the sample with higher Si NC concentration.](image)

As can be concluded from the presented experimental results, the excitation dependence EQY of the 0.8 eV Er-related PL band sensitized by Si NCs exhibits a threshold-governed increase with the excitation energy. While both the
threshold energy value $E_{\text{th}}$ and the rate of the subsequent enhancement depend on material parameters, these two basic features are omnipresent.

### 4.3 Hot-carrier mediated Er excitation

As already mentioned in the introduction, past investigations of the Si NC sensitization of Er-related PL revealed a hot-carrier mediated excitation process of Er$^{3+}$ ions [32,43]. Such carriers appear in Si NCs upon absorption of high energy photons. In an Auger process involving a fast intraband transition, a hot carrier may efficiently transfer energy to a proximal Er$^{3+}$ ion, which can then be promoted directly to the first $^4I_{13/2}$ excited state responsible for the 0.8 eV emission. (This excitation mechanism is a direct analog of the impact excitation of Er$^{3+}$ ions in bulk Si [22]). The hot-carrier induced energy transfer is then responsible for the ultrafast appearance of Er-related PL, within nanoseconds after the laser pulse, illustrated by the high-resolution PL decay dynamics for one of the samples investigated in this study ($d_{\text{NC}} = 3$ nm, $[\text{NC}] = 2.1 \times 10^{18}$ cm$^{-3}$, $[\text{Er}^{3+}] = 2.7 \times 10^{19}$ cm$^{-3}$), as shown in the previous chapter (Fig. 3.2).

![Figure 4.6: Decay dynamics of 0.8 eV Er-related emission for the first 300 ns after the excitation pulse. The fast component appears for above-threshold excitation and increases with higher excitation energies. The inset shows the integrated Er-related emission at 0.8 eV as a function of the initial amplitude of the fast decaying signal. All data has been obtained for the same sample with $d_{\text{NC}} = 3$ nm, $[\text{NC}] = 2.1 \times 10^{18}$ cm$^{-3}$ and $[\text{Er}^{3+}] = 2.7 \times 10^{19}$ cm$^{-3}$.](image)

While the efficient Er excitation process experiences strong reversal due to the energy back-transfer to free carriers available in a NC, some of the excited
dopants escape this non-radiative recombination (possibly also due to a resonant energy diffusion within the Er$^{3+}$ ions network), and contribute to the 0.8 eV emission; this is illustrated by the fact that the initial fast PL signal does not decay to zero. In that way, the total experimentally measured intensity of the Er-related PL contains contributions from Er$^{3+}$ ions excited by the two excitation channels – the slow exciton-related one and the ultrafast one, which is enabled by hot carriers. The contribution of the impact excitation will be proportional to the initial amplitude of the fast decaying PL. Figure 4.6 illustrates the initial decay dynamics, experimentally measured for several excitation energies, normalized to an equal (and low) photon flux. As can be seen, the fast decaying component indeed appears for the above-threshold pumping and then increases at still higher energies. This is confirmed in the inset to Fig. 4.6, which shows the total (time integrated) PL intensity observed over the entire investigated excitation energy range as a function of the initial PL amplitude of the corresponding transient. A linear dependence between the two is found which proves that the total enhancement of EQY at higher pump energies arises due to the hot-carrier excitation mechanism.

### 4.4 Microscopic model

Excitation mechanisms that can be responsible for the observed step-like enhancement of 0.8 eV Er-related PL will be discussed now. For this purpose, the EQY of one of the samples with $d_{\text{NC}} = 3 \text{ nm}$, is plotted in Fig. 4.7. The observed excitation energy dependence of EQY is divided into four regions, corresponding to the individual steps in the experimentally obtained data. For a better illustration, the proposed interpretations of the relevant threshold energies are depicted in the lower panel, by displaying the appropriately shifted PL spectrum; in that way the size distribution, and consequently the bandgap energy distribution, of Si NCs are taken into account.

#### 4.4.1 Slow excitation process

Range #1 in Fig. 4.7 corresponds to the excitation region where only the exciton-mediated excitation of Er$^{3+}$ ions is possible. In this range, photons with energies exceeding the NC bandgap $h\nu > E_{\text{PL}}$ are absorbed by Si NCs and generate (low energy) electron-hole pairs (excitons). The non-radiative recombination of these excitons in Si NCs can transfer energy to Er$^{3+}$ ions bringing these into one of the higher excited states corresponding to exciton energy, with or without phonon participation. The characteristic transfer time $\tau_1$ of this process depends on the NC-Er distance and for Er$^{3+}$ ions situated within a NC or close to its surface is of the order of nanoseconds (or even shorter) [69]. After that, however, internal relaxation to the $^4I_{13/2}$ state is still required before emission at 0.8 eV can appear.
The relevant relaxation time $\tau_2$ is of an order of microseconds [32,69]. Combination of these two time constants is responsible for the slow rise of Er-PL within several microseconds after the excitation pulse – see dynamics of 0.8 eV Er-related PL in Fig. 3.2 (previous chapter). Therefore, in the excitation energy range #1, independent of its energy, a single photon absorbed by a Si NC can excite, at most, a single Er$^{3+}$ ion. This explains the flat character of the measured EQY dependence. For the sample whose data are depicted in Fig. 4.7, the EQY of the exciton-mediated excitation is \(~1\%\), but varies from sample to sample, as can be concluded from the experimental results of this study. The proposed interpretation of the excitation mechanism taking place for energies in range #1 is shown schematically in Fig. 4.8.

![Figure 4.7: EQY of 0.8 eV Er-related PL at different excitation energies. Different regions are assigned to different excitation processes and the lower panel shows the Si NCs PL shifted appropriately to illustrate the responsible excitation route.](image-url)
Figure 4.8: Schematic illustration of Er$^{3+}$ excitation in the energy range #1. Non-radiative recombination of the (low-energy) exciton in the Si NC brings the near Er$^{3+}$ ion into one of the higher states ($\tau_1$), after which an internal relaxation to the emitting state follows ($\tau_2$). At maximum, only a single Er$^{3+}$ ion can be excited per one absorbed photon. The illustration is for 3 nm sized Si NCs.

4.4.2 Fast excitation process

As discussed before, the intraband cooling of hot carriers facilitates the second excitation channel for Er$^{3+}$ ions, directly into the first excited state $^4I_{13/2}$ responsible for the 0.8 eV PL. Past theoretical modeling [69] has shown that for the fastest transitions in a NC with diameter $d_{NC} = 3$ nm, the time scale of this excitation can reach ~ 0.5 ns for Er$^{3+}$ ions located on the NC surface. It has also been established [43] that a major part – ~ 50% or more – of all the Er dopants can receive energy in this way; this in contrast to the exciton-mediated mechanism which reaches only a minor part of Er contents. It is therefore not surprising that the fast excitation process is responsible for the experimentally observed enhancement of EQY. At the same time, the fast and efficient excitation of an Er$^{3+}$ ions provides a unique opportunity to extract the excess energy of hot carriers generated in Si NCs. The fast excitation process requires free carriers with a certain excess energy, and therefore appears only upon excitation with photon energies exceeding a threshold value given by $E_1 = E_{PL} + E_{Er1} + \Delta$, corresponding to the NC “optical” bandgap (emission energy), the energy of the first excited state of Er$^{3+}$ ion (equal to 0.8 eV), and some additional
Optical extraction of hot-carrier energy

energy required to enable the transfer process, respectively. This implies that the threshold energy value is directly related to the emission spectrum of NCs, as indeed can be concluded from the data in Fig. 4.3: where the threshold energy for the sample with the smaller NCs is somewhat higher, similarly as its PL spectrum. For the sample whose EQY is depicted in Fig. 4.7, the threshold energy is $E_1 \approx 2.2$ eV; taking into account the corresponding PL spectrum, this implies that the energy loss is $\Delta = 0.1-0.2$ eV. For excitation energies $E_{\text{exc}} > E_1$, the excess energy of a hot carrier is sufficient for impact excitation of an Er$^{3+}$ ion, and now two Er$^{3+}$ ions can be excited upon absorption of a single photon. This increases the total EQY, as the threshold excitation energy is gradually exceeded for more NCs within the ensemble. Interestingly, the absolute value of EQY which is achieved in range #2, is more than twice that of range #1; this directly implies that more NCs participate in the hot-carrier mediated “fast” excitation than in the “slow” process, and is consistent with its much faster dynamics, as indeed experimentally observed in Fig. 4.6. The proposed hot-carrier mediated excitation process activated in range #2 following the first threshold is schematically shown in Fig. 4.9 (a).

\[ \text{Two excitations per photon} \]

(a) Si NC

(b) Si NC

\[ \text{Er}^{3+} \]

Figure 4.9: Schematic illustration of Er excitation process at higher pump energies. The proposed process of excitation of two Er$^{3+}$ ions per absorbed photon by a combination of exciton recombination and hot-carrier cooling with energy transfer to (a) the first excited state of Er$^{3+}$, range #2, and (b) the second excited state of Er$^{3+}$, followed by internal relaxation, range #3.
The next threshold in the EQY dependence in Fig. 4.7 is found at $E_2 \approx 2.5$ eV. We propose to relate it to the fact that at this point, carrier excess energy reaches the value of the second $^4I_{11/2}$ excited state of Er$^{3+}$ ion of 1.2 eV: $E_2 = E_{PL} + E_{Er2} + \Delta = E_1 + 0.4$ eV. Therefore in range #3 impact excitation becomes possible not only to the first, but also to the second excited state, $^4I_{11/2}$ [70]. While in this range still 2 Er$^{3+}$ ions can be excited by a single photon, reaching this threshold slows down the increase of the population rate of the $^4I_{13/2}$ state responsible for 0.8 eV PL, as not all Er$^{3+}$ ions excited to the $^4I_{11/2}$ state will eventually relax to $^4I_{13/2}$. The excitation scheme considered for range #3 is schematically illustrated in Fig. 4.9 (b).

![Three excitations per photon](image)

*Figure 4.10: Range #4: excitation of three Er$^{3+}$ ions per absorbed photon, with two possible scenarios – either direct excitation of three Er$^{3+}$ ions or the sharing of energy between 2 Er$^{3+}$ ions.*

Upon further increase of pump energy – range #4 – hot carriers capable of excitation of 2 (and more) Er$^{3+}$ ions are being generated. The lowest possible threshold for that is given by $E_3 = E_{PL} + 2E_{Er1} + \Delta$. From data in Fig. 4.7 that is $E_3 \approx 3.2$ eV. Following that threshold, excitation of three Er$^{3+}$ ions per absorbed photon becomes possible, two by the hot-carrier mediated fast process and one by the exciton recombination. Moreover, in that range also an alternative process is possible, when first a hot carrier excites a nearby Er$^{3+}$ ion into still higher excited state ($^4I_{9/2}$ or higher), which subsequently shares part of its energy with
another proximal Er$^{3+}$ ions [70]. This process is a reversal of the concentration quenching, well known for heavily Er-doped materials [71]. Therefore, instead of a direct excitation of three Er$^{3+}$ ions from Si NC, there appears an indirect transfer path through Er$^{3+}$ ions. In Fig. 4.10 both these scenarios possible in range #4 are schematically illustrated. For pumping with energies $E_{\text{exc}} > E_3$, a single photon might excite 3 (and then more) Er$^{3+}$ ions, which is then responsible for the experimentally measured further increase of EQY. Subsequent threshold energies are difficult to distinguish, as more and more possibilities for multiple Er excitations might appear.

### 4.5 Theoretical support

In order to rationalize the proposed microscopic model for the step-like enhancement of EQY at higher pump energies, we note that Er-excitation involving hot carriers competes with other carrier relaxation processes, and, prominently electron-phonon scattering. According to the general understanding, the energy relaxation of hot carriers is determined by the emission of optical phonons [72,73]. To estimate the phonon relaxation rate, the Monte-Carlo simulations of the energy relaxation by phonon scattering in Si NC with $d_{\text{NC}} = 2.5$ nm are shown in Fig. 4.11.

![Figure 4.11: Monte-Carlo simulation of excess energy relaxation of hot electrons in Si NCs with $d_{\text{NC}} = 2.5$ nm. Black dashed line depicts the relaxation rate without phonon recycling taken into account. Taking that into account can only make the relaxation slower. – See other lines for phonon reabsorption with (red, dashed) and without (blue) decay.](image)

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Optical extraction of hot-carrier energy
At each step of the simulation the emission and absorption of phonons by an electron and phonon decay are considered. The black/dashed line shows the excess energy dependence on time for the electrons with the initial energy 3 eV above the bottom of the conduction band. As can be seen, the extrapolation gives the relaxation time of approximately 13 ps, with the average relaxation rate of about 0.8 eV per 5 ps. Taking into account the Si NC – Er\(^{3+}\) energy transfer time of an order of 0.5 ns [69], we arrive to efficiency of the hot-carrier mediated excitation of an order of 1 \%, in reasonable agreement with the experimental results. Moreover, the cooling time significantly increases when a possibility of phonon reabsorption (dotted line) is considered, even when a (reasonable) model of phonon decay is taken into account (solid line). Further, the rate of Er-excitation due to intraband transition is expected to decrease for smaller NCs, being proportional to \(d_{\text{NC}}^{-4}\) [32]; this is indeed confirmed by the experimental results, which show reduction of the EQY value upon increase of the NC size - see Fig. 4.3.

### 4.6 Outlook

From all the presented experimental results it can be concluded that, in order to maximize the energy extraction from hot carriers (i) the ratio of [NC]/[Er\(^{3+}\)] should be high and (ii) a smaller diameter of NCs with superior crystalline quality is preferred. The EQY for a sample prepared according to this preliminary and crude guidance (\(d_{\text{NC}} = 2\) nm, [NC] = \(2 \times 10^{19}\) cm\(^{-3}\), [Er\(^{3+}\)] = \(2 \times 10^{20}\) cm\(^{-3}\)) is depicted in Fig. 4.12: in this case ~ 9% of EQY is induced by the hot-carrier energy, which is a ~ 15-fold increase over the investigated energy range.

The EQY of 9% at excitation of 4.25 eV implies that we get 9 photons of 0.8 eV per absorption of 100 photons of 4.25 eV. In the absolute terms we get then 7.2 eV of optically extracted energy per 245 eV of excess energy of hot carrier generated in Si NCs with a bandgap of 1.8 eV. This gives then the experimentally demonstrated net external extraction efficiency of hot carrier excess energy of 3%.

Efficient conversion of a single high-energy photon into multiple photons of lower energy could find interesting applications in, e.g., optoelectronics and photovoltaics. The first step then would be the improvement of the initial flat/baseline in EQY – range #1. Since the excitonic energy transfer is rather slow, it is only possible for Si NCs with sufficiently long exciton lifetime, i.e. those which would recombine radiatively in the absence of Er. Therefore, EQY in the range #1, indirectly reflects the level of the ‘optical activity’ of Si NCs [74]. In the investigated material the optical activity of Si NCs is quite low and needs to be improved. Past investigations have indicated that the optical activity
Optical extraction of hot-carrier energy

of Si NCs can reach 60% in carefully optimized materials [75]. Future work must show whether reaching such a high degree of optical activity will also be possible for Er-doped materials. To this end the low temperature post annealing in H$_2$ environment could be explored, since it has been shown to enhance the optical activity within ensembles of Si NCs, reducing the number of the so-called ‘dark’ NCs undergoing fast non-radiative quenching of excitons [74]. For the improvement of EQY in regions #2-4 the hot-carrier mediated excitation must be optimized. In the present case, the large initial amplitude of the hot-carrier mediated Er PL evident in temporal dynamics – see, Fig. 4.6 – proves that the energy transfer is actually nearly 100% efficient, and points out that further research has to concentrate on elimination of the non-radiative quenching of the (originally high) excited Er population, which reverses the excitation process in materials investigated in this study.

![Figure 4.12: EQY of a Er-related PL in a sample with high concentration of Er$^{3+}$ ions, showing a ~ 15-fold increase in EQY over the investigated energy range. (d$_{NC}$ = 2 nm, [NC] = 2×10$^{19}$ cm$^{-3}$, [Er$^{3+}$] = 2×10$^{20}$ cm$^{-3}$).](image)

### 4.7 Photovoltaics prospect

When the sufficiently high level of EQY has been reached, then SiO$_2$ layers with Si NCs and Er$^{3+}$ ions could form the basis for a light conversion layer (‘solar shaper’ [76]) specifically targeted for extraction of hot-carrier energy. This energy is typically lost to heat in solar cells, and its harvesting is generally recognized as a very promising route towards the next generation photovoltaics. The upper limit for the energy conversion efficiency of the discussed process can be evaluated. For this purpose we take the experimentally found step-like
characteristics of EQY and assume that all other recombination processes in Si NCs have been eliminated and all the absorbed energy is being stream-lined to Er$^{3+}$ ions and transformed into 0.8 eV photons. The result is shown in Fig. 4.13, and compared to what could be achieved with a Si layer (and what indeed takes place in a standard Si solar cell).

As can be seen, for the blue edge of the solar spectrum the theoretical energy conversion efficiency reaches 75-80 %, with a single photon being converted into 4 photons of 0.8 eV. This is approximately 3 times higher than for Si and illustrates the theoretical efficiency limit of this conversion mechanism. Finally, we note that the considered spectral transformation represents an optical equivalent of the multiple carrier generation at the optimal energy of 0.8 eV; the theoretical limit of the conversion efficiency is in this case ~ 45 % [37], considerably above the Shockley-Queisser limit [1]. This constitutes then also the theoretical limit of efficiency of the solar device making use of the mechanism described here.

![Figure 4.13](image)

**Figure 4.13:** The maximal theoretically available energy conversion efficiency of the proposed spectral shaper (solid red circles) calculated as the ratio of the total energy of the maximum number of photons that can be emitted by Er$^{3+}$ ions to that of the absorbed photon. Blue line illustrates the result of the similar evaluation for crystalline Si used in standard solar cells. Reference solar spectra AM 1.5 and AM 0 are indicated in green and light green, respectively; the shaded region represents parts of the spectra which could be targeted with the shaping layer discussed in this work.

For material parameters as used in this study, a layer of ~ 8 μm would be sufficient to absorb 95% of all the photons with energies above 3 eV. The lower
energy photons pass through the active layer and undergo photovoltaic conversion in the Si cell, while the IR photons generated in the top layer pass through the Si cell and convert in a low bandgap (e.g., Ge) cell underneath, depicted in Fig 4.14.

![Figure 4.14: Schematic illustration of a possible device making use of Er excitation by the “optical cooling” of hot carriers. A thin active layer of SiO₂ doped with Si NCs and Er³⁺ ions converts high energy photons into a stream of IR photons. The lower energy photons pass through the active layer and are absorbed in a Si cell. The IR photons generated by the top layer pass through the Si cell and undergo photovoltaic conversion in the low bandgap cell underneath.](image)

By adjusting size and concentration of Si NCs, Er³⁺ ion concentration and the layer thickness, the absorbance of the active layer can be tuned for the optimal division of the solar photon flux between the Si and the Ge parts of the proposed device. The ‘solar shaper’ allows to harvest a substantial part of the solar energy inaccessible to a standard cell and in that way the overall photovoltaic conversion efficiency can increase exceeding the Shockley-Queisser limit. Naturally, before a practical realization of the proposed scheme may be attempted a rigorous further optimization of the material for the conversion layer is required.

### 4.8 Conclusion
The absolute EQY of 0.8 eV Er-related PL from Er-doped SiO₂ sensitized with Si NCs as a function of excitation energy is determined. EQY is constant at low
pump energies and increases in a step-like manner above certain threshold of excitation energy. Both the threshold energy and the increase rate of EQY depend on material parameters – Si NC average diameter and concentration, and the Er-to-NC doping ratio. The threshold energy is given by the sum of the bandgap energy of Si NCs and the 0.8 energy of 1st excited state of Er$^{3+}$ ion, plus a minor loss of 0.1-0.2 eV. The subsequent enhancement of EQY is exclusively related to the increased contribution of the hot-carrier mediated excitation of Er$^{3+}$ ions. The characteristic steps in the EQY dependence are related to specific thresholds of this excitation mechanism, as different excited states of Er$^{3+}$ are approached and/or multiple Er$^{3+}$ ions addressed. In the highest investigated pump energy range, a single photon absorbed by a Si NC can excite up to 4 Er$^{3+}$ ions. With the internal photon energy conversion efficiency reaching ~ 80 %, when fully developed, this system could be interesting for photovoltaics, providing a path for an optical extraction of excess energy of hot carriers, and thus offering an ‘optical’ alternative to the hot-carrier solar cell concept [61].