Step-like increase of quantum yield of 1.5 μm Er-related emission in SiO2 doped with Si nanocrystals

Published in:
Journal of Applied Physics

DOI:
10.1063/1.4907759

Citation for published version (APA):
Step-like increase of quantum yield of 1.5 μm Er-related emission in SiO₂ doped with Si nanocrystals

S. Saeed, E. M. L. D. de Jong, and T. Gregorkiewicz
Van der Waals-Zeeman Institute, University of Amsterdam, Science Park 904, NL-1098 XH Amsterdam, The Netherlands

(Received 16 October 2014; accepted 25 January 2015; published online 9 February 2015)

We investigate the excitation dependence of the efficiency of the Si nanocrystals-mediated photoluminescence from Er³⁺ ions embedded in a SiO₂ matrix. We show that the quantum yield of this emission increases in a step-like manner with excitation energy. The subsequent thresholds of this characteristic dependence are approximately given by the sum of the Si nanocrystals bandgap energy and multiples of 0.8 eV, corresponding to the energy of the first excited state of Er³⁺ ions. By comparing differently prepared materials, we explicitly demonstrate that the actual values of the threshold energies and the rate of the observed increase of the external quantum yield depend on sample characteristics—the size, the optical activity and the concentration of Si nanocrystals as well Er³⁺ ions to Si nanocrystals concentration ratio. In that way, detailed insights into the efficient excitation of Er³⁺ ions are obtained. In particular, the essential role of the hot-carrier-mediated Er excitation route is established, with a possible application perspective for highly efficient future-generation photovoltaics. © 2015 AIP Publishing LLC.

I. INTRODUCTION

Due to their attractive properties, featuring sharp and temperature-stable emission bands, rare-earth (RE) doped optical materials are widely investigated for the development of light sources. In parallel, RE ions are also being explored for the purpose of photon down- and up-conversion for lighting and photovoltaics. In down-conversion, absorption of a single photon of sufficiently large energy results in excitation transfer and subsequent emission of two (or more) lower energy photons.¹⁻³ RE-based phosphors utilizing this principle are commonly used, e.g., in white light diodes, converting ultraviolet photons into the visible range. Also up-conversion, the reverse of this process, comprising emission of high-energy photons upon sequential excitation at lower energy, has been demonstrated and its potential to increase the efficiency in photovoltaics has been explored.⁴⁻⁶ However, the common disadvantage of all the RE-based solutions is the extremely low absorption cross-section, due to the marginally allowed character of optical transitions within the (internal) ⁴f-electron shell governing the optical properties of RE ions.⁴

This difficulty can be circumvented using indirect excitation enabled by a semiconducting host. In this case, RE ions are excited by nonradiative recombination of excitons efficiently generated due to band-to-band absorption.⁷⁻¹¹ However, extensive investigations, conducted especially for the highly desired semiconductor-RE system Si:Er,¹²⁻¹⁵ identified a very efficient excitation reversal and, in spite of an enormous research effort, stable bright emission at room temperature could not be achieved.

A more successful approach is by making use of the sensitization effect introduced by Si nanocrystals (Si NCs),¹⁷⁻¹⁹ which enable indirect excitation of Er³⁺ ions. In that way, the effective excitation cross-section is increased by several orders of magnitude.²⁰,²¹ Indeed, the efficient infrared emission at 0.8 eV from Er-doped SiO₂ sensitized with Si NCs has been extensively investigated in order to understand and explore its full capabilities. When Si NCs are incorporated in SiO₂ together with Er³⁺ ions, they act as sensitizers of Er excitation. Since the absorption cross-section of the Si NCs is much higher than that of Er³⁺ ions, the incident light is initially absorbed by the Si NCs, generating electron-hole pairs. These can recombine radiatively, giving rise to the NCs-related photoluminescence (PL) band. Alternatively, an excited Si NC can recombine non-radiatively, transferring its energy to neighboring Er³⁺ ions, bringing them into one of the higher excited states. Following internal relaxation, this energy transfer results in Er emission, mainly from the ⁴¹₁₃/₂ state at 1.5 μm (0.8 eV). Detailed time-resolved spectroscopy of Si NC-mediated PL of Er³⁺ ions revealed two major energy transfer mechanisms leading to the 0.8 eV emission, distinguishable by their dynamics: a slow one (microseconds), due to nonradiative combination of an exciton, and a fast one, due to intraband transitions of hot carriers (sub-nanosecond range).¹⁹,²²,²³ The hot-carrier-mediated excitation requires the sufficiently large excess energy of free carriers, and therefore appears only at high excitation energies, or at high fluxes of low-energy photons, as Auger recombination of multiple excitons generated in the same NCs also produces hot carriers. The most direct evidence for the coexistence of the two excitation mechanisms has been found from evaluation of the external quantum efficiency of Er-related PL in the Er-Si NCs system.²⁴,²⁵ In the present study, we confirm the initial findings by showing that at low flux excitation, the initial fast component in dynamics of Er-related PL appears only upon high energy excitation. We follow by conducting detailed investigations of the external quantum yield (EQY) (defined as the ratio between the
numbers of emitted and absorbed photons) of Er-related PL and demonstrate that it increases above a certain threshold of excitation energy, as the excitation channel by hot-carriers is activated. We discuss in detail the effects of material characteristics (size of Si NCs, concentration of Si NCs and Er$^{3+}$ ions) on the EQY of Er-related PL. In this way, we provide detailed insights into the excitation and energy transfer processes taking place in this material. Finally, we comment on a possible practical application of the NCs-sensitized Er-related PL for development of “solar shapers” for the next generation photovoltaics.

II. EXPERIMENTAL DETAILS

A. Samples

The investigated $\sim$2 $\mu$m thick layers containing Si NCs with Er$^{3+}$ ions in SiO$_2$ have been fabricated on a quartz substrate by radio frequency co-sputtering. The sputtering procedure was followed by annealing for 30 min in N$_2$ atmosphere at 1100 °C or 1200 °C, leading to precipitation of high-quality Si NCs. More details on sample preparation can be found in Ref. 17. By changing the amount of excess Si, the annealing temperature and the number of Er tablets on the sputtering target, 17 samples with different average NC sizes and various concentrations of NCs and Er$^{3+}$ ions have been produced (see Ref. 26 for more details on the sample preparation). For microscopic structural characterization on nanometer scale, some of the prepared samples were studied by transmission electron microscopy. The average nanocrystal size was estimated from the relevant PL spectrum. 28

In this study, three categories of samples have been investigated:

(i) Two samples having the same concentration of Si NCs and Er$^{3+}$ ions of $\lbrack$NC$\rbrack \approx 2.1 \times 10^{18}$ cm$^{-3}$ and $\lbrack$Er$^{3+}$ $\rbrack \approx 2.8 \times 10^{19}$ cm$^{-3}$, but different average Si NCs diameters of $d_{\text{NC}} \approx 3$ nm (1100°C annealed) and 4 nm (1200°C annealed).

(ii) Three samples (1100°C annealed) with the same Si NCs concentration of $\lbrack$NC$\rbrack \approx 4.1 \times 10^{18}$ cm$^{-3}$ and average Si NCs diameter of $d_{\text{NC}} \approx 3$ nm, but different Er$^{3+}$ ions concentrations: $\lbrack$Er$^{3+}$ $\rbrack \approx 0.5 \times 10^{19}$, 1.1 $\times 10^{19}$, and 2.8 $\times 10^{19}$ cm$^{-3}$.

(iii) Two samples with the same Er$^{3+}$ ions concentration of $\lbrack$Er$^{3+}$ $\rbrack \approx 2.8 \times 10^{19}$ cm$^{-3}$ and average Si NCs diameter of $d_{\text{NC}} \approx 3$ nm, but different Si NCs concentration $\lbrack$NC$\rbrack \approx 2.1 \times 10^{18}$ and $5.5 \times 10^{18}$ cm$^{-3}$ (1100°C annealed).

B. Optical characterization

Photoluminescence spectra measurements were performed under continuous wave excitation either with Nd:YVO$_4$ laser (Millennia, Spectra Physics), operating at 532 nm or 150 W Xenon lamp (Hamamatsu L2273) coupled to a double pass monochromator (Solar MSA-130), capable of producing multiple wavelengths. The PL signal was recorded with an 1 m f/8 monochromator (Jobin-Yvon THR-1000) coupled to an infrared Ge detector (Edinburgh Instruments) with a DSP lock-in amplifier (Signal Recovery SR7265). A complete PL spectrum (showing Si NCs and Er-emission bands) for one sample is shown in supplementary Fig. S1 and typical Er-emission bands at different excitation energies are depicted in supplementary Fig. S2. All the measurements were corrected for the spectral response of the system. A photomultiplier tube (Hamamatsu R5509–73, 300–1700 nm) working in time-correlated single-photon-counting mode coupled to an 1 m f/8 monochromator (Jobin-Yvon THR-1000) was used to measure PL life times. These measurements were performed under pulsed excitation at different energies, provided by a tunable optical parametric oscillator pumped by the third harmonic of a Nd:YAG laser, with a pulse duration of $\sim$10 ns and a repetition rate of 100 Hz. A Perkin Elmer Lambda 950 UV-VIS-NIR spectrometer was used to measure the linear absorption of the samples, with tungsten-halogen and deuterium lamps in combination with a PMT and a Peltier-cooled PbS detector providing a detection range of $\lambda_{\text{det}} = 175$–3300 nm. To avoid contributions of the substrate to data obtained with this setup, the signal of a bare substrate was separately measured and subtracted. An integrating sphere was incorporated in the setup to account for scattering effects. A typical absorption spectrum for one of the samples is shown in Supplementary Fig. S2. All measurements in this study were performed at room temperature.

C. EQY of Er-related PL

The EQY, the ratio between the number of emitted and the number of absorbed photons, of the studied samples was determined based on a method originally described in Ref. 30. Light from a 150 W Xenon lamp (Hamamatsu L2273) coupled to a double pass monochromator (Solar MSA-130) was directed onto a sample placed in an integrating sphere. In order to calculate the number of absorbed photons, the unabsorbed excitation light was recorded at different excitation energies using a CCD (Hamamatsu S10141–1108S, 200–1100 nm) coupled to a monochromator (Solar M266). The reference (quartz substrate) and the investigated samples were subsequently placed in the integrating sphere, and from the integrated decrease of the signal the absorption in the active layer of the investigated samples was obtained. In order to determine the number of emitted photons, the 0.8 eV emission signal of Er$^{3+}$ ions was recorded using a Ge detector (Edinburgh Instruments, 900–1700 nm) together with a lock-in amplifier (Signal Recovery SR 7265). Since the absorption and emission signals were recorded using two different detection systems, it was important to scale their efficiencies. The first step was to measure the correction curves for both systems by using a combination of tungsten-halogen and deuterium lamps. The next step was to measure the EQY of a sample emitting in the overlapping detection range of the two detectors. For this purpose, a colloidal sample of Si NCs dispersed in ethanol with emission in the 700 nm to 1100 nm range has been used. After measuring the PL spectra of this sample with both detectors, the PL spectra were first corrected using the sensitivity correction curves and then properly scaled. This
scaling factor was then used to correct all the calculations for the determination of the EQY of Er-related PL. Another important notion here is that the EQY calculated for Er-related PL was a relative measurement because instead of actual number of emitted photons the integrated PL signal at 0.8 eV was used. Now, to convert this number to the absolute number of photons, we again made use of the same Si NCs dispersed in ethanol sample and measured the EQY of this sample by both methods—the relative (two detection system) and the absolute (single detection system). This gives another scaling factor which is then used to convert the relative number into the absolute QY.

III. RESULTS

In this study, we investigate the excitation energy dependence of the EQY of Er-related PL at 0.8 eV sensitized by Si NCs. We observe that Er-related PL itself is independent of the excitation energy—See Fig. S2, supplementary information. By performing measurements on differently prepared samples, we follow changes of EQY upon variation of material parameters—Si NC size and concentration as well as Er doping level.

A. EQY dependence on Si NCs sizes

Figure 1 compares the EQY of Er-related PL measured at 0.8 eV as a function of the energy of the incident photons for two samples which are characterized by identical concentrations of Si NCs and Er$^{3+}$ ions, of [NC] $\approx 2.1 \times 10^{18}$ cm$^{-3}$ and [Er$^{3+}$] $\approx 2.8 \times 10^{19}$ cm$^{-3}$, respectively, but with different average size of Si NCs—with average diameters of $d_{NC} \approx 4$ nm (panel a) and $d_{NC} \approx 3$ nm (panel b).

As can be seen, the EQY for both materials is characterized by a constant value for low excitation energies up to a certain threshold, after which it increases. For the 4 nm sized Si NCs, the onset energy is $E_{th} \approx 2.0$ eV, while for smaller Si NCs of 3 nm this onset is somewhat higher, at $E_{th} \approx 2.2$ eV. Inset of both figures shows the excitonic emission spectra for the investigated samples, with the emission bands peaking at $E_{PL} \approx 1.37$ eV and $E_{PL} \approx 1.55$ eV for Si NC diameter of $d_{NC} \approx 4$ nm and $d_{NC} \approx 3$ nm, respectively. It is clear that the shifts of the emission peak $E_{PL}$ (and therefore the nanocrystals sizes) and the EQY threshold energy $E_{th}$ are correlated with each other. Other than different thresholds, we note that the absolute values as well as the enhancement rate of EQY at higher excitation energies are also sample-dependent. For the material with $d_{NC} \approx 4$ nm, the EQY of Er-related PL rises within the investigated excitation energy range from $\sim 0.5$% to $\sim 4.5$%, showing for an excitation of 4 eV an increase of $\sim 4$%. For the sample with $d_{NC} \approx 3$ nm, the absolute EQY is higher, rising from $\sim 1$% to $\sim 6.5$%, i.e., by $\sim 5.5$%. In addition, we also note that for the sample with the smaller linewidth of the emission band ($E_{PL} \approx 1.55$ eV, $d_{NC} \approx 3$ nm, indicating a more narrow NC size distribution), the EQY dependence has a step-like character; we recall that a step-like behavior has been previously observed for carbon nanotubes$^{31}$ and Si NCs,$^{32}$ and was also theoretically modeled for the multiple exciton generation in semiconductor nanocrystals.$^{33}$ The steps are not so evident for the sample with the larger linewidth of the emission band ($E_{PL} \approx 1.37$ eV, $d_{NC} \approx 4$ nm, indicating a broader NC size distribution). As discussed before, the step-like increase of the EQY smears out for the broader size distribution.$^{32}$

B. EQY dependence on concentration of Er$^{3+}$ ions and Si NCs

Figure 2(a) compares the EQY of 0.8 eV Er-related PL for three samples with identical size ($d_{NC} \approx 3$ nm) and concentration ([NC] $\approx 4.1 \times 10^{18}$ cm$^{-3}$) of Si NCs, but different Er content of [Er$^{3+}$] $\approx 0.5$, 1.1 and $2.8 \times 10^{19}$ cm$^{-3}$. The inset to Fig. 2(a) shows the EQY value at excitation energy of 4.25 eV versus Er contents. With increasing Er$^{3+}$ ions concentration, the mutual Er-to-NC contents ratio is increasing (from $\sim 1.2$ to $\sim 7$), and one can anticipate that the NC-to-Er energy transfer might be enhanced. As can be seen, a similar threshold-governed increase of EQY is observed for all the three samples, with the similar initial value of the EQY of $\sim 1$% and a threshold energy of $E_{th} \approx 2.2$ eV. The subsequent enhancement of EQY for higher energies, however, is clearly different, increasing with Er$^{3+}$ ions concentration.

FIG. 1. The EQY of Er-related PL from the samples with average Si NC diameters of $d_{NC} \approx 4$ nm (a) and $d_{NC} \approx 3$ nm (b). Both samples have same concentrations of Si NCs ([NC] $\approx 2.1 \times 10^{18}$ cm$^{-3}$) and Er$^{3+}$ ions ([Er$^{3+}$] $\approx 2.8 \times 10^{19}$ cm$^{-3}$). Insets show the excitonic PL spectra recorded for Si NCs from Er-doped samples under 532 nm (low flux) continuous wave excitation.
The EQY of 0.8 eV Er-related PL for two samples with identical Si NCs size ($d_{\text{NC}} \approx 3$ nm) and concentration of $\text{Er}^{3+}$ ions ($[\text{Er}^{3+}] \approx 2.8 \times 10^{19}$ cm$^{-3}$), but with different Si NCs concentration is compared in Fig. 2(b). Step-like behavior is observed for both samples, with a similar threshold energy of $E_{\text{th}} \approx 2.2$ eV, but with the subsequent enhancement being clearly higher for the material with the lower concentration of Si NCs. The inset to Fig. 2(b) plots the EQY value at excitation energy of 4.25 eV versus Si NCs concentration. We could speculate that this is related to reduction of energy transfer among Si NCs, or to a better crystalline quality/lower defect level of the layer with a lower concentration of Si NCs.

**IV. DISCUSSION**

As can be concluded from the presented experimental results, the excitation dependent 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 materials parameters, these two basic features are omnipresent. We first discuss the origin of the enhancement of the EQY and then its characteristics in relation to the energy transfer mechanism between Si NCs and $\text{Er}^{3+}$ ions and material parameters.

**A. Hot-carrier mediated Er-excitation**

As already mentioned in the introduction, past investigations on the Si NC sensitization of Er-PL revealed two channels of energy transfer from Si NCs to $\text{Er}^{3+}$ ions responsible for the excitation and eventual emission of 0.8 eV photons; the “slow” one (microsecond) involving nonradiative recombination of an electron-hole pair in the NC core and the “fast” one (sub-nanosecond) due to intraband cooling of hot carriers with a sufficiently large excess energy. 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 $\text{Er}^{3+}$ ion, which can then be promoted directly to the first $^4I_{13/2}$ excited state responsible for the 0.8 eV emission (we note that this excitation mechanism is a direct analog of the impact excitation of $\text{Er}^{3+}$ ions in bulk Si[16]). The hot-carrier induced energy transfer is then responsible for the ultrafast appearance of Er-related PL, within nanoseconds after the laser pulse, as illustrated by the high-resolution PL decay dynamics for one of the samples investigated in this study in the inset of Fig. 3(a), for the sample characterized by $d_{\text{NC}} \approx 3$ nm, $[\text{NC}] \approx 2.1 \times 10^{18}$ cm$^{-3}$ and $[\text{Er}^{3+}] \approx 2.8 \times 10^{19}$ cm$^{-3}$. While this efficient Er excitation process experiences strong reversal due to the energy back-transfer to free carriers available in NCs (see the fast quenching of Er-PL within the first microsecond after the excitation in the inset), some of the excited dopants escape this nonradiative recombination (possibly by resonant energy diffusion within the $\text{Er}^{3+}$ 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, as can be seen in the inset. In this way, the total experimentally measured intensity of the Er-related PL contains contributions from $\text{Er}^{3+}$ ions excited by the two excitation channels—the slow exciton-related one and the ultrafast one, enabled by hot carriers. We also note that the contribution of the impact excitation will be proportional to the initial amplitude of the fast decaying PL.

Figure 3(a) shows the initial amplitude of Er-related PL transient versus excitation energy for the investigated sample whose PL decay transient is given in the inset. A substantial increase at higher excitation energies can be seen, which suggests that the hot-carrier mediated excitation of $\text{Er}^{3+}$ ions becomes more efficient and therefore could be responsible for the observed EQY enhancement. This is further supported by Fig. 3(b), which shows the total (time integrated) PL intensity in the investigated excitation energy range as a function of the initial PL amplitude of the corresponding transient. A linear dependence between the two is concluded; this provides direct evidence that the enhancement of EQY at higher excitation energies arises entirely due to the hot-carrier mediated excitation mechanism.

**B. Excitation transfer model**

Now, we turn our attention to the excitation route that can be responsible for the observed step-like enhancement of the 0.8 eV Er-related PL. For this purpose, we plot in more
detail the excitation dependence of the EQY for one sample with $d_{NC} \approx 3 \text{ nm}$ in Fig. 4.

We divide the observed excitation energy dependence of the EQY in four regions, corresponding to the individual steps in the experimentally obtained data. For better illustration, the proposed interpretations of threshold energies are depicted in the lower panel, by displaying the appropriately shifted PL bands simulated from the measured spectrum; in that way the size, and consequently the bandgap energy distribution of Si NCs, is taken into account. We discuss separately the contributions of the slow (due to nonradiative excitonic recombination) and the fast (due to hot-carrier intraband transitions) Er excitation mechanisms.

1. “Slow” excitation process

Range #1 in Fig. 4 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 $\hbar \nu > E_{PL}$ are absorbed by Si NCs and generate (low energy) electron-hole pairs (excitons). The nonradiative recombination of this exciton in the Si NCs can transfer energy to an Er$^{3+}$ ion bringing it into one of the higher excited states corresponding to exciton energy, with or without phonon participation. The characteristic transfer time of this process depends on the NC-Er distance and for Er$^{3+}$ ions situated within a NC or close to its boundary this transfer time $\tau_1$ can be of the order of nanoseconds (or even shorter). After that, however, internal relaxation to the $^4I_{13/2}$ state is required before emission at 0.8 eV can appear. This relaxation time $\tau_2$ is of the order of microseconds. The combination of these two time constants is responsible for the slow rise of the Er-related PL within several microseconds after the excitation pulse—see the inset to Fig. 3(a). In that excitation energy range, a single photon (independent of its energy) absorbed by a Si NC generates a single low-energy exciton and can excite, at most, a single Er$^{3+}$ ion. This explains the flat character of the measured EQY dependence. The initial/base EQY value depends on the percentage of NCs capable of supporting an exciton. For this particular sample, the EQY of the exciton-mediated excitation is $\sim 1\%$, but varies from sample to sample, as can be concluded from the experimental results presented in Sec. III. The proposed interpretation of the excitation taking place for energies in range #1 is shown schematically in Fig. 5.

2. “Fast” excitation process

As discussed, 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. The efficiency of this process follows the $(d_{NC})^{-4}$
dependence of the intraband transition rate,19 which explains the larger increase of the EQY for smaller NCs. Past theoretical modeling34 has shown that for the fastest transitions in a NC with diameter $d_{NC} \approx 3 \text{ nm}$, the time scale of this excitation can reach $\sim 0.5 \text{ ns}$ for Er$^{3+}$ ions located on the NC surface. It has also been established22 that a major part—$\sim 50\%$ or more—of all the Er dopants can receive energy in this way; this is 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 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 exceeding a threshold value given by $E_{th1} = E_{PL} + E_{Er1} + \Delta$, 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 energy required to enable the transfer process, respectively. This implies that the threshold energy value is directly related to the emission spectrum of Si NCs, as indeed can be concluded from the data in Fig. 1, where the threshold for the sample with smaller NCs is somewhat higher, similarly as its NC emission energy. For the sample whose EQY is depicted in Fig. 4, the threshold energy is $E_{th1} \approx 2.2 \text{ eV}$; taking into account the corresponding NC PL spectrum, this implies the enabling energy of $\Delta = 0.1–0.2 \text{ eV}$. At a higher excitation energy $E_{exc} > E_{th1}$, excess energy of hot-carriers 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 the 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, which is consistent with its much faster dynamics, as indeed experimentally observed in the inset of Fig. 3(a). The hot-carrier mediated excitation process activated in range #2 following the first threshold is schematically shown in Fig. 6(a).

The next threshold in the EQY dependence in Fig. 4 is found at $E_{th2} \approx 2.5 \text{ eV}$. We postulate that at this point, carrier excess energy reaches the value of the second $^4I_{15/2}$ excited state of Er$^{3+}$ ion, $1.2 \text{ eV}$: $E_{th2} = E_{PL} + E_{Er2} + \Delta = E_1 + 0.4 \text{ eV}$. In that excitation range (#3), impact excitation becomes possible not only to the first, but also to the second excited state $^4I_{15/2}$.25 While now still two Er$^{3+}$ ions can be excited by a single photon, reaching this threshold slows down the increase of the generation rate of the $^4I_{15/2}$ state responsible for 0.8 eV PL, as not all Er$^{3+}$ ions excited to the $^4I_{15/2}$ state will eventually relax to $^4I_{13/2}$ and contribute to the investigated PL at 0.8 eV. The excitation scheme considered for range #3 is schematically illustrated in Fig. 6(b).

Upon further increase of excitation energy—range #4—hot-carriers capable of excitation of two (and more) Er$^{3+}$ ions are being generated. The threshold for that is given by $E_{th3} = E_{PL} + 2(E_{Er1} + \Delta)$. From the data in Fig. 4, we find that $E_{th3} \approx 3.2 \text{ eV}$. Above this energy threshold, excitation of three Er$^{3+}$ ions per absorbed photon becomes possible, two by the hot-carrier mediated fast process and one by exciton recombination. Moreover, in that range also an alternative process is enabled, when a hot-carrier excites a nearby Er$^{3+}$ ion into a still higher excited state $^4I_{9/2}$ or higher, which subsequently shares part of its energy with another proximal Er$^{3+}$.35 This process is a reversal of the concentration quenching, well known for heavily Er-doped materials.36 Therefore, instead of direct excitation of three Er$^{3+}$ ions from Si NC, there appears an indirect excitation by energy exchange between Er$^{3+}$ ions. Fig. 6(c) schematically illustrates both scenarios, available in range #4. For excitation with energies $E_{exc} > E_{th3}$, a single photon might excite three (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 excitation of multiple Er$^{3+}$ ions appear.

3. “Fast” excitation process versus carrier cooling

In order to rationalize the proposed microscopic model of hot-carrier mediated energy transfer as being responsible for the step-like enhancement of EQY at higher excitation energies, we briefly consider carrier dynamics in Si NCs. We note that Er-excitation involving hot-carriers compete with other carrier relaxation processes, and prominently with electron-phonon scattering. According to the general understanding, the energy relaxation of hot-carriers is determined by the emission of optical phonons.37,38 From Monte-Carlo simulations, the energy relaxation time by phonon scattering in Si NCs with $d_{NC} = 2.5 \text{ nm}$ was estimated to be approximately 13 ps, with an average relaxation rate of about 0.8 eV.
per 5 ps.\textsuperscript{39} Taking into account the Si NC-to-Er\textsuperscript{3+} energy transfer time of an order of 0.5 ns,\textsuperscript{34} we arrive to an efficiency of the hot-carrier mediated excitation of an order of 1%, in reasonable agreement with our experimental results. We note that the cooling time significantly increases when a possibility of phonon re-absorption is considered, even when a (reasonable) model of phonon decay is taken into account,\textsuperscript{39} enhancing efficiency of this transfer process.

V. APPLICATION POTENTIAL

So far, we have discussed Er excitation routes which could account for the observed step-like increase in EQY of Er-related PL at 0.8 eV. Now, we will comment on the possible material modifications which could be introduced in order to increase the EQY. This is important since efficient conversion of a single high energy photon into multiple photons of lower and predefined energy could find interesting applications in, e.g., optoelectronics and photovoltaics. The first step would be the improvement of the initial flat/base line in EQY—range #1. Since the excitonic energy transfer is rather slow, this excitation mechanism is effective only for Si NCs with sufficiently long exciton lifetime, i.e., those which would recombine radiatively in the absence of Er. Therefore, the EQY in range #1 indirectly reflects the level of the “optical activity” of Si NCs.\textsuperscript{40} In the investigated material, the optical activity of Si NC is quite low and can be improved. Past investigations have shown that in carefully optimized materials the optical activity of Si NCs can reach 60%.\textsuperscript{41} Future work must show whether reaching such a high degree of optical activity will be possible for Er-doped materials as well. To this end, the low temperature post-annealing in H\textsubscript{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 nonradiative quenching of excitons.\textsuperscript{40} For improvement of EQY in regions #2–4, the hot-carrier mediated excitation must be optimized. Here, the current study provides clear guidance, suggesting that the highest efficiency can be expected for materials with moderate concentrations of relatively small NCs of superior crystalline quality, and a high Er-to-NC concentration ratio.

Finally, we shortly comment on the application potential of the investigated materials. When the sufficiently high level of EQY is realized, then Er-doped SiO\textsubscript{2} with Si NCs could form the basis for a light conversion layer (“solar shaper”\textsuperscript{42}) 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 the most promising route towards increasing conversion efficiency in the next generation photovoltaics. Different strategies of hot-carrier solar cells have been considered and theoretically modelled in the past.\textsuperscript{43–51} Based on the results of the present study, we propose the use of a thin layer of an optimized SiO\textsubscript{2} doped with Si NCs and Er\textsuperscript{3+} ions to absorb the high energy photons, whose conversion efficiency in a standard Si cell is the lowest, and transform them into a stream of 0.8 eV photons, while the lower energy photons would pass through that layer to undergo photovoltaic conversion in a conventional cell. On the other hand, the 0.8 eV photons generated in the top layer would not be absorbed by the Si cell and could be directed to a dedicated low energy bandgap cell, e.g., positioned underneath. In that way, the total conversion efficiency would be enhanced, since the “blue” photons for which most of the energy is wasted to heat in a standard configuration, would be transformed and used to the fullest. By adjusting the thickness of the conversion layer, its absorbance could be tuned, so as to optimize the division of the solar radiation between the two conversion routes.

VI. CONCLUSIONS

We have successfully measured excitation energy dependence of the absolute EQY of 0.8 eV Er-related PL from Er-doped SiO\textsubscript{2} sensitized with Si NCs. The EQY is constant at low excitation energies and increases in a step-like manner above a certain threshold. Both the threshold energy and the further increase rate of EQY depend on

FIG. 6. Schematic illustration of Er excitation processes at higher excitation energies. The proposed process of excitation of two Er\textsuperscript{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\textsuperscript{3+}, range #2, and (b) the second excited state of Er\textsuperscript{3+} followed by internal relaxation, range #3. (c) Range #4: excitation of three Er\textsuperscript{3+} ions per absorbed photon, with two possible scenarios—either direct excitation of three Er\textsuperscript{3+} ions or in two stages, sharing of the energy between Er\textsuperscript{3+} ions.
material parameters—Si NC 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 eV energy of first excited state of Er$^{3+}$ ion, plus a minor loss of $\sim$0.1–0.2 eV. The subsequent enhancement of EQY is exclusively provided by the increased contribution of the hot-carrier mediated excitation of Er$^{3+}$ ions. The characteristic steps in the EQY dependence are related to specific excitation paths, as different excited states of Er$^{3+}$ are approached and/or multiple Er$^{3+}$ ions addressed. In the highest investigated excitation energy range, a single photon absorbed by a Si NC can excite up to 3 Er$^{3+}$ ions.

ACKNOWLEDGMENTS

This work has been financially supported by Stichting voor de Technologische Wetenschappen (STW) and Stichting voor Fundamenteel Onderzoek der Materie (FOM), the Netherlands.

29See supplementary material at http://dx.doi.org/10.1063/1.4907759 for the complete PL spectrum (Si NCs and Er-related emission bands) and absorption spectra for one of the samples. The excitation dependence of the Er-related PL band is also given for the same sample.
48M. A. Green, Third Generation Photovoltaics (Springer-Verlag, Berlin, 2003).