Towards optical amplification for silicon photonics

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Chapter 6

Using of Si NCs as optical sensitizers

We present evidence of a novel mechanism for the indirect excitation of Er\textsuperscript{3+} ions in a SiO\textsubscript{2} matrix sensitized with Si quantum dots (SiQDs). The proposed process enables the simultaneous and rapid excitation of two proximal Er\textsuperscript{3+} ions upon absorption of a single high-energy photon in a SiQD. The experimental evidence leading to the identification of this energy transfer path is obtained from investigations of the photoluminescence quantum yield of two Er-related emission bands at 1.54 and 0.98 \textmu m in SiO\textsubscript{2} layers doped with small (~ 2 nm diameter) SiQDs and a high concentration of Er\textsuperscript{3+} ions, prepared by sputtering on hot substrates. In contrast to the previously considered mechanisms for indirect excitation of Er\textsuperscript{3+} ions in SiO\textsubscript{2}, this excitation process offers an advantage of efficient suppression of the most important channels of nonradiative de-excitation - the Auger energy transfer to free carriers as well as the so-called energy backtransfer of excitation reversal. This feature revives hopes for practical application of Er-doped SiO\textsubscript{2} sensitized by SiQDs. With the use of quantum cutting in SiO\textsubscript{2}:Si,Er materials, smaller fraction of the Er\textsuperscript{3+} ion emission energy can cover almost 80\% of the solar spectrum.

6.1 Photon cutting for excitation of Er\textsuperscript{3+} ions

6.1.1 Introduction

Rare-earth (RE) ions are favorite “optical dopants” frequently used to tailor optical properties of insulating and semiconducting hosts. Following the success of neodymium-doped yttrium aluminum garnet (Nd:YAG), most attention has been given to Er-doped crystalline Si due to its emission wavelength coinciding with the absorption minimum of telecommunication networks. The research is motivated by prospective applications in Si photonics and optoelectronics [1, 99]. Unfortunately, while much information has been gathered and many interesting effects have been observed (e.g., [149, 96]), broader applications of Si:Er remain limited due to the thermal instability of emission. Among insulating hosts, the SiO\textsubscript{2} matrix doped with Er\textsuperscript{3+} ions (SiO\textsubscript{2}:Er) is also well investigated, as the basis for the development of optical amplifiers. However, due to the fact that the optical properties of RE ions...
are determined by the intra-4f electron shell, the SiO$_2$:Er - based amplifiers require high-power resonant pumping, which is cumbersome and expensive.

Excitation of photo- and electro-luminescence of Er$^{3+}$ ions in SiO$_2$ can be effectively sensitized by Si quantum dots (SiQDs) [71, 72, 73, 74, 75]. In this case, room-temperature 1.54-μm Er-related emission can be induced by a non-resonant excitation process via band-to-band absorption in SiQDs. Since the indirect band structure of Si is preserved also in its nanocrystalline form [76], electron-hole pairs generated in this way are characterized by a relatively long lifetime, enabling energy transfer to Er$^{3+}$ ions located in the vicinity. Making use of the band-to-band absorption, this indirect excitation process is relatively efficient, with an (effective) excitation cross-section of $\sigma \approx 10^{-17} - 10^{-16}$ cm$^2$. As a result, an increase of a factor $\sim 10^3$ in $\sigma$ is found in comparison with SiO$_2$:Er [74], while at the same time it is $\sim 10^3$ times lower than for Si:Er [45]. It can be therefore concluded that the solid state dispersion of SiQDs in Er-doped SiO$_2$ matrix - SiO$_2$:(Er,SiQDs) - to a certain extent combines positive features of Er-doped crystalline Si with the advantages of Er-doped SiO$_2$: the high excitation cross-section and the temperature-stable emission.

However, despite of continuous developments in the preparation, only a relatively small proportion of all the Er$^{3+}$ ions is usually available for indirect excitation via SiQDs [79, 80]. This limitation is the main obstacle in attaining a high concentration of excited Er$^{3+}$ ions and population inversion, which is necessary for optical amplification [81]. Obviously, this problem relates to the microscopic details of the indirect excitation mechanism. Dedicated experiments [82, 83] have revealed that the excitation of Er$^{3+}$ ions in the SiO$_2$:(Er,SiQDs) system involves mechanisms operating on different time scales, from several microseconds down to below 100 ns. In particular, the Förster (dipole-dipole) mechanism - Förster resonant energy transfer (FRET) - [84, 85] has been proposed in order to explain the “slow” (microsecond time scale) energy transfer from SiQDs to Er$^{3+}$ ions [86], and the microscopic location of Er with respect to SiQDs has been considered [77, 78]. In addition to this relatively slow excitation, the presence of a much faster (sub-100-ns range) process has been conclusively established [87, 82]. As for its physical origin, a process analogous to hot-carrier impact excitation of Er in bulk Si has been put forward [82, 83]. In this mechanism a hot carrier loses (part of) its excess energy by intraband relaxation with energy transfer to an Er$^{3+}$ ion.

In this work, we present investigations of the optical excitation of Er$^{3+}$ ions in the SiO$_2$:(Er,SiQDs) material with a high Er concentration. We demonstrate evidence of a very specific and thus far unidentified energy-transfer path, in which two Er$^{3+}$ ions are excited simultaneously by a single photon of sufficiently high energy absorbed in a SiQD. This excitation mechanism is enabled by the proximity of Er dopants and bears a strong similarity to quantum cutting observed for RE
ions [150]. It operates parallel to the earlier reported Förster dipole-dipole process and Auger-facilitated energy transfer mechanisms. The identification is based on the analysis of the quantum yield of two Er-related emission bands at 1.54 and 0.98 μm, appearing due to the radiative recombination from the first (\( ^4I_{13/2} \rightarrow ^4I_{15/2} \)) and second (\( ^4I_{11/2} \rightarrow ^4I_{15/2} \)) excited states of Er\(^{3+} \) ions, respectively.

### 6.1.2 Experimental

The study has been performed on a series of SiO\(_2\):(Er,SiQDs) thin films supplied by Dr. S. Cueff in the group of Prof. R. Rizk in Centre de Recherche sur les Ions, Université de Caen, France. The films were prepared by radio-frequency magnetron co-sputtering on hot (500 °C) quartz substrates. The thickness of the epitaxial layer is about 1-2 μm. A Si-excess of ≈8.5 at. % and an Er concentration of [Er] \( \approx 1-2 \times 10^{20} \) cm\(^{-3} \) were estimated via energy-dispersive X-ray spectroscopy (EDX). Subsequently, the samples were annealed at temperatures ranging from 600 to 1100 °C. The combination of the hot substrate growth and high-temperature annealing resulted in the elimination of defect centers and the formation of small Si nanoclusters of ≈ 2 nm diameter. Further details of the sample preparation procedure and material characterization can be found elsewhere [151, 152]. Following preliminary selection, samples with the most intense 1.54-μm Er-related emission have been chosen for the investigation of optical properties.

The tunable excitation in the UV-Vis range has been provided by a system of two coupled optical parametric oscillators pumped by the third harmonic of a Nd:YAG laser, delivering 5-ns pulses with a repetition rate of 10 or 100 Hz (Solar Laser Systems). The photoluminescence (PL) signals were collected in a monochromator - either THR-1000, f/8, 900 grooves/mm (Jobin-Yvon) or f/3.8, 600 grooves/mm (Solar Laser Systems). The signals were detected by a nitrogen-cooled InGaAs photomultiplier tube (Hamamatsu R5509-72) or a germanium detector (Edinburgh Instruments) in combination with a lock-in amplifier (Signal Recovery SR7265) and/or a digital oscilloscope (Tektronix TDS3000). The analysis has been based on time-integrated PL signals. All experiments were carried out at room temperature.

In order to evaluate quantum yield for a particular PL band, PL intensity measured at different excitation wavelength has been scaled to an equal number of absorbed photons. The average number of absorbed photons per unit area at a certain excitation wavelength \( \lambda \) is given by:

\[
N_{\text{abs}}(\lambda) = \Phi(\lambda) \times (1 - e^{-OD(\lambda)ln10}) ,
\]  

where \( \Phi(\lambda) \) is the pumping flux, and \( OD(\lambda) \) is the optical density, determined from the Lambert–Beer absorption profile using a UV-Vis Lambda900 spectrometer in combination with an integrating sphere (data not shown). The excitation power for
Figure 6.1: PL spectra of the samples annealed temperature at 600 and 900 °C. The increase of Er-related PL is accompanied by the decrease of SiQDs PL intensity. This sensitising role had been well described in the Förster resonance energy transfer (FRET) [84].

A certain excitation photon energy $E_{\text{exc}}$ was tuned using the following relation:

$$P(\lambda) = \Phi(\lambda) \times E_{\text{exc}} \propto \frac{E_{\text{exc}}}{1 - e^{-OD(\lambda)\ln 10}} .$$

(6.2)

6.1.3 Results and discussion

As mentioned previously in the introductory paragraph, the SiQD-assisted indirect excitation of Er$^{3+}$ ions in SiO$_2$ is a multichannel process, with different mechanisms operating in parallel. For a particular material, with fixed SiQD size and distribution, and a certain concentration of Er$^{3+}$ ions, the relative contributions of these excitation channels are expected to vary with the excitation photon energy. Fig. 6.1 shows PL spectra of the two samples, with the same Er concentration and excess Si concentration, annealed at 600 and 900 °C. The increase of Er-related PL follows by the decrease of SiQDs PL intensity. This sensitizing role had been well described by the FRET [84] and discussed in the introductory chapter (Chapter 1).

In the Förster energy transfer process, the nonradiative recombination of an electron-hole pair in the core of a SiQD is accompanied by the excitation of a ad-
adjacent Er$^{3+}$ ion via the dipole-dipole interaction. The energy mismatch is compensated by phonon emission, which reduces efficiency of the transfer. This process is relatively slow and critically dependent on the mutual separation between the SiQD and Er$^{3+}$ ion. In the present case, the maximum of the PL spectrum of SiQDs in the investigated material is around 1.8 eV (see the inset to Fig. 6.2). Therefore, in view of the energy conservation, the Förster energy transfer into the first $^4I_{13/2}$ is highly improbable, and will proceed through the second $^4I_{11/2}$, the third $^4I_{9/2}$ or even higher excited states of the Er$^{3+}$ ion, depending on the optical bandgap of the involved SiQD. Thus, the 1.54-μm emission can only appear following the internal relaxation of the 4f-electron shell into the emitting $^4I_{13/2}$ state, which takes place on a microsecond time scale. Therefore, in the case that the Förster energy-transfer process would be the only available excitation path for Er$^{3+}$ ions, the intensity ratio of emissions from the first (at 1.54 μm) and the second (at 0.98 μm) excited states should be independent on excitation photon energy, being solely governed by the internal relaxation of the inner 4f-electron shell. This is not observed in the experiment. The intensity ratio of the Er-related PL bands at 1.54 and 0.98 μm as measured under excitation with different photon energies $E_{\text{exc}}$ is presented in the main panel of Fig. 1. As can be seen, the relative intensity of the 1.54-μm band rises with the excitation energy, until $E_{\text{exc}} \approx 2.1$ eV. We conclude that in our material the Förster energy transfer is not the only excitation mechanism, and must be accompanied by another process transferring energy directly into the $^4I_{13/2}$ state. This situation changes for even higher excitation photon energies $E_{\text{exc}} \gtrsim 2.1$ eV, as the intensity ratio of the two bands becomes constant.

The increased emission at 1.54 μm could be induced by the aforementioned Auger process of impact excitation by hot carriers. According to previous investigations [82, 83], the impact excitation process requires a minimum excess energy of the excited carrier of 0.81 eV, necessary to bring an Er$^{3+}$ ion into the $^4I_{13/2}$ state. In that case, the minimum excitation photon energy marking the onset of the impact excitation should be $E_{\text{exc}}^{\text{imp}} = E_g + 0.81$ eV, where $E_g \approx 1.8$ eV is the “optical bandgap” of SiQDs facilitating the process. Such a threshold value indeed has been confirmed in the past for a SiO$_2$:(Er,SiQDs) material with a (lower) Er concentration of [Er] ≈ 2.8 × 10$^{19}$ [128].

In the present case $E_g \approx 1.8$ eV, as determined from the excitonic emission of the investigated sample in the inset to Fig. 6.2, leading to $E_{\text{exc}}^{\text{imp}} \approx 2.6$ eV. From Fig. 6.2, we see that the PL intensity ratio changes already for excitation photon energies that are much below this estimated value, with the increase practically commencing just above the optical bandgap $E_g$. We conclude that the previously proposed impact excitation mechanism cannot account for the current results, and that a different explanation has to be sought.

Looking for a possible excitation process which could account for the experi-
Figure 6.2: The ratio between the PL intensities of the first (1.54 µm) and the second (0.98 µm) excited states of Er$^{3+}$ ions in SiO$_2$-(Er,SiQDs) as a function of excitation photon energy. The complete PL spectrum of the investigated sample is shown in the inset, with the indication of energy levels of excited states of Er$^{3+}$ ions in comparison with the photon emission energy. The Er$^{3+}$ ($i = 1 \div 5$) correspond to the $^4I_{13/2}$ (0.81 eV), $^4I_{11/2}$ (1.26 eV), $^4I_{9/2}$ (1.55 eV), $^4F_{9/2}$ (1.9 eV), and $^2H_{11/2}$ (2.38 eV) excited states of the Er$^{3+}$ ions, respectively.
mental findings, we recall that in the past also an excitation mechanism involving participation of a not well specified type of defect center has been proposed for Er in Si-rich SiO$_2$ [153]. However in the present case the formation of defects in the investigated materials has been purposefully suppressed, by the use of the hot substrates and post-growth high-temperature annealing. The hot substrate growth (similar to hot substrate implantation) allows for substantial ordering of material already during deposition. Therefore the presence of a sufficiently large number of defect centers to facilitate an efficient excitation route is unlikely.

In order to gain further insight into the possible microscopic mechanism responsible for the experimental observations, we have investigated the (external) quantum yield (QY) of both Er-related PL bands, in the energy range where their intensity ratio varied, below the estimated threshold for impact excitation. The results are depicted in Fig. 2. The experiments were conducted under the condition of an equal number of absorbed photons and in the low excitation flux regime, to exclude non-linear effects. For a simple comparison, the QY values obtained for both bands have been normalized for the lowest excitation energy. (In fact, the QY of the 1.54-μm band was found to be two orders of magnitude higher than that of the 0.98-μm emission). We see that the QY of the 1.54-μm band increases practically over the whole range of the investigated excitation energies. In contrast, QY of the 0.98 μm band remains constant for lower energy pumping and increases only above the threshold value of ~ 2.1 eV.

We point out that the QY data depicted in Fig. 6.3 are fully consistent with the PL intensity ratio given in Fig. 6.2, and show that additional excitation below the estimated threshold for impact excitation process takes place not only into the lower $^4_{13/2}$ but also into the higher $^4_{11/2}$ state of the Er$^{3+}$ ions.

Before proposing a new physical mechanism, we note that a high-energy carrier in SiQD can be generated also by sequential absorption of two low-energy photons; it is possible that a photo-generated carrier might absorb another photon (intraband absorption), and attain a higher excited state, enabling the impact excitation mechanism. As a result, the threshold for the hot carrier impact excitation process might be shifted to a lower excitation photon energy. In order to exclude this possibility, we investigated the QY of the 1.54-μm band for all photon energies under low and high flux conditions. Both dependencies were linear and practically identical in the measured energy range, directly scaling with the flux ratio ($5 \times$). We conclude that the generation of hot carriers due to intraband absorption can be neglected. Therefore, the increase of the QY observed for excitation energies below the impact excitation threshold indicates the presence of a different, and thus far unidentified excitation mechanism.

The proposed energy-transfer process which can account for the experimental findings reported in this study is schematically depicted in Fig. 6.4. In the first step
Figure 6.3: The dependence of quantum yield (QY) of emission bands at 0.98 μm (blue circles) and 1.54 μm (red squares) on the excitation photon energy, under the condition of an equal number of absorbed photons per pulse (9 × 10^{10} cm^{-2}), in the low excitation regime. The dashed lines, indicating the quantum yield onsets, serve only as a guide to the eye.
6.1. Photon cutting for excitation of Er\(^{3+}\) ions

A photon of energy larger than the bandgap is absorbed by a SiQD generating an exciton, possibly with some excess energy. The excitation process proceeds by a Coulombic interaction of an exciton in the ground state and the nearest Er\(^{3+}\) ion [154]. In this case, one of higher excited states of the Er\(^{3+}\) ion acts as a virtual state enabling the process - the \(i\)-th excited state in the inset to Fig. 1. It is the second-order perturbation process, in which the next step involves an immediate transfer of part of the energy to the second Er\(^{3+}\) ion in close proximity, enabled in our material by the high concentration of Er dopants. Thus the final state of the process comprises two Er\(^{3+}\) ions in excited states, while the possible energy excess is compensated by (multi-)phonon emission.

The efficiency of the proposed process is higher for a smaller energy mismatch \(\Delta\) between the exciton and the virtual state (see Fig. 6.1.3) and depends also on the oscillator strength of the involved excited state of Er\(^{3+}\). As can be seen from the sketch in the inset of Fig. 6.2, the state \(^{4}\text{I}_{11/2}\) (2.38 eV or 520 nm) has the highest oscillator strength in the considered photon energy range. This effect will modulate the experimentally measured excitation energy dependence of the PL quantum yield.

In contrast to the impact excitation, in the present case no free carriers are left after the excitation is completed, thereby limiting de-excitation by the Auger process. At the same time, the fact that Er\(^{3+}\) ions are excited into the lower excited states while the bandgap energy of the SiQDs is relatively large, limits the excitation reversal by the so-called back-transfer process [57], in which the energy disperses back to SiQDs. The probability of the excitation process via a virtual state can compete with excitation into the real Er\(^{3+}\) state of lower energy, as it involves the higher states of the Er\(^{3+}\) ions with higher oscillator strengths and is assisted by lower numbers of the emitted phonons, and increases dramatically with Er concentration.

The process depicted in Fig. 6.4 provides an additional efficient Er excitation channel that can account for the QY enhancement. Excitons in the ground state of SiQDs with bandgap energies above 1.62 eV can excite two Er\(^{3+}\) ions into the first excited state (\(E_g > 2 \times 0.81\) eV), upon a single photon absorption, explaining the rise of its QY in Fig. 2. The excitons in SiQDs with a bandgap energy larger than the sum of the first and the second excited states of the Er\(^{3+}\) ions (\(E_g > 0.81 + 1.24\) eV = 2.05 eV) can facilitate the excitation process in which one Er\(^{3+}\) ion attains the first excited state - \(^{4}\text{I}_{13/2}\), giving rise to the 1.54 \(\mu\)m emission - while the second one goes to the second excited state \(^{4}\text{I}_{11/2}\), enhancing the 0.98 \(\mu\)m PL, stabilizing the ratio of 1.54 and 0.98 \(\mu\)m emission intensities shown for higher energies (Fig. 6.2).

6.1.4 Conclusion

In conclusion, the current study shows that the indirect excitation of Er\(^{3+}\) ions in SiO\(_2\) facilitated by SiQDs is a complex multichannel process with the participation of different physical mechanisms. Their individual contributions depend on the
Figure 6.4: Schematic illustration of the non-resonant excitation mechanism, via the high excited state of Er as the virtual state (second order perturbation process), leading to the simultaneous excitation of two neighboring Er ions in the first excited state (Er<sup>1</sup> under absorption of a single photon. ∆ is the energy mismatch between the exciton ground state and the virtual state involved.
pumping photon energy but also on material characteristics. In particular, for the SiO₂(Er,SiQDs) system with small SiQDs and a sufficiently large Er concentration, we identify a unique energy-transfer mechanism in which two Er³⁺ ions can be simultaneously excited upon absorption of a single photon of sufficiently high energy. The process involves direct photon energy transfer into two Er³⁺ ions, assisted by a SiQD.

In comparison with previously identified excitation mechanisms taking place in the SiO₂(Er,SiQDs) system - the impact excitation and energy transfer by the dipole-dipole interaction (Förster) - the proposed mechanism offers the important advantage of suppressing the most important processes of nonradiative de-excitation that hamper the practical potential of this material for applications - the Auger process of energy transfer to free carriers and excitation reversal by back-transfer. Finally, we note that the proposed mechanism bears some similarity with the previously reported quantum cutting taking place between two types of different rare-earth ions or the Er³⁺ ions themselves [155], while removing the disadvantage of resonant pumping, thanks to the band-to-band absorption in SiQDs.

6.2 Monocolor solar cell

Spectral mismatch of the energy distribution of photons in the solar spectrum and the fixed bandgap energy of semiconductor materials is the main reason for losses of energy taking place in photovoltaic conversion in solar cells. Photons with energies smaller than the semiconductor bandgap are not absorbed, and their energy is totally lost. Photons with energy larger than the band gap are absorbed, but the excess energy above the bandgap is converted to heat. In a Si-based solar cell, the spectral mismatch accounts for the total loss of more than 50%. One way to reduce the energy loss is by carrier multiplication (CM), in which several electron-hole pairs can be generated per an incident photon, for photon energies larger than twice the band-gap energy of the solar cell material.

The results shown in the previous part have identified a new excitation mechanism, which could be of great fundamental and application impact. It is based on Coulombic interaction but distinguishes itself in several major points from the previously classified FRET process:
- It is non-resonant;
- It involves one of the high excited states of Er³⁺ ions as a virtual state;
- It results in efficient quantum cutting, which does not compete with internal relaxation of the Er³⁺ ion;
- It is characterized by a low energy threshold for quantum cutting, which is very different from the previously observed quantum cutting in the SiO₂(Er,SiQDs) system in Ref. [128];
Figure 6.5: The coverage of solar spectrum AM1.5 (National Renewable Energy Laboratory, NREL, USA), by bulk Si conversion and Er cutting under an assumption of 100% quantum cutting efficiency. The fraction of AM1.5 spectrum (red) that can be covered into usable energy by a crystalline silicon solar cell (violet), and Er$^{3+}$ ions of 100% down conversion or quantum cutting efficiency (green). As can be seen, due to the smaller energy of the first excited state of Er$^{3+}$ ions, almost 80% of the AM1.5 spectrum can be covered.

- Since quantum cutting follows immediately upon the energy transfer, the so-called back-transfer process is not possible.

Moreover, upon completion of the energy transfer process, no free carriers are left in SiQDs and therefore also Auger quenching is not possible. In contrast to the impact excitation of Er$^{3+}$ ions by hot carriers in SiQDs, this novel excitation process appears in the investigated materials due to combination of two parameters (a) excellent position of SiQDs bandgap energies with respect to higher excited states of Er$^{3+}$ ions, and (b) high Er concentration, enabling Er-Er interactions (and quantum cutting).

Our findings open new possibilities towards the conversion of the solar light into a single wavelength - 1.54 μm, as the threshold energy of the excitation mechanism spans into the lower range of the solar spectrum in the visible. This might have an impact for applications in light emitters and amplifiers for optoelectronics and photonics at 1.54 μm, due to the high absorption cross-section of SiQDs and absence of
6.2. Monocolor solar cell

the back-transfer. Further, we note that the 1.54 \( \mu \text{m} \) wavelength is at the theoretical maximum of solar spectrum conversion by carrier multiplication [156]. This opens applications in photovoltaics for the so-called monocolor solar cell, optimized for a single wavelength only. The solar spectrum will be converted into 1.54\( \mu \text{m} \) with the use of quantum cutting in SiO\(_2\):(Er,SiQDs) material, and eventually guided into such a solar cell. By this way, the monocolor solar cell using SiO\(_2\):(Er,SiQDs) material can cover a larger portion of the solar spectrum as illustrated in Fig. 6.5. The red spectrum represents the AM1.5 solar spectrum as given by by National Renewable Energy Laboratory, USA. Bulk Si absorption spectrum (violet) covers about 50\% of the AM1.5 solar spectrum. Due to smaller energy of the first excited state of Er\(^{3+}\) ion, almost 80\% of the AM1.5 spectrum can be covered.