Optical spectroscopy of carrier multiplication by silicon nanocrystals

Timmerman, D.

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Optical Spectroscopy of carrier Multiplication By silicon nanocrystals

Dolf Timmerman
Optical spectroscopy of carrier multiplication by silicon nanocrystals

ACADEMISCH PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de University of Amsterdam
op gezag van de Rector Magnificus
prof. dr. D. C. van den Boom
ten overstaan van een door het college voor promoties ingestelde commissie, in het openbaar te verdedigen in de Agnietenkapel
op vrijdag 22 juni 2012, te 14.00 uur.

door

Dolf Timmerman

geboren te Hoorn
Promotiecommissie

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Faculteit der Natuurwetenschappen, Wiskunde en Informatica

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Deadline

I know this desk
Every scratch
Every circled stamped coffee stain.
Finally
"Optical spectroscopy of carrier multiplication by silicon nanocrystals"
Cornered blank paper, mind bending flatlands, wander in the back of my head.
No blinking cursor
No consciousness
A digital mind set.
“Sorry sir.” strikes my brain destructively
My fingers stop.
“You have to move your desk.”
I breath
The smell of paint
I look up
A man with a bucket white paint and a brush in his hands.
“Can’t this wait!” I yell at his speckled face.
“No sir, the perpetual motion is on his way and I paint his path.”
I look behind my desk
A white line divides the floor in two
“Are you mad!” and I stare deep in his eyes
“Don’t forget to look at your horizon, it moves faster than you think.”
Baffled, I watch him bend over, walk backward and paint his perpetual lie.
smaller smaller and smaller.

“I decide!”

To Loïs
kleine onderzoeker
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<th>Units</th>
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<tbody>
<tr>
<td>$a$</td>
<td>Lattice constant</td>
<td>m</td>
</tr>
<tr>
<td>$A_{s,in,out,f}$</td>
<td>Area of sphere, entrance port, exit port, fiber core</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$c$</td>
<td>Velocity of light in free space</td>
<td>$2.9979 \times 10^8$ m s$^{-1}$</td>
</tr>
<tr>
<td>$d$</td>
<td>Depth</td>
<td>m</td>
</tr>
<tr>
<td>$D$</td>
<td>Diameter</td>
<td>m</td>
</tr>
<tr>
<td>$E_{C,V,NC}$</td>
<td>Energy of conduction\valence band\nanocrystal bandgap</td>
<td>J</td>
</tr>
<tr>
<td>$E_{h\nu,p,g}$</td>
<td>Energy of photon, phonon, bandgap</td>
<td>J</td>
</tr>
<tr>
<td>$f_{Si}$</td>
<td>Filling fraction silicon</td>
<td></td>
</tr>
<tr>
<td>$I_{em,ex}$</td>
<td>Emission and excitation intensity</td>
<td>counts</td>
</tr>
<tr>
<td>$I_{0,1}$</td>
<td>Incident and transmitted intensity</td>
<td>counts</td>
</tr>
<tr>
<td>$J_{pump}$</td>
<td>Pump pulse fluence (number of photons per pulse per cm$^{-2}$)</td>
<td>cm$^{-2}$</td>
</tr>
<tr>
<td>$\mathbf{k}$</td>
<td>Electron wave vector</td>
<td>m$^{-1}$</td>
</tr>
<tr>
<td>$k_{R,NR}$</td>
<td>Radiative, non-radiative rate</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$l$</td>
<td>Layer thickness</td>
<td>m</td>
</tr>
<tr>
<td>$L_s$</td>
<td>Radiance of sphere</td>
<td>J s$^{-1}$ sr$^{-1}$ m$^{-2}$</td>
</tr>
<tr>
<td>$N$</td>
<td>Maximum number of e-h pairs that can recombine radiatively</td>
<td></td>
</tr>
<tr>
<td>$N^*$</td>
<td>Number of e-h pairs that can recombine radiatively</td>
<td></td>
</tr>
<tr>
<td>$N_{NC(\text{Er})}$</td>
<td>Total number of nanocrystals (erbium ions) in volume</td>
<td></td>
</tr>
<tr>
<td>$N_{NC(\text{Er})}^*$</td>
<td>Excited number of nanocrystals (erbium ions) in volume</td>
<td></td>
</tr>
<tr>
<td>$N_{abs}$</td>
<td>Total amount of absorbed photons</td>
<td></td>
</tr>
<tr>
<td>$N_{PL}$</td>
<td>Total amount of emitted photons</td>
<td></td>
</tr>
<tr>
<td>$N_x$</td>
<td>Number of nanocrystals that have absorbed $x$ photons</td>
<td></td>
</tr>
<tr>
<td>$\langle NC^* \rangle$</td>
<td>Average number of photons absorbed per nanocrystals</td>
<td></td>
</tr>
<tr>
<td>$[NC]$</td>
<td>Concentration of nanocrystals</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$p$</td>
<td>Momentum</td>
<td>Js</td>
</tr>
<tr>
<td>$S_{abs}$</td>
<td>Fraction of photons that are absorbed</td>
<td></td>
</tr>
<tr>
<td>$S_{PL}$</td>
<td>Time-integrated photoluminescence signal</td>
<td>counts</td>
</tr>
</tbody>
</table>
# List of Symbols and Abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t )</td>
<td>Time</td>
<td>s</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>Absorption coefficient</td>
<td>cm(^{-1})</td>
</tr>
<tr>
<td>( \beta )</td>
<td>Stretch parameter</td>
<td></td>
</tr>
<tr>
<td>( \gamma_{PL} )</td>
<td>photo-excitation efficiency</td>
<td></td>
</tr>
<tr>
<td>( \zeta )</td>
<td>Proportionality factor</td>
<td></td>
</tr>
<tr>
<td>( \eta )</td>
<td>Quantum yield</td>
<td></td>
</tr>
<tr>
<td>( \lambda )</td>
<td>Wavelength</td>
<td>m</td>
</tr>
<tr>
<td>( \mu )</td>
<td>Mean</td>
<td></td>
</tr>
<tr>
<td>( \nu_{EHPM} )</td>
<td>Electron-hole pair multiplication efficiency</td>
<td></td>
</tr>
<tr>
<td>( \rho )</td>
<td>Reflectance</td>
<td></td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Standard deviation</td>
<td></td>
</tr>
<tr>
<td>( \sigma_{ex,PL} )</td>
<td>Excitation, photoluminescence cross-section</td>
<td>cm(^2)</td>
</tr>
<tr>
<td>( \tau_{PL,R} )</td>
<td>Photoluminescence, radiative lifetime</td>
<td>s</td>
</tr>
<tr>
<td>( \Phi )</td>
<td>Flux</td>
<td>s(^{-1}) m(^{-2})</td>
</tr>
</tbody>
</table>

## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>BBO</td>
<td>Beta-barium borate</td>
</tr>
<tr>
<td>CM</td>
<td>Carrier multiplicative</td>
</tr>
<tr>
<td>CMOS</td>
<td>Complementary metal oxide semiconductor</td>
</tr>
<tr>
<td>e-h</td>
<td>Electron–hole</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron energy loss spectroscopy</td>
</tr>
<tr>
<td>FCC</td>
<td>Face centered cubic</td>
</tr>
<tr>
<td>FRET</td>
<td>Förster resonant energy transfer</td>
</tr>
<tr>
<td>HAADF</td>
<td>High angle annular dark field</td>
</tr>
<tr>
<td>HR-TEM</td>
<td>High-resolution transmission electron microscopy</td>
</tr>
<tr>
<td>LED</td>
<td>Light emitting diode</td>
</tr>
<tr>
<td>MEG</td>
<td>Multiple exciton generation</td>
</tr>
<tr>
<td>NA</td>
<td>Numerical aperture</td>
</tr>
<tr>
<td>NC(s)</td>
<td>Nanocrystal(s)</td>
</tr>
<tr>
<td>OD</td>
<td>Optical density</td>
</tr>
<tr>
<td>OPO</td>
<td>Optical parametric oscillator</td>
</tr>
<tr>
<td>PL(E)</td>
<td>Photoluminescence (excitation)</td>
</tr>
<tr>
<td>PMT</td>
<td>Photo multiplier tube</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic(s)</td>
</tr>
<tr>
<td>QD</td>
<td>Quantum dot</td>
</tr>
<tr>
<td>QY</td>
<td>Quantum yield</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>rf</td>
<td>Radio-frequency</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>SHG</td>
<td>Second harmonic generation</td>
</tr>
<tr>
<td>SRSO</td>
<td>Silicon-rich silicon oxide</td>
</tr>
<tr>
<td>(SS)QC</td>
<td>(Space-separated) quantum cutting</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 Silicon age

The term “Silicon Age” is popularly used to describe the current period, similar as the archaeological ages were named after specific materials which were prevalently used. While you can dispute that this term would be classified within scientific nomenclature used for historical periods, silicon is certainly the most important material with respect to present-day microelectronic technology with far leading consequences into almost all aspects of everyday life. This is a direct result of the invention of the fundamental building block of electronic devices - the transistor. Interestingly enough, the transistor effect was discovered by Bardeen, Brattain and Shockley in December 1947 in a different material, namely germanium. Since the bandgap of germanium is only 0.7 eV, the use of this material in practical transistors is limited to not too high temperatures, and therefore also to lower power applications. Another disadvantage of germanium is the chemical activity of its surface, making it necessary to enclose the structures with other materials for stable operation, increasing the cost.

Silicon is a group IV element, like germanium, and has very similar electronic properties, but crystalline silicon has a larger bandgap of 1.1 eV. This fact started research into the use of silicon for transistors, as it could potentially operate at higher powers and temperatures. In 1954 “Bell Labs” succeeded in realization of the first silicon transistor. This was the starting point of the continuous miniaturization, cost reduction and technological development that has brought us into the “Silicon Age”. To give some idea of the enormous progress made in integrated circuits, currently (2012) commercial chips are available, which contain ~1 billion transistors, each having a typical dimension down to 20 nm. Another result of the studies on silicon transistors at “Bell Labs” was the development of a silicon based photovoltaic (PV) cell. It turned out to have much higher conversion effi-
ciency (of \(\sim 6\%\)) than the long known selenium based cells used at that time. The very beneficial bandgap of silicon, close to the theoretical optimum for a solar light conversion material as it turned out later [1], made it very interesting for PV applications. Since then increasing technological level of silicon fabrication and processing technologies has improved efficiencies and reduced costs of silicon PV cells considerably. Conversion efficiencies have been shown to reach values of \(\sim 25\%\) [2], close to the theoretical maximum of \(\sim 30\%\).

For electronic applications on both the very large scale (PV) and the small scale (microelectronics) Si has proven to be the dominant material. Another field which could possibly greatly benefit of the technological superiority of Si, is that of photonics. Efficient Si based light emitters are in this case a necessity, and although long sought for, are still non existing.

The next section discusses the optical properties of Si and the reason why light emission is very poor.

### 1.2 Optical properties of Si

Silicon has four valence electrons, and crystals will form in a diamond structure. Its valence electrons are derived from the \(s\) and \(p\) orbitals (electronic configuration \(1s^22s^22p^63s^23p^2\)) and in the crystalline structure \(sp^3\) hybridized orbitals form covalent bonds between the atoms. From the level ordering it becomes clear that the conduction band has \(s\)-like character derived from \(s\) anti-bonding states, while the top of the valence band is \(p\)-like, derived from \(p\) bonding states [3]. This means that electronic transitions between conduction and valence band are dipole allowed and in principle could be efficient. However, when we look at the bandstructure of crystalline Si, it turns out to be an indirect gap semiconductor; the conduction band minimum is not at the Brillouin zone centre (\(\Gamma\)-point), but at approximately 85% of the \(\Gamma\)–\(X\) distance (See Fig. 1.1a). As a result, transitions at the band edge must be accompanied by a large change in the electron \(\vec{k}\)-vector \(0.85X\), where \(X = (\pi/a) (\pm 1,0,0), (0,\pm 1,0)\) or \((0,0,\pm 1)\) (= 6-fold). For the lattice constant of \(a = 0.543\) nm, we can calculate the momentum difference with the top of the valence band at \(\vec{k} = 0\) to be \(0.85 \times 2\hbar/a = 2 \times 10^{-24}\) Jsm\(^{-1}\). When we compare this with the momentum associated with a photon having an energy the size of the bandgap 1.13 eV = \(p \cdot c\), we get a value of \(p = 6 \times 10^{-28}\) Jsm\(^{-1}\). It is obvious that this transition cannot take place by itself. The most probable way to have a radiative transition without breaking the momentum conservation, is by addition of phonon absorption or emission. As a result, the transition can take place, but the probability is 4-6 orders of magnitude smaller than for the direct (in \(\vec{k}\)-space) transition. The photon energies associated with this transition are given by \(E_{h\nu} = E_g \pm E_p\), where \(E_g = E_C - E_V\), the difference between energy associated with bottom of conduction band \(E_C\) and top of valence band \(E_V\). \(E_p\) indicates the
1.2. OPTICAL PROPERTIES OF SI

Figure 1.1: (a) Brillouin zone of Si. Some important symmetry points and directions are indicated. (b) Bandstructure of Si. The energy dispersion is drawn for different directions connecting the points of high symmetry. $E_C$ and $E_V$ indicate the energy associated with the bottom of the conduction band and top of the valence band, respectively. Note that the $E_C$ is associated with $\vec{k} = 0$.

Energy of the phonon accompanying the transition, where the sign depends on the creation or consumption of a phonon in the process. Probabilities of absorption and emission near the silicon band edge are very small, as can be seen by the small absorption coefficient for values close to the bandgap, orders of magnitude smaller than for direct bandgap materials, and slowly increasing for larger energies – see Fig. 1.2. The radiative lifetime, typically $\sim 1$ ms which compares to $\sim 1-10$ ns for direct bandgap semiconductors [4]. For luminescence this indirect bandgap is disastrous. For example optically excited carriers with initially high energy relax rapidly by emitting phonons. Since electron-phonon coupling is very strong this process takes typically place on timescales of $\sim 100$ fs, bringing the carriers quickly to the bottom of the conduction band, before radiative transitions can take place [6]. From there they can emit a photon by the process mentioned above, or recombine non-radiatively for example via defects. Since the radiative carrier lifetime is very long, the chance for a carrier to undergo a non-radiative process is very large, limiting the luminescence efficiency. Nevertheless it is fair to mention that a silicon light emitting diode with an efficiency as high as 1% has been presented [7]. In this case a high quality crystal was used, which had very few contaminations and special surface treatments were employed to remove a large part of non-radiative centers.
1.3 Why silicon nanocrystals?

1.3.1 Quantum confinement effects

In the beginning of the 1990s it was discovered that light emission can take place from porous Si [8, 9] and from ultrafine nanoparticles [10], which suggested that limitations of the Si band-structure on light emission might be overcome in Si nanocrystals in wide-bandgap dielectric matrices. Carriers inside a NC experience a strong confining potential, localizing the electronic states considerably. The so-called quantum confinement regime, the size for which carrier localization alters the electronic states, is determined by the “Bohr-radius” (following the analogy size of an electron-hole pair to that of a hydrogen atom) inside the confined material, for Si this radius is approximately 4.5 nm. Localization of electronic states also leads to spread in momentum distribution, which follows from Heisenberg uncertainty relation. Since the wave functions consist of plane waves covering all possible wave vectors including \( \vec{k} \sim 0 \) for electrons and \( \vec{k} \sim \vec{k}_\Delta \) for holes, there is a nonzero probability of \( \Delta - \Gamma \) radiative transitions, without additional momentum conserving (quasi)-particles. This leads to a substantial decrease of the radiative recombination time, which is observed in photoluminescence lifetime experiments. In general, stronger confinement in smaller crystallites gives rise to shorter radiative times as quasi-direct transitions become increasingly probable (from \( \sim \text{ms} \) to \( \sim \mu \text{s} \) for the smallest Si NCs). However, even for small nanocrystals the momentum conservation law is not fully broken, which can be seen for example in PL radiative lifetime for very small Si nanocrystals, which is still longer than several microseconds. Even more, PL spectra of single Si NCs show multiple peaks indicating that the quasi-direct transition is not the only means.

![Figure 1.2: Optical absorption of Si at 300 K. Data taken from Ref. [5]](image)
1.3. WHY SILICON NANOCRYSTALS?

of emission, but there are also momentum conserving phonons involved [11].
Another typical feature of the energetic structure in such “quantum confined”
systems is that the energy difference between the valence and conduction band
increases when the nanoparticle size decreases. In absorption and emission spec-
troscopy the terminology “blueshift” is employed, since the wavelength of emitted
and absorbed photons shift to shorter wavelengths. The simplest explanation of
this phenomenon can be found in the “particle in a box” model, where an infinitely
high potential barrier is located at the nanocrystal boundary. The energy of car-
rriers (electrons and holes) inside such a nanocrystal are proportional with $D^{-2}$,
where the $D$ is the diameter. It is obvious that this model is an oversimplification
of the real behavior, but it gives some insight into what is happening on these
scales. Additional effects, like electron-hole Coulomb interaction ($D^{-1}$) and the
non-infinite barrier at the nanocrystal, relax the dependence considerably. From
experimental studies where the relation between the energy-gap and nanocrystal
size was examined, it was mostly found that the scaling is proportional to $D^{-b}$,
with $1 < b < 1.5$ [12, 13, 14, 15, 16]. The differences between the individual re-
sults from the studies are mostly attributed to preparation procedure, structure,
surrounding matrix, surface bonds etc. Especially surface phenomena can play an
important role in small nanocrystals, since the surface-to-volume ratio increases
quickly. For example for Si nanocrystals with a diameter of 3 nm it can be esti-
mated that more than 50% of the atoms are located at the surface. A important
experimental study into the effect of surface termination on PL properties can
be found in Ref. [17]. In this case hydrogen terminated silicon nanocrystallites in
porous Si was slowly oxidized. Oxidation decreases the size of nanocrystals and,

![Figure 1.3: Electronic states in Si nanocrystals as a function of cluster size and
surface passivation (from Wolkin et al. [17]).](image-url)
following quantum confinement, a blue-shift of PL spectra was observed. But for the smaller particles luminescence stabilized at a longer wavelength. The model proposed to explain these results invoke that some dangling bonds are passivated into Si=O double bonds. Simulations of the energy bands of Si NCs with Si=O double bonds at the surface (Fig. 1.3) indicate the importance of oxygen states for the energetic structure. For hydrogen passivated NCs, quantum confinement holds up and luminescence originates from recombination of excitons. For oxidized NCs the smaller NCs (Zone II and III) show levels that appear inside the bandgap and electrons and holes will be trapped on these surface states, so that luminescence originates from transitions between them. This model is widely assumed to explain the behavior of oxidized Si NCs, and shows the importance of surface chemistry in these systems.

The wide tunability range of emission energies, from UV-emitting (350 nm) chemically synthesized NCs \cite{18}, via visible wavelengths (porous silicon \cite{17}) into infrared up to 1100 nm (oxidized, gas-phase fabricated \cite{14}) and even to longer wavelengths by means of doping (see Chapter 8), shows the enormous versatility of silicon nanocrystals.

1.3.2 Non-equilibrium carriers

Another consequence of quantum confinement in nanostructures is a reduction of density of states, which results in discrete electronic states instead of continuous bands of bulk materials \cite{19}. This notion raised a lot of interest, as non-equilibrium carrier dynamics can be severely influenced, and controlled. Photo-generated carriers created with energies above conduction and valence band edges, will thermalize rapidly and convert their excess energy into heat. In NCs the distance between individual electronic states increases, and at the same time density of phonon modes decreases, so that transitions between the electronic states by means of phonon emission decrease in probability \cite{20}. This so-called “phonon-bottleneck” has been proposed theoretically \cite{21} and which should not appear if hot-carrier cooling occurs via longitudinal-optical phonon emission. However, there are also other mechanisms by which hot carriers can release their excess energy. An Auger mechanism that transfers the energy to a hole, which thermalizes quickly because of the smaller level spacing and larger effective mass \cite{22} can break the phonon bottleneck. But also other mechanisms, like electron-hole scattering \cite{23}, acoustical-optical phonon emission, \cite{24} and impact ionization, could achieve this \cite{25}. Experimentally the slowing down of cooling rates has been observed in a number of different types of NCs, but was also absent in many others (see Ref. \cite{26} for an overview). For silicon NCs it has not been observed.
1.4 Synergy of this thesis

In this thesis, fundamental investigation of optical excitation and de-excitation processes are described. The prior paragraphs give a general introduction to the properties of the material of choice: silicon. Quantum confinement in nanostructures increase the optical activity with respect to its bulk counterpart, and this introduces also other (beneficial) properties. The experimental approaches that are used to study optical excitation and emission processes as well as sample preparation procedures and structural characterization techniques are described in Chapter 2. Determination of photoluminescence quantum yield is a specific characterization technique that is widely employed throughout this work. The exact definition and ambiguities thereof as well as the details of the experimental procedures can be found in Chapter 3. The limits of the optical performance of silicon nanocrystals prepared by thin film deposition technique, are investigated in the next chapter. For short wavelengths, the approach to these limits was found to be different, as excitation cross-sections turned out to grow faster than anticipated. This effect is more elaborately studied and discussed in the second part of Chapter 4, where it is found that the relative quantum yield of photoluminescence increases for shorter excitation wavelengths. The model to describe this effect, termed space-separated quantum cutting, is introduced and its application potential is discussed. The strong demand from the nano-optics community and also possible demonstration of applicability of the above effect led to dedicated investigation of absolute photoluminescence quantum yield (Chapter 5). The expansion to differently prepared silicon nanostructures in this chapter shows that the identified carrier multiplication mechanism is a general feature of densely packed silicon nanocrystal structures. Since optical properties of such ensembles are strongly influenced by size distribution and also saturation effects; an elaborate study dedicated to these specific effects is presented in Chapter 6. Erbium is a much studied optical dopant and silicon nanocrystals are known for their effective sensitization of excitation of these rare earth ions. Different energy transfer processes between these species can be observed, where most strikingly the quantum cutting effect is also noted, with erbium as the receiving species (Chapter 7). Finally, in the quest to enable a shift of the quantum cutting process to smaller photon energies, a system of phosphorous and boron co-doped silicon nanocrystals is studied. These show emission with energies below that of bulk Si bandgap energy values and might enhance the effective range for quantum cutting to even smaller photon energies.
This chapter discusses the various instrumental and experimental details of the investigations described in this thesis. Firstly, the various instruments for optical spectroscopy are presented and specific features of these are elaborated on. Secondly, details about the sputtering technique used for sample preparation are given and, thirdly, the characterization of the samples by different techniques, as well as simulations of material properties, are discussed. For higher optical densities there will be a large difference in excitation conditions dependent on the position of the nanocrystals relative to the surface where light is incident. The influence this effect has on the spatial distribution of excited states and consequences of that for experimental findings are discussed as well.

2.1 Photoluminescence measurements

The most important characterization technique used throughout this study, is that of photoluminescence spectroscopy. Samples are illuminated by a light source and photons that are absorbed by the sample bring the material from equilibrium conditions to an excited state. Subsequently, the material will return to equilibrium, which can be accompanied by the emission of photons. These emitted photons can be detected and their properties, like energy and dynamics, can give information about specific features of the material. Since we are interested in dependence of luminescence on excitation photon energies, different tunable light sources have been employed. The details of these are discussed in the next two paragraphs.
CHAPTER 2. EXPERIMENTALS

Figure 2.1: Layout of the OPO laser system. The 3\textsuperscript{rd} harmonic of a Nd:YAG laser can be converted via different OPO’s and SHG-units in order to generate wavelengths in the range from 210-2480 nm. Different wavelength ranges are indicated for each pathway and the arrows present horizontal or vertical polarization.

2.1.1 OPO setup

For generation of coherent light with tunable wavelength a setup comprising a Nd\textsuperscript{3+}:YAG laser and nonlinear optical crystals was employed. A simplified optical scheme can be found in Fig. 2.1. For nonlinear conversion of light it is essential to have large photon fluxes, which is obtained by a Q-switching technique. The Nd\textsuperscript{3+}:YAG laser in the left of the figure comprises a ring resonator containing the active medium and a Q-switch unit (Pockells cell), which can change the Q-factor of the optical resonator. Initially the Nd\textsuperscript{3+}:YAG is pumped by a xenon flash-lamp, which induces population inversion, but there is no laser operation as the feedback of the resonator is poor (low Q-factor). When the medium is gain-saturated, the Q-switch rapidly changes to high Q, allowing feedback and starting optical amplification. The build up energy in the gain medium will now quickly be released and generate a short (∼10 ns) intense light pulse at the lasing wavelength of 1064 nm. Part of this light pulse is guided through an optical amplifier to generate even higher intensities (typically 200 mJ in a pulse). This light pulse is frequency doubled in a “second harmonic generation unit” (SHG) inside the laser housing. Further, by subsequent nonlinear frequency mixing of the residue of the fundamental and the generated second-harmonic, the third harmonic, with wavelength 354 nm, is rendered. The pulse energy after the nonlinear conversion steps is approximately 55 mJ, enough to drive nonlinear conversion in the optical parametric oscillators (OPO’s). In Fig. 2.1 we see that the horizontally polarized pulse from the Nd:YAG laser can go to two different OPO’s in which down conversion can take place. This process is based on a second-order nonlinear effect in beta-barium borate (BBO) crystal, similar to the second harmonic generation in the pump laser. In down conversion, however, the pump frequency ω\(_p\) is converted in radiation of two smaller frequencies: ω\(_s\) (signal) and ω\(_i\) (idler). Conservation of energy ω\(_s\) + ω\(_i\) = ω\(_p\), and momentum \(\vec{k}_s + \vec{k}_i = \vec{k}_p\), in the process determine the signal and idler frequencies. Collinear beams in crystals satisfy ω\(_p\) \cdot n\(_p\) = ω\(_s\) \cdot n\(_s\) + ω\(_i\) \cdot n\(_i\), where n\(_p\), n\(_s\) and n\(_i\) are the refractive indexes at the wavelength of pump, signal and idler. The BBO crystals
2.1. PHOTOLUMINESCEENCE MEASUREMENTS

feature an angular dependence of birefringence and thus allow for selection of the three wavelengths. Since the pump wavelength is constant, changing the angle of the crystal relative to pump radiation will alter phase matching condition and thus the signal and idler wavelengths. The crystals in OPO I and OPO II are both cut differently as to be optimized for different wavelength ranges. Signal and idler wavelengths are perpendicularly polarized, indicated in the figure with horizontal and vertical arrows, which makes selection relatively easy. A Glan-Thompson prism can pass either horizontally or vertically polarized light, and these wavelengths can than be used. If shorter wavelengths than 415 nm are imminent, the radiation from the OPO’s can be frequency doubled in SHG units. For this process each wavelength has a certain angle of synchronism of the non-linear crystal with the incoming radiation, where SHG efficiency is optimal. This requires that the SHG units be synchronized with the OPO units in order to double the frequency most efficiently. Another requirement is that the incoming light is horizontally polarized; for this reason a $\lambda/2$ retarder plate is implemented in the setup to rotate the polarization of the idler by 90°. Note that the frequency-doubled light from the SHG units is vertically polarized.

2.1.2 Xenon lamp

For some experiments there are more stringent conditions on the stability of the excitation light source. The combination of a high stability xenon lamp coupled to a low-straylight double beam monochromator accomplished this. A 150 Watt xenon (Hamamatsu L2273) lamp inside a forced air-cooled lamp housing (Hamamatsu E7536), shows very high stability, better than 0.3 % peak-to-peak and drift of <0.5 % per hour. The lamp emits a broad “white light” spectrum, with a color temperature of 6000 K, covering the 185-2000 nm wavelength range. Light from the lamp is collimated and coupled into a double pass monochromator (Solar MSA-130). The monochromator combines effectively two monochromators with focal length of 130 mm, and in this way acts as a low-stray-light-filter with tunable bandwidth (0.2-40 nm). For broad band sources stray light can be a nuisance, as typically $10^{-4}$ of light directed inside a monochromator will be scattered randomly which is quite considerable. The MSA-130 is characterized by a value for stray light of $10^{-9}$, diminishing this contribution.

2.1.3 Detection

After optical excitation the samples start to emit light, which needs to be collected and detected. Different emission wavelength ranges require different detectors. First, the luminescence is guided into a spectrograph for dispersion into its components (either Triax 320, or Solar M266), which contain different gratings, each optimized for specific wavelength ranges and different dispersions. Diffraction on
the gratings takes always place in multiple orders. To remove higher order contributions of residual light in the detected emission, it is important to use high pass filter - before entrance (Triax 320), or inside the spectrograph (Solar M266). For detection of light, either a liquid-nitrogen-cooled Ge photodiode (Edinburgh Instruments, 0.9—1.7µm), or similarly cooled photo multiplier tube (PMT) (Hamamatsu R5509-73, 0.3 — 1.7µm) was used for the infrared region. In the visible region a different type of PMT (Hamamatsu R9110 185 — 900 nm) or a one-stage thermoelectric-cooled charge-coupled device (CCD) (Hamamatsu S10141-1108S, 200 — 1100 nm) was utilized. These latter two detectors are preferred as they benefit from a higher sensitivity and a better signal-to-noise ratio. Both PMT’s allow for fast time-resolved spectroscopy, with typical time resolutions of ~1 ns. In photon counting mode, an excitation laser pulse is detected by a diode, which triggers a clock in a fast time-of-flight multiscaler (Fast Comtec P7887). Subsequently, light detected by a PMT is converted to an electric signal and fed to the multiscaler, which registers the temporal difference of these signals. In this way it is possible to get dynamics of emission after a pulsed excitation. We note here again the preference for the R9110 over R5509-73, as gain values are 20 times better, whereas dark current is 8 times less.

2.1.4 Integrating sphere optics

As an important part of this thesis concerns experiments employing an integrating sphere, we dedicate a paragraph to the theory and considerations concerning that. Light inside an integrating sphere is reflected many times by the diffusely reflecting inner surface before it is collected and detected. This eliminates much of the emission anisotropy and will give a good measure of the total emitted radiant power [27]. For a mathematical treatment we consider a sphere with total area $A_s$, input port area $A_{in}$ and output port area $A_{out}$, in which light with flux $\Phi_i$ (in Watts) will be perfectly diffused by an initial reflection on the surface (Fig. 2.2 (a)) [28, 29]. In this case the sphere’s interior is illuminated by a uniform irradiance

$$\frac{\Phi_i \rho (1 - f)}{A_s} \left( \frac{W}{m^2} \right), \quad (2.1)$$

where $f$ is the port fraction $(A_{in} + A_{out})/A_s$ and $\rho$ the reflectance. The sphere surface reflects $\rho$ of this with a Lambertian distribution, so the contribution of this reflection to the radiance $L_s$ is

$$\frac{\Phi_i \rho^2 (1 - f)}{\pi A_s} \left( \frac{W}{m^2\text{sr}} \right). \quad (2.2)$$

For each subsequent reflection there will be a fraction $(1-f)$ that does not leave the sphere, multiplied by the fraction $\rho$ that is left after the next reflection contributing to the surface radiance. This process is repeated for each reflection, so
2.1. PHOTOLUMINESCENCE MEASUREMENTS

Figure 2.2: Cross section of an integrating sphere. (a) Light enters from the top entrance port (area $A_{in}$) with flux, $\Phi_i$. The surface scatters the light randomly with efficiency $\rho$. (b) An optical fiber with core area $A_f$ coupled to an integrating sphere. Red lines indicate cone of acceptance.

the total radiance of the sphere’s wall is

$$L_s = \frac{\Phi_i \rho^2}{\pi A_s} [1 + \rho(1 - f) + \rho^2(1 - f)^2 + \cdots]. \quad (2.3)$$

This geometric sequence can be expressed as

$$L_s = \frac{\Phi_i}{\pi A_s} \frac{\rho^2}{1 - \rho(1 - f)}. \quad (2.4)$$

This equation relates the radiance of the integrating sphere to a given input flux, port surface and sphere size. When we compare this equation with Eq. (2.1), we see that the total radiance of the sphere surface is actually larger than that only due to the input ($\rho$ and $f$ are between 0 and 1). In Eq. (2.4) the second part can be seen as the sphere multiplier

$$M = \frac{\rho^2}{1 - \rho(1 - f)}, \quad (2.5)$$

which is an important parameter of an integrating sphere. Typical parameters of integrating spheres ($0.95 < \rho < 0.99$ and $0.02 < f < 0.05$) result in values for $M$ in the range of 10-30. It is also important to note that the spectral dependence of $\rho$, leads to a spectral dependence of $M$. For example for a Spectralon® coating, $\rho$ changes from 0.99 to 0.95 for wavelengths from 400 till 250 nm from, altering $M$ by approximately 60 %.

When an optical fiber is used to collect the light (Fig. 2.2 (b)) the output port diameter is given by the fiber core diameter, $A_f$. An important parameter of the
optical fiber is the numerical aperture (NA), which determines effectiveness of light coupling. The projected solid angle is:

$$\Omega = \pi (\text{NA})^2.$$  

(2.6)

Since the optical fiber will have losses at the air/fiber interface, the reflectance $R$ should also be considered when determining the total flux that enters the fiber, $\Phi_f$, which is then given by

$$\Phi_f = L_s A_f (\text{NA})^2 (1 - R).$$  

(2.7)

For typical experiments done throughout this thesis, a sample was placed inside the integrating sphere and excited by light. For a good determination of the radiance it is important that the viewed area of the sphere, determined by the position and numerical aperture of the fiber, is not directly irradiated. The light should have undergone at least two reflections before detection. Fig. 2.3 shows how this is accomplished when the sample (square) is placed in the center of the sphere. The output fiber is placed off center, so that its acceptance cone does not include emission, or scattered excitation light, from the sample directly. A highly diffusive reflective baffle on the left and underside of the sample prevents emission and scattered light from the sample to go directly to viewed area. A second baffle on the inside of the sphere prevents the first reflections from the excitation light from the bottom to enter the field-of-view.

Figure 2.3: Cross section of an integrating sphere with a square sample placed in the center. Baffles prevent scattered excitation light and emitted light from the sample to go directly to the field of view of the optical fiber, indicated by the red lines.
2.2. SAMPLES

2.2 Samples

2.2.1 Sputtered layers

The larger part of the work in this thesis has been performed on samples fabricated by radio-frequency (rf) co-sputtering method. Different structures and compositions of the deposited films are possible in this way. Preparation procedures of the different batches are discussed in this section.

Si NCs in SiO$_2$

Two batches were fabricated here, which are indicated by Si$_A$TB and Si$_A$t$_C$TB. These samples have been fabricated in a single target sputtering apparatus. A pure SiO$_2$ target with a diameter of 4 inch was topped with $p$-type Si chips (10 Ω-cm, [B]=10$^{15}$-10$^{16}$ cm$^{-3}$) with a size of 5×15×0.5 mm. The number of Si chips is denoted by $A$ in the sample labeling. These materials were then co-sputtered in Ar gas with a pressure of 40 mPa, at a background pressure of 10$^{-3}$ mPa, and with rf power of 200 W. The deposited silicon-rich silicon oxide (SRSO) films were subsequently annealed in a tube furnace purged with N$_2$ gas (2 liter/min) at temperatures in the range 1100-1250 °C ($B$ in sample labeling) for 30 minutes. The thermally induced aggregation of Si atoms results in formation of Si NCs whose sizes are determined by the composition of the deposited layer and the annealing temperature (see section 2.3). The thickness of deposited layers is $\sim$2 µm for the first batch. The thickness of the 2$^{nd}$ batch is determined by the parameter $C$, ranging from 2-14, which indicates the deposition time in minutes. The deposition rate of $\sim$50 nm/min thus resulted in layers with 100-700 nm thickness. NB: all samples with $C = 2$ showed only negligible absorption after the annealing procedure.

Er$^{3+}$ + Si NCs in SiO$_2$

In Chaps. 5 and 7 samples have been used that are co-doped with Er$^{3+}$ ions. These have been prepared by the same method as described above, with the only difference being the inclusion of Er$_2$O$_3$ tablets during sputtering. In this way concentrations of [Er$^{3+}$]=7 × 10$^{18}$ – 6 × 10$^{19}$ cm$^{-3}$ have been obtained in the deposited layers.

Multi-layers

In a multiple target sputtering apparatus it is relatively easy to deposit different types of layered structures. Each gun contains a different target material and by changing the relative power to each of the guns, different compositions of materials can be easily made. Alternating the active guns in a deposition sequence generates a superlattice of the deposited layers. For alternating SRSO and SiO$_2$
layers this results in self-limited NC growth in the SRSO layer during annealing, dependent on the layer thickness, as the surrounding SiO$_2$ layers act as buffers preventing the excess Si to diffuse outside [30].

**B-P-doping**

In Chapt. 8 the influence of $n$- and $p$-type doping of Si NCs has been studied. For this purpose a batch of samples with different deposition parameters has been prepared, which were either single layer SiO$_x$ (SL, 500 nm thickness) or multi-layer (ML, 4 nm SiO$_x$ + 10 nm SiO$_2$; total 50 layers). Different concentration of excess silicon in the Si-rich layer indicated by 3, 5, 7 or 9 (5.8, 27.8, 40.7 and 45.1 volume % excess Si, respectively) and doping levels (P$_2$O$_5$ and B$_2$O$_3$, concentrations of both either 0, 1.1 or 2.2 volume %). All samples have been annealed in a N$_2$ atmosphere for 30 minutes at a temperature of 1200 °C.

**2.2.2 Porous silicon**

Porous silicon grains suspended in ultraviolet-grade ethanol, made by electrochemical etching of crystalline silicon, have been investigated as Si NC containing system as well. The preparation consists of several steps. First a p-type wafer (B-doped, 0.075-0.100 Ωcm, <100>-oriented, etched area $\sim$10 cm$^2$), was electrochemically etched under constant current density of 1.6 mA cm$^{-2}$ for 2 hours. Platinum was used as the top electrode and the bath was stirred. The etching bath consisted of hydrofluoric acid (HF) and UV-grade ethanol (EtOH) in ratio HF (50%) : EtOH (99.9%)=1:2.85. After intense rinsing in pure (99.9%)
2.3. SAMPLE CHARACTERIZATION

EtOH and slow drying in air, the resulting nanocrystalline layer was mechanically scraped-off the substrate and underwent 30-60 min ultrasonic treatment in UV-grade EtOH. The final product was contained in Suprasil quartz cuvettes of 3.5 ml volume. The different steps in sample preparation are shown schematically in Fig. 2.4. After sedimentation and filtering the colloidal suspension contains grains of po-Si with a typical size of 1 micrometer. Each grain consists of a large number of closely spaced oxidized silicon NCs with a typical size of 1-3 nm. They embody a dense sponge-like network in which some NCs may be interconnected. Fig. 2.5 shows HR-TEM image of this structure, where the individual NCs can clearly be seen. The distribution of sizes of individual Si NCs as determined from HR-TEM image is shown in the right panel.

2.2.3 Freestanding colloidal Si quantum dots

Freestanding silicon quantum dots (Si-QDs) were prepared via a wet-chemical method [33]. Magnesium-silicide (Mg$_2$Si) was oxidized with bromine (Br$_2$) in refluxing n-octane for 3 days. The bromine-terminated Si-QDs formed in this way were passivated using n-buthyl-lithium, resulting in n-buthyl terminated Si QDs. These samples have been obtained through collaboration with the group of Prof. Zuilhof from the University of Wageningen.

2.3 Sample characterization

There are a number of important parameters that will determine the final properties of the material which have been studied. In this section we will treat some different characterization techniques that have been employed to study material
properties like NC size, crystalline quality, composition, etc; also simulations are made to determine important material properties for further investigations.

2.3.1 Scanning transmission electron microscopy

To get detailed information about the structures on nanometer sizes, some samples were studied by scanning transmission electron microscopy (STEM). These measurements were performed in collaboration with Oak Ridge National Laboratory and the University of Cadiz. The images are taken in a NION UltraSTEM using a voltage of 100 kV. In Fig. 2.6 the images of bright field STEM are shown for two different samples. Random distributions of nanocrystals, with varying crystalliographic orientation can be seen with a fairly similar size, which is around 3.5 nm for Si8Er4T1150 and 5 nm for Si8Er4T1200. In order to get information of the composition and distribution of elements a combination of electron energy loss spectroscopy (EELS) and high angle annular dark field (HAADF) STEM was employed. The HAADF technique is very sensitive to variations in the atomic number of atoms in the sample and can be used to produce Z-contrast images. Typical HAADF images of a NC are shown in Fig. 2.7a and 2.8a. Along the green line electron energy loss spectra are obtained, which contain information about the composition. By comparing the obtained EELS spectra with reference of standards for Si, SiO2 and Er, the distributions of these elements along the line can be found. From Figs. 2.7b and 2.8b we can clearly see that the contents of oxygen, which is directly related to the O-K (the electron K shell of oxygen) peak, decreases inside the NCs. At the same time the first peak of Si-L2,3 (crystalline Si) disappears outside the NCs. The remaining intensity of the O-K edge can originate from the Si-Ox above and below the NCs.

![Figure 2.6: Bright field STEM images of (a) Si8Er4T1150 and (b) Si8Er4T1200](image-url)
2.3. SAMPLE CHARACTERIZATION

The distribution of Er ions is more difficult to obtain. In a study on similar materials it was found that Er tends to cluster and distribute similarly as the Si NCs [34], but concentrations were about an order of magnitude larger. In Fig. 2.8b the signal related to Er-N$_{4,5}$ edge is also shown. It shows that Er is preferentially located in the amorphous matrix. In the typical STEM HAADF images there are bright spots present, which could indicate large Er concentrations or clusters, as intensity is approximately proportional to the square of atomic number Z. By simultaneous recording of HAADF and bright field STEM images (Fig. 2.9) distributions of NCs and Er can be seen; there is no correlation between the two. From the presence of the Er-N$_{4,5}$ peak in EELS spectrum we know that Er is present, and this opens the possibility that the bright spots could be corresponding to Er clusters. Fig. 2.10 depicts a spectral image from Er-N$_{4,5}$ edge, which shows distribution of Er atoms. The same area as HAADF image shows that the bright spots are not related to Er ions, which indicates that Er is homogeneously distributed and does not form clusters. A similar elemental analysis of a very bright spot in HAADF image of Si$_4$Er$_4$T$_{1200}$ gives the grayscale chemical map of Fig. 2.11. The distributions of the elements around and inside the brightest particle is the same as that shown in Figs. 2.7b and 2.8b. This is again a confirmation that the bright spot is not related to a cluster of Er atoms, but probably is a Si NC with an orientation which produces a channeling effect.

The main results of this STEM study are:

- Crystalline Si particles are found in all samples.
- The size of NCs varies for different samples, but the distribution of sizes

Figure 2.7: (a) HAADF image of a NC in Si$_8$Er$_4$T$_{1150}$, the green line indicates the path followed by the beam (line scan). (b) Normalized EELS intensities of peaks related to Si-L$_{2,3}$ and O-K signal along the line.
Figure 2.8: HAADF image of a NC in Si4Er4Ti200, the green line indicates the path followed by the beam. (line scan) (b) Normalized EELS intensities of peaks related to Si-L\textsubscript{2,3}, Er-N\textsubscript{4,5} and O-K signal along the line.

within one sample is not too large.

- Erbium is randomly distributed in the amorphous matrix surrounding the Si NCs.

- There is no indication that the location of Er ions are correlated with Si NCs.

Figure 2.9: left: HAADF image of the silica matrix with bright spots. right: Bright Field STEM image simultaneously taken. The red circle indicates the location of a Si NC in both figures.
2.3. SAMPLE CHARACTERIZATION

Figure 2.10: *left*: Spectrum image of erbium concentration extracted from Er N$_{4.5}$ edge. *right*: HAADF image simultaneously recorded, showing bright spots.

Figure 2.11: Grayscale map of (a) Si-L$_{2,3}$ first peak, (b) Er-N$_{4.5}$ and (c) O-K.

- There are no Er clusters found.
- (Nearly) every visualized Si NC has a neighbor in close proximity, at a distance comparable to its radius.

2.3.2 PL properties and deposition parameters

In section 2.2.1 the employed sputtering technique was discussed, and how the different parameters determined composition of the deposited material. In this section we will look how the PL properties of the Si NC layers formed by annealing of the sub-stoichiometric silicon dioxide depend on the composition and annealing temperature. All PL data are obtained under continuous-wave excita-
Figure 2.12: PL spectra for a series of Si NCs in SiO$_2$ with different composition of the deposited precursory layer and identical annealing parameters.

Typical PL spectra are shown in Fig. 2.12 for a series of Si NC films with different composition, but identical annealing procedure. All spectra show a broad band with a typical full width at half maximum of $\sim$150 nm. Furthermore, it is observed that the intensity and the emission wavelength vary for all samples in this series. Generally there is a blueshift of the emission wavelength as the NC size decreases [35, 36]. The broadening of the spectra is thus an indication of the size distribution within the samples, a deeper analysis in this matter is given in section 2.3.3.

The spectral position of the entire spectrum is an indication for the average size of the NCs. To gain some better understanding about how the NC size is determined by fabrication parameters we have determined PL spectra for a range of different compositions and annealing temperatures, which were varied between 1100 - 1250 °C. An illustration of the influence of the excess Si concentration and annealing temperature on the emission can be found in Fig. 2.13. This data is taken for the Si$^A_{4}T_{B}$ series, where $A = 4, 6, 8$ or 10 (4.8%, 8%, 12.6% and 17.2% excess Si, respectively) and $B$ the annealing temperature (1100, 1150, 1200 or 1250 °C). Since photon energies are inversely proportional to the size of NCs, two main trends can be deduced from the figure:

- In the compositional direction it is apparent that smaller NCs occur on the silicon-poor side of the map.
2.3. SAMPLE CHARACTERIZATION

Figure 2.13: Photon energies associated with the peak of PL spectra and dependence on the excess Si concentration and annealing temperature.

- The size of NCs increases for higher annealing temperatures.

Another observation is that both parameters are not mutually independent and that their combination determines the final NC characteristics. This complicates for example the fabrication of layers with same NC size and size distribution, but different concentration, which are desirable for some later parts in this research. A separate series of Si NCs in SiO$_2$ was produced to fabricate samples with exactly these features, but also to extend the composition more to the Si deficient side. A mapping of the peak energy, as well as the integrated PL intensity, as function of composition and annealing temperature can be found in Fig. 2.14. In the left part of the figure we see that at even smaller Si excess, the PL peak shifts still

Figure 2.14: **left**: Photon energies associated with the peak of PL spectra and dependence on the excess Si concentration and annealing temperature for SiA t14 TB series. **right**: Relative PL intensity map.
more to the higher energies, indicating the occurrence of even smaller NCs. From the intensity map it is concluded that there exists a “sweet” spot, which reaches maximum intensity. The drop in intensity for the low excess Si side is due to the lower density of Si NCs, while at the Si-rich side it is caused by opening of non-radiative pathways in large and possibly interconnected clusters.

### 2.3.3 Size distribution

A relation between emission energy and size of NCs determined by high-resolution transmission electron microscopy (HR-TEM) has been obtained in the past \[16\]. It is found that there is a good fit for these data for the optical gap \(E_g(D) = E_{Si} + 1.86/D^{1.39}\), where \(E_{Si}\) is the bandgap of bulk Si and \(D\) the NC diameter, similar as the theoretical dependence determined in \[37\]. When an intrinsic yield of PL of 100% is assumed \[38, 39\], we can convert the PL spectrum directly to a size distribution. This type of NCs commonly have sizes whose logarithm is normally distributed \[12, 40, 41\] as described by

\[
I(D) = \frac{1}{D\sigma\sqrt{2\pi}} e^{-\frac{(\ln(D) - \mu)^2}{2\sigma^2}},
\]

(2.8)

where \(\mu\) and \(\sigma\), are the mean and standard deviation, respectively, of the diameter \(D\)’s natural logarithm. By fitting the measured PL spectra with this equation we can determine these important parameters for the different samples. In Fig. 2.15 we show experimental data and accompanying fitting parameters of Eq. (2.8).

![Figure 2.15: Size distribution as determined from PL spectra (black lines) and fits with Eq. (2.8) (gray dashed lines). Fitting parameters, which indicate the mean \(\mu\) and \(\sigma\) are also indicated.](image)
2.3. SAMPLE CHARACTERIZATION

2.3.4 Separation between Si NCs

Since a large part of the research on the thin films considers energy transfer between individual NCs, knowledge about distribution of distances between the NCs is highly desirable. There is only little information about the microscopic distribution of Si atoms in such layers [42]. This work shows that the phase separation in SRSO layers is ~100%, all Si atoms are part of NCs, but there is no conclusive information about the average distance between these NCs. In this section we develop a model, which describes the distance between Si NCs. Some assumptions have to made as to simplify the model, so that the obtained values are not absolutely correct, but give the upper limit and allow us to determine the trend in NC-NC distance as function of NC size and excess Si fraction.

For the model we assume a full phase separation of the excess Si, which is reasonable according to [42], and Si NCs to be spheres with a single size. At the optimum packing of spheres, in the face centered cubic (FCC) structure, a unit cell contains 4 spheres of volume $V$ and the filling fraction $f_{Si}$, which indicates the silicon excess fraction, is given by:

$$f_{Si} = \frac{4 \times V}{a^3} = \frac{2\pi D^3}{a^3}, \quad (2.9)$$

where $D$ is the sphere diameter and $a$ the length of a unit cell edge (see Fig. 2.16). The distance between the surfaces of spheres, $d_{ss}$, can be expressed as

$$d_{ss} = a\sqrt{2} - 2D = \frac{a}{\sqrt{2}} - D. \quad (2.10)$$

Combining Eqs. (2.9) and (2.10) gives than the relation between $d_{ss}$, $D$ and $f_{Si}$,

$$d_{ss} = D[(\frac{\pi}{3f_{Si}})^{\frac{1}{3}}2^{\frac{1}{3}} - \frac{1}{3} - 1]. \quad (2.11)$$
A visual representation of this equation is depicted in Fig. 2.17. Typical ranges of both parameters in our samples are $3 < D < 5$ nm and $0.05 < f_{Si} < 0.2$. We can see that in this case the distance between the NCs is between 1 and 7 nm. Of course in a real system the self-assembled NCs will not be oriented in such a structure, but more randomly, so there will be a distribution of nearest neighbor distances. For a given $f_{Si}$ and $D$ randomizing the distribution of Si NCs will lower the average distance between them, the FCC assumption yields a maximum.

Now we will take a look at the other side of the spectrum and analyze randomly distributed NCs. Again we assume all the NCs to be spherical and have a identical size. Torquato et al. [43] developed a general expression for a nearest-neighbor distribution function $H(r)$ in a system of interacting spheres and compared these with Monte Carlo simulations. From their results we can find another important measure for such systems, the so-called “mean nearest-neighbor distance” $l$, which is defined as

$$l = \int_0^\infty rH(r)dr.$$  \hfill (2.12)

We can convert this value to the “mean nearest-neighbor surface-to-surface distance” $d_{ss,av}$ by subtracting the diameter of the particles from $l$. From their simulations we now get the empirical relation

$$d_{ss,av} = \left(\frac{1}{f_{Si}} - 1\right)0.0277D,$$  \hfill (2.13)

which is valid for $0 < f_{Si} \leq 0.5$. It is obvious that the distances are much smaller in the case of random distribution of the NCs. In the region of interest $d_{ss,av}$ varies between $\approx 0.2$ and $\approx 2$ nm, but we also have to keep in mind that this is a mean value, with particles having smaller and large distances. The purpose of this section is to show the behavior of different distributions and what are the typical values of the distances between individual NCs. It is very difficult to get “real” values, as an experimental determination of the real space distribution is extremely difficult and scarce. Furthermore, it is even more complicated by other aspects, like size and shape distributions, which are typical for self-assembled systems.
Figure 2.17: (a) Contourplot of the dependence of the NC surface-to-surface distance in a FCC lattice on the NC diameter and excess silicon fraction. Lines indicate regions of identical $d_{ss}$, where boxed values are in nm. (b) Contourplot of the mean nearest-neighbor surface-to-surface distance in a system of randomly distributed NCs.
Chapter 3

Photoluminescence quantum yield

The quantum yield of photoluminescence is an important parameter of the studied optically active materials. This chapter describes the exact terminology which is employed, followed by the experimental details that have been considered and the conditions necessary for a reliable determination of this parameter. Furthermore, the setup and method used for the determination of the absolute photoluminescence quantum yield are introduced. Different origins of error in this determination procedure are considered, and their contributions are estimated. Finally, the procedure for calibration of the system, and optimization hereof, are discussed.

3.1 Definition of PL QY

In this section we will describe the considerations concerning the determination of the quantum yield of photoluminescence. For clarity we start with the definition that we shall use throughout this work:

\[
\text{Quantum yield of photoluminescence} = \frac{\text{number of emitted photons}}{\text{number of absorbed photons}}. \quad (3.1)
\]

Note that this is the \textit{external} QY, which considers all the photons that are absorbed and emitted in a macroscopic amount of material. This quantity can be determined as a product of the efficiency of photoexcitation (number of generated excitons per absorbed photon, \(\gamma_{PL}\)) and the ratio of radiative \((k_R)\) and non-radiative \((k_{NR})\) recombination rates. Similarly it can be described by the ratio of the lifetime of luminescence \((\tau_{PL})\) and the radiative lifetime \((\tau_R)\), (the
luminescence lifetime in absence of non-radiative decay),

\[ QY = \gamma_{PL} \cdot \frac{k_R}{k_R + k_{NR}} = \gamma_{PL} \cdot \frac{\tau_{PL}}{\tau_R}. \] (3.2)

For ensembles of nanoparticles, the determination of these parameters is however not evident. The radiative lifetime is not well-defined, as opposed to a molecular or bulk system, since there is a distribution of sizes and shapes of the particles, with different radiative rates. When a quantum yield is deduced from the PL lifetime, it is important to acknowledge that by this method the internal quantum yield is determined \[39, 38\], so that is only for those particles that are optically active. For example excitons in nanocrystals with dangling bonds on their surface will undergo a fast non-radiative interaction and do not contribute to luminescence at all. These so-called “dark” nanocrystals will however not change the decay characteristics of the optically active part of distribution, as the non-radiative lifetime associated with these NCs are much smaller than the radiative lifetime. If there would not be any dark nanocrystals then, in this definition, the internal QY would be equal to the external QY.

We note that the definitions used here for internal and external quantum yields are different than that used in, for example, photovoltaics. In that case the internal quantum efficiency determines how efficient absorbed photons are converted in electrons, while the external quantum efficiency indicates the total incident photons to electrons efficiency. It is also important to understand that quantum efficiency is not equivalent of energy efficiency, since the individual energy of the particles are not considered, just their numbers. Energy conversion efficiencies will always be smaller than quantum efficiencies.

### 3.2 Experimental considerations

The spectral dependence of the external quantum yield of photoluminescence of silicon NCs was determined experimentally by comparing the total number of emitted and absorbed photons, by a method based on that originally developed in Ref. \[44\]. Our experimental set-up to determine the absolute external QY of PL is shown schematically in Fig. 3.1. Light from an excitation source is directed onto a sample placed inside an integrating sphere. The unabsorbed excitation light and photoluminescence emitted due to radiative recombinations in the NCs are guided to an imaging spectrometer and detected with a CCD detector for subsequent data analysis. The external quantum yield of PL is determined as the ratio of the number of emitted photons (given by the integrated PL signal, which is the increase of signal in the region of PL compared with that of a reference sample comprising only the substrate) and the number of absorbed photons (integrated decrease of signal from the excitation source). In both cases
the PL intensity is divided by the appropriate photon energy:

\[
QY = \frac{\sum_{em\,band} [I_{Si}^{em}(E_{em}) - I_{ref}^{em}(E_{em})]C(E_{em})/E_{em}}{\sum_{ex\,band} [I_{ref}^{ex}(E_{ex}) - I_{Si}^{ex}(E_{ex})]C(E_{ex})/E_{ex}}; \quad (3.3)
\]

\(I^{em}\) and \(I^{ex}\) are the measured emission and excitation intensities for the Si NCs and reference sample (denoted by subscripts ‘Si’ and ‘ref’). \(C\) is the correction for system spectral sensitivity, which has been separately determined with a calibrated light source (see Section 3.4), and \(E_{em}\) and \(E_{ex}\) are the emission and excitation photon energies. The validation of the experimental procedure and test on a reference sample can be found in Appendix A. It is important to note that the value of external quantum yield determined with this method acts as a lower limit. It is known from the literature that individual silicon NCs with an internal quantum yield of \(\sim 100\%\) are available [38], but non-radiative recombination and effects such as photocharging and carrier trapping lower the ensemble quantum yield. This also holds for multiphoton absorption, another notorious source of error for quantum yield determination, as multiple electron-hole pairs in a single nanocrystal will undergo fast Auger recombination [45] and in this way lower the external quantum yield. The results obtained here for po-Si were backed up by a comparative method, in which luminescence intensity was compared with a standard (see Appendix A).

3.3 Error Analysis

3.3.1 Error for low absorption region

One part of the determination of QY of PL comprises optical detection of the excitation intensity and lowering thereof upon introduction of an absorbing medium. The difference between these two gives a measure for the absorption and can be related to a number of absorbed photons. Since the excitation source will always fluctuate, it is important to estimate the contribution of this effect on the error of the calculated QY. This paragraph gives a mathematical description of this error. We note that the analysis done here considers Gaussian statistics, which are only valid for the region where there is little absorption.

The QY is determined by the ratio of the number of emitted and absorbed photons:

\[
QY = \frac{N_{PL}}{N_{Abs}}. \quad (3.4)
\]

The number of absorbed photons is determined by the difference between the intensity of the excitation source without NCs and that with NCs. It is assumed that the fluctuations of the excitation light are Gaussian with an average intensity \(\mu_1\) and a standard deviation of \(\sigma_1\). Upon introduction of an absorbing medium,
CHAPTER 3. PHOTOLUMINESCENCE QUANTUM YIELD

Figure 3.1: Experimental set-up for quantum yield determination. The excitation source (xenon lamp with a monochromator, LED, or tunable OPO laser system) excited the samples placed inside an integrating sphere. Homogeneously scattered (within the sphere) emission and non-absorbed excitation light are guided by a UV-grade optical fiber to an imaging spectrometer and registered by a CCD detector.

the measured intensity drops to a new average $\mu_2$ with a standard deviation determined by the relative error of the source

$$\sigma_2 = \frac{\sigma_1}{\mu_1} \mu_2.$$  \hfill (3.5)

In this case the absorption of the medium is determined by the difference between $\mu_1$ and $\mu_2$;

$$\mu_{Abs} = \mu_1 - \mu_2,$$  \hfill (3.6)

with the accompanying deviation given by

$$\sigma_{Abs} = \sqrt{\sigma_1^2 + \sigma_2^2}.$$  \hfill (3.7)
A part of the absorption will lead to emission; this part is determined by the $QY$ of PL. The PL signal is thus given by

$$\mu_{PL} = QY \mu_{Abs},$$

(3.8)

with uncertainty

$$\sigma_{PL} = \frac{\sigma_1}{\mu_1} \mu_{PL}.$$  

(3.9)

Since $N_{PL} \propto \mu_{PL}$ and $N_{Abs} \propto \mu_{Abs}$, then combined with Eq. (3.4) we can derive the following expression for the expectation value

$$\mu_{QY} = \frac{\mu_{PL}}{\mu_{Abs}},$$

(3.10)

with an error given by

$$\sigma_{QY} = \mu_{QY} \sqrt{\left(\frac{\sigma_{Abs}}{\mu_{Abs}}\right)^2 + \left(\frac{\sigma_{PL}}{\mu_{PL}}\right)^2}.$$  

(3.11)

Now using Eqs. (3.6-3.9) and substituting them in Eq. (3.11), we find that the relative error in determination of $QY$ is given by:

$$\frac{\sigma_{QY}}{\mu_{QY}} = \sqrt{\frac{2\sigma_1^2 (\mu_{Abs}^2 - \mu_{Abs} + 1)}{\mu_{Abs}}},$$

(3.12)

Figure 3.2: Relative error of $QY$ in low absorption regime as function of excitation source stability and the absorbed fraction of light. The continuous lines indicate values of constant error.
and thus is only dependent on the fluctuation of the pump $\sigma_1$ and the fraction of absorbed excitation light $\mu_{Abs}$.

Figure 3.2 depicts the error in determination of QY as a function of both these parameters. The continuous lines show values of $\mu_{Abs}$ and $\sigma_1$ for an error of 5, 10, 25 and 50%. In the low absorption region, it can be seen that the uncertainty becomes quite large due instability of the excitation source. For the xenon lamp (Hamamatsu L11033), values of the stability supplied by the manufacturer are $\pm 0.2\%$ with a drift of $\pm 0.5\%$ per hour. For relatively short integration times the drift is not so important, but for the comparison of intensities of NCs and substrate it is very much of importance, since there is a considerable time between the two individual measurements. A typical value of the standard deviation of intensity based on statistics of 100 individual measurements of the lamp intensity yielded a value of $\sigma_1 = 0.0027$, close to the specifications. By substituting this value in Eq. (3.12) we get the dependence of the error on the absorption, as shown in Fig. 3.3. It is obvious that the uncertainty of QY increases very steeply for small values of $\mu_{Abs}$ putting strict constraints on the determination of QY in the low absorption region.

### 3.3.2 Stray light, PL intensity, spectral sensitivity

In this section other sources of error are introduced and their contributions and reduction thereof are qualitatively discussed.

1. **Stray light:** This is a problem for broadband excitation sources like the xenon lamp. The monochromator providing selection of wavelengths used for excitation can also pass other wavelengths, not in the intended region, typically $10^{-4}$ for a single grating monochromator. The stray light can
overlap with PL spectra of the emitting species, thereby introducing a false notion of PL. Since the xenon lamp is a very bright source and PL intensity can be quite weak, the relative contribution of stray light can be substantial. While the experiment intrinsically removes the contribution of stray light, since the spectrum of the reference substrate is subtracted from that of the NCs, this is not necessary fully neutralized due to differences in reflectivity, scattering or absorption of stray light between the sample and the reference. The relative contribution of stray light to PL intensity can be estimated relatively easy, since the xenon lamp has very distinct peaks in its spectrum. Nevertheless it is advisable to reduce the stray light as much as possible, for example by using a double pass monochromator.

2. **PL intensity:** The absolute PL intensity is very important and, especially for thin films, can be very low. This limits accuracy of QY determination in different ways; the contribution of stray light competes with PL and low intensities require long integration times giving rise to more thermal noise in the CCD. PL intensity is in general dependent on the type of NCs used, but for the QY experiment it is always small on both sides of excitation spectrum. For short wavelengths this is a result of limiting excitation intensities available in this range. For longer wavelengths the absorption is smaller, resulting in a lower number of excited NCs that contribute to the PL.

3. **Spectral sensitivity:** The correction procedure for the spectral sensitivity of the entire system, as explained in the next paragraph, is essential for obtaining reliable results.

### 3.4 Spectral sensitivity calibration procedure

The entire system for QY determination needs to be calibrated for its spectral sensitivity; i.e., the detection efficiency light detected as a function of the wavelength. All components of the detection system have a certain spectrally dependent efficiency and the combined response to light must be taken into account. The broad spectral range over which the PL QY is determined makes this a relatively complicated procedure. As the relative sensitivity of the entire system varies over few orders of magnitude and will directly determine the final QY, it is important that this is done very accurately. In the described experiments, two light sources with calibrated spectral profile have been used to cover the entire range: Oriel tungsten-halogen lamp (45 W) for the visible range and Newport deuterium source (Model 63979, 30 W) for the UV. The documentation of the tungsten-halogen lamp gives the spectral profile for wavelengths >250 nm, but actually the intensity below 350 nm is too low for practical use, and it is advisable
not to use it below 400 nm. The lamp is placed 50 cm from the entrance of the integration sphere and its spectrum is determined, $I_T(\lambda)$ (note that it is important to have no direct light entering the optical fiber). The same procedure is applied for the deuterium lamp, where $I_D(\lambda)$ is determined. Since the efficiency of the entire system decreases rapidly for wavelengths shorter than 300 nm, it is important to not only subtract the dark signal, but also determine the stray-light signal as Fig. 3.4 shows the measured spectra for the lamp (red) and with a glass plate used as a high pass filter, removing light with a wavelength below $\sim 280$ nm. It can be seen that part of the intensity for shorter wavelengths is actually a result of stray-light. A polynomial fit to this signal is subtracted from the original measurement, to get the value of $I_D(\lambda)$. Dividing the calibrated intensity, known for both lamps, by the determined $I_T(\lambda)$ and $I_D(\lambda)$ gives now the inverse sensitivity, $C(\lambda)$. For the experiment of measuring PL QY, it is only important to have a relative sensitivity of the entire range. In practice the two ranges for the different lamps will not match exactly (mostly due to instability of calibration lamps), so the above notion allows to scale the ranges to match the two in the region where calibration data is available for both lamps. In the region 350-400 nm, both lamps have enough intensity to have a good signal, making it the best region for matching both ranges and getting the final $C(\lambda)$. Fig. 3.5 shows the experimentally determined spectral (inverse) sensitivity. It can be seen that the sensitivity varies over 4 orders of magnitude. Around 600 nm the system has its
Figure 3.5: Typical determined inverse sensitivity spectrum for PL QY setup.

maximum efficiency, which decreases for shorter and longer wavelengths.
Chapter 4

Luminescence saturation and quantum cutting by silicon nanocrystals

The first part of this chapter presents a photoluminescence excitation study of silicon nanocrystals in an SiO$_2$ matrix. It is shown that although the excitation cross-section is wavelength-dependent and increases for shorter wavelengths, the maximum time-integrated photoluminescence signal for a given sample saturates at the same level independent of the excitation wavelength or amount of electron-hole pairs generated per nanocrystal after a laser pulse. An explicit demonstration that saturation is achieved when every nanocrystal has absorbed at least one photon is given. In nanocrystals where several electron-hole pairs have been created during the excitation pulse, fast non-radiative recombinations reduce their number, leading to the situation that only a single electron-hole pair per nanocrystal can recombine radiatively, producing one photon and contributing to the photoluminescence. In this way a natural limit is set for photoluminescence intensity from an ensemble of Si nanocrystals excited by a laser pulse of duration much shorter than the radiative lifetime of electron-hole pairs.

The second part of this chapter demonstrates results of a study on the relative quantum yield of photoluminescence for different excitation wavelengths. From these it is concluded that for excitation photon energies above a certain threshold, there arises a additional mechanism increasing the excitation efficiency. This is explained by the redistribution of the absorbed photon energy over multiple proximal nanocrystals, generating electron-hole pairs that are separated in space. Effectively, this mechanism cuts the energy of the incoming photon. This effect is then very similar as the multiple exciton generation process, where multiple
electron-hole pairs are generated in one nanocrystal upon absorption of a single photon. Different mechanisms are discussed that might underly the cutting process, and also the beneficial properties for applications are considered.

4.1 Luminescence saturation

4.1.1 Introduction

In case of PL from Si NCs, the generation of an e-h pair arises due to photon absorption and therefore depends on the absorption cross-section, which is dependent on the size of NCs (see section 2.3) and generally increases for shorter wavelengths [46]. Consequently, it is frequently inferred that short excitation wavelengths are necessary for effective PL from Si NCs. In this section we show that the maximum PL intensity which can be obtained from a Si NC layer after a pulsed excitation is independent of the excitation wavelength. We argue that this is caused by an efficient exciton-exciton non-radiative recombination resulting in a maximum of one radiative e-h recombination per NC per excitation pulse. Therefore, under the condition that the duration of the laser pulse is much shorter than the radiative lifetime of e-h pairs in NCs, the PL intensity limit is set by the density of NCs and the radiative lifetime of excitons in Si NCs only.

4.1.2 Experimental details

The photoluminescence excitation (PLE) study has been performed on thin films of Si NCs embedded in a matrix of SiO₂ which had been produced by a radio-frequency co-sputtering method followed by annealing in N₂ atmosphere. In this study, Si NC layers with different parameters (size and concentration of NCs and layer thickness) have been investigated and similar conclusions have been reached for all of them. Here we present results obtained for two specific samples: Sample #1 is characterized by an average NC diameter $D_1 = 3.5 \pm 0.5$ nm and concentration of NCs $[\text{NC}]_1 = 4.1 \times 10^{18}$ cm$^3$; for Sample #2 these values are $D_2 = 2.5 \pm 0.4$ nm and $[\text{NC}]_2 = 1.3 \times 10^{18}$ cm$^3$. - see Chapter 2 for more details on sample preparation and characterization. The PLE has been investigated in the range of 420 - 650 nm using a tunable OPO, which was pumped by the third harmonic of a pulsed Nd:YAG laser with a pulse duration of 5 ns and a repetition rate of 10 Hz. In this excitation range all the NCs in the ensemble can absorb light and contribute to the PL. The emerging PL was resolved with a Jobin-Yvon TRIAX 320 monochromator and detected with a Hamamatsu R5509-72 near-IR photomultiplier tube connected to a digital scope where the “slow” microsecond PL signal could be visualized and integrated over a few hundred $\mu$s. Variations of PL intensity and kinetics were investigated at a wavelength set to the peak intensity of PL spectrum. For absorption measurements, a Varian Cary-
50 UV-VIS spectrophotometer was used. All measurements have been performed at room temperature and the illuminated area of the sample during the PLE measurements was kept constant by using a pinhole.

4.1.3 Results and discussion

The time-integrated PL spectrum of Sample #1 is depicted in the inset A of Fig. 4.1. The spectrum is independent of excitation wavelength, as long as there is no saturation effect (see Chapt. 6), consistent with earlier findings \[47\]. In the first experiment, the PL intensity related to Si NC exciton recombination was monitored at a wavelength of 914 nm, the peak value of the PL spectrum (indicated in inset A with an arrow), as a function of excitation pump pulse fluence \(J_{pump}\), the number of photons per cm\(^2\) per pulse. Results hereof are depicted in Fig. 4.1, where the excitation power dependence of the PL intensity for five different pump wavelengths is given. All curves show an initial linear rise followed by a saturation at an identical PL intensity level. Taken together with the notion that the decay time of PL does not change with excitation wavelength \((\tau \approx 100 \mu s, \text{see inset B of Fig. 4.1})\), this result indicates that the maximum attainable PL signal is independent of excitation wavelength. In contrast, the growth rate of the PL intensity in the initial “linear” regime clearly increases with photon energy. To describe the PL intensity dependence on the pump pulse fluence, we use a simple two-level model of Si NC excitation \[48\]. We assume that every emitted photon originates from a single e-h pair. Further, in view of the observed saturation of PL intensity, we introduce \(N\); the maximum number of e-h pairs which can recombine radiatively in our system. In that case, the number of e-h pairs capable of radiative recombination that have been induced during the laser pulse \(N^*\) can be described by the following differential equation:

\[
\frac{dN^*}{dt} = \sigma_{ex} \phi(N - N^*) - \frac{N^*}{\tau},
\]

(4.1)

with \(\tau\) being the effective lifetime of the e-h pairs, \(\sigma_{ex}\) an excitation cross-section and \(\phi\) the excitation photon flux. Since the duration of the laser pulse \((\Delta t \approx 5 \text{ ns})\) is much shorter than the lifetime of e-h pairs in the NCs \((\tau \approx 100 \mu s)\) we assume that no recombination takes place during the laser pulse and we ignore the last term. At the end of the pulse the number of e-h pairs capable of recombining radiatively is thus given by:

\[
N^* = N(1 - e^{-\sigma_{ex}\phi\Delta t}).
\]

(4.2)

In this relation, the number of photons per cm\(^2\) per pulse, given by \(\phi\Delta t\), can be denoted by \(J_{pump}\). For low pump pulse fluence, i.e., in the initial “linear” regime of the PL intensity dependence, we can expand Eq. (4.2) in \(J_{pump}\) and get the relation: \(N^* = NJ_{pump}\sigma_{ex}\). Since the time-integrated PL signal \(S_{PL}\) is
CHAPTER 4. LUMINESCENCE SATURATION AND QUANTUM CUTTING BY SILICON NANOCRYSTALS

Figure 4.1: Dependence of the NC-related PL on the pump pulse fluence for different excitation wavelengths. For shorter excitation wavelengths, the slope of the initial part, related to the excitation cross-section $\sigma_{ex}$, increases, while the saturation level is identical for all excitation wavelengths. The solid lines are fits to the data using Eq. 4.2 Inset A: Room-temperature PL spectrum of Sample #1. Inset B: RT transients of the NC PL for Sample #1 for three different excitation wavelengths. For easy comparison the transients have been shifted vertically relative to each other. All transients show a similar decay time of $\tau \approx 100 \mu s$.

Propotional to the number of radiatively recombining $e-h$ pairs $N^*$, we get for the derivative of the integrated PL signal with respect to the pump pulse fluence in the low power region:

$$\frac{dS_{PL}}{dJ_{pump}} \propto \sigma_{ex}. \quad (4.3)$$

Therefore from the data in Fig. 4.1 we conclude that the excitation cross-section $\sigma_{ex}$ is wavelength-dependent and increases for shorter wavelengths. The mechanism behind the linear dependence between the number of the incoming and emitted photons is indeed expected since emission of a photon follows from radiative recombination of an $e-h$ pair generated by an absorbed photon - the efficiency of this process is generally of a few percent for ensembles of NCs, but can be as high as 60% [49]. (We note that in view of the excitation photon energies used in this study, we disregard a possibility of creating two $e-h$ pairs per photon by multiple exciton generation [50, 51, 52]). It is clear from this mechanism that the intensity of exciton-related PL should be correlated with the absorption of...
4.1. LUMINESCEENCE SATURATION

Photons in the NCs. This is indeed the case for low excitation fluence, as evidenced by the linear dependence observed for this regime in Fig. 4.1. For larger fluences, the dependence of the PL intensity deviates from linearity, indicating there is a maximum to the amount of radiative e-h pair recombinations in the system; saturation effects set in. Fig. 4.1 displays this saturation of the PL intensity; solid lines represent fits of the experimental data with Eq. (4.2) for each excitation wavelength.

For the linear regime of the PL intensity dependence on pump pulse fluence it can also be shown that this proportionality between the number of absorbed and emitted photons is independent of excitation wavelength. In order to demonstrate this behavior, we compared the results of linear absorption measurements with the PLE data of Fig. 4.1. The absorption spectrum of Sample #1 is shown in the inset to Fig. 4.3. In this case, the fraction of photons that are absorbed per pump pulse $S_{abs}$, is given by $(I_0 - I_1)/I_0$, where $I_0$ is the incident and $I_1$ the transmitted pump beam intensity, respectively (see Fig. 4.2). The total number of absorbed photons $N_{abs}$ can be calculated by the product of the pump pulse fluence $J_{pump}$, the illuminated area of the sample $A$ and the absorbed fraction $S_{abs}$:

$$N_{abs} = J_{pump} AS_{abs}.$$  \hspace{1cm} (4.4)

Each absorbed photon can contribute to the PL signal with an efficiency $\mu$, giving a total amount of emitted photons

$$N_{PL} = \mu N_{abs} = \mu J_{pump} AS_{abs}.$$  \hspace{1cm} (4.5)

The emitted photons are subsequently detected and give rise to the luminescence signal $S_{PL}$, which is proportional to the number of photons emitted:

$$S_{PL} = \chi N_{PL} = \chi \mu J_{pump} AS_{abs}.$$  \hspace{1cm} (4.6)

Here $\chi$ is a function of the geometry of the setup, the efficiency of the photodetector and other experimental factors. We define now the PL yield as the derivative of the PL intensity with respect to pump pulse fluence

$$Y_{PL} = \frac{dS_{PL}}{dJ_{pump}} = \chi \mu AS_{abs},$$  \hspace{1cm} (4.7)
CHAPTER 4. LUMINESCENCE SATURATION AND QUANTUM CUTTING BY SILICON NANOCRYSTALS

Figure 4.3: Dependence of the excitation cross-section $\sigma_{ex}$ on the absorbed fraction $S_{abs} = (I_0 - I_1)/I_0$ determined for different wavelengths for Sample #1. The solid gray line represents a linear fit. Inset: Absorption spectrum of Sample #1.

where $\chi$ is constant and $\mu$ could possibly be wavelength-dependent. This equation can be compared to Eq. (4.3) and it follows that

$$\chi \mu A S_{abs} \propto \sigma_{ex}.$$ (4.8)

Note that the above mathematical treatment is only valid in the linear regime. In Fig. 4.3 the values of $\sigma_{ex}$, as determined from the experimental data with Eq. (4.2), are plotted versus the independently measured $S_{abs}$ for different excitation wavelengths. A linear dependence between $S_{abs}$ and $\sigma_{ex}$ is observed for the whole investigated wavelength range. We conclude that although the absorption of photons is dependent on the excitation wavelength, the mechanism leading to radiative recombinations of e-h pairs after absorption of a photon is wavelength-independent.

We will now address the PL saturation observed for large fluence in Fig. 4.1. In order to investigate this effect in detail we apply simple statistical analysis of the absorption. This was realized in Sample #2, which shows similar saturation behavior as Sample #1 - see Fig. 4.4. The absorption of Sample #2 is however much smaller ($<1\%$ over the whole investigated photon energy range), so we can assume a constant photon flux throughout the layer, which justifies the use of our analysis. (see Section 6.2 for modeling for the case where absorption is considerable and nonlinear effects become important). The number of NCs that have absorbed $x$ photons after an excitation pulse, $N_x$, is determined by the Poisson
distribution function:

\[ N_x = P_x N_{NC} \]  

(4.9)

with

\[ P_x = \langle NC^* \rangle^x e^{-\langle NC^* \rangle} \frac{1}{x!}, \]  

(4.10)

where \( \langle NC^* \rangle \) is the average number of photons absorbed per NC and \( N_{NC} \) is the number of NCs in the illuminated volume; \( N_{NC} = A_l[NC] = 1.0 \times 10^{12} \), where \( l \) is the thickness of the NC layer. The average number of photons absorbed per NC will be given by the ratio of absorbed photons and the number of NCs under illumination:

\[ \langle NC^* \rangle = \frac{N_{abs}}{N_{NC}} = \frac{J_{pump}AS_{abs}}{1.0 \times 10^{12}}. \]  

(4.11)

Fig. 4.4 shows the excitation power dependence of the NC-related PL of Sample #2 for three different excitation wavelengths. The lower horizontal axis indicates the number of absorbed photons per pulse, \( N_{abs} \), and the top axis shows the accompanying average number of photons absorbed per NC \( \langle NC^* \rangle \). The green continuous line depicts the number of NCs which have absorbed at least one photon \( x \geq 1 \), where Eqs. (4.11) and (4.9) were used and by scaling the total number of NCs \( N_{NC} \) to match the saturation level. A good agreement with the experimental data can be concluded. For comparison, we also show the distribution for the case \( x \geq 2 \) - which clearly deviates from the experiment. We conclude that the PL intensity saturates when every NC has absorbed at least one photon, and therefore has been given an opportunity to emit a photon. This evidences not only that the number of illuminated NCs determines the maximum PL intensity, but also that only a single \( e-h \) pair per NC might recombine radiatively. The scenario which can explain our experimental findings has been discussed before \([53]\), but here we demonstrate this mechanism to occur quantitatively. In the linear regime of the excitation power dependence, only a small percentage of the NCs are excited, and therefore these mostly contain only one \( e-h \) pair, which can eventually recombine radiatively. In this range, increasing the excitation flux will proportionally increase the number of NCs with a single \( e-h \) pair and, accordingly, linearly increase the observed PL intensity. At still higher pump pulse fluences multiply excited NCs will appear. However, the small volume of NCs results in high carrier densities and enhanced Coulomb interactions, leading to increased Auger recombination rates \([54]\). Elaborate calculations for spherical Si NCs show Auger recombination times to be in the range of 0.1 to 1 ns for NCs with sizes investigated in this study \([53]\). This is much faster than the radiative lifetime of \( \tau \approx 100 \mu s \). Therefore, the fast Auger recombination process will remove all excess carriers and leave only a single \( e-h \) pair per NC to recombine radiatively, contributing to the measured integrated PL signal. The validity of this scenario finds direct confirmation in the PL dynamics measured for Sample #2 for the three different excitation levels indicated in Fig. 4.4: in the linear regime, at the
CHAPTER 4. LUMINESCENCE SATURATION AND QUANTUM CUTTING BY SILICON NANOCRYSTALS

Figure 4.4: PL-intensity dependence of Sample #2 on the amount of absorbed photons per pulse \( N_{\text{abs,}\lambda} = J_{\text{pump,}\lambda} A S_{\text{abs,}\lambda} \) for three different excitation wavelengths. On the top axis the average amount of absorbed photons per NC is indicated. The cumulative Poisson distribution from Eq. (4.9) for \( x \geq 1 \) and \( x \geq 2 \) for a NC diameter of 2.5 nm is shown by the two continuous lines, the value of \( N_{\text{NC}} \) has been scaled to match the saturation value of the PL. Inset: RT PL-transients of Sample #2 obtained for 3 different pump pulse fluences as indicated by color-coded arrows.

onset of saturation, and in the saturation regime. The results have been obtained by a time-correlated photon counting method and are illustrated in the inset of Fig. 4.4. As can be seen, identical decay dynamics are observed regardless of the pumping level. (We note that due to the experimental resolution, the effect of the fast non-radiative recombination is contained within the bin size of 256 ns). Finally, we briefly comment on the previous reports of PL saturation from Si NCs. Studies on porous silicon under continuous excitation revealed saturation for higher excitation intensities (>2 W/cm²) [55]. In this case, the measured PL lifetime showed a strong decrease for higher excitation fluxes. This effect has been related to the Auger process which appears when a second \( e-h \) pair is created in a NC during the lifetime of the first one. On the other hand, measurements performed on single Si NCs under cw excitation, and also on dilute solutions of Si NCs under pulsed excitation, showed that the initial linear dependence of PL intensity on excitation pump pulse fluence was followed by a sublinear increase for the region where, on average, more than one \( e-h \) pair is created per NC per pulse [56]. The explanation of this behavior has been sought in the blinking of
NCs and the possible shortening of the “off” periods which might appear under intense pumping. These effects are clearly not observed in Si NCs investigated in this study. While blinking could play a role also for our samples, we consider this effect not to be of importance for the saturation behavior; it could influence only the maximum PL intensity, since different times of blinking for different NCs will be averaged out on ensemble of NCs.

4.1.4 Conclusions

We have performed PLE studies on Si NCs in a SiO$_2$ matrix and found that the maximum level of time-integrated PL after a pulsed excitation is independent of excitation wavelength and is reached when each NC has absorbed at least one photon. This demonstrates that the PL intensity for an ensemble of NCs is limited by the amount of NCs. We argue that at high excitation intensities the NCs that are multiply excited undergo a fast non-radiative Auger recombination. Therefore only the “last” e-h pair in each NC can subsequently recombine radiatively and contribute to the observed PL. In this way, the maximum intensity of PL from an ensemble of Si NCs after a pulsed excitation is restricted to a maximum of one photon per NC.

4.2 Quantum cutting

4.2.1 Relative quantum yield of PL

In Section 4.1 it was shown that there is a maximum of one exciton per nanocrystal which can contribute to photon generation after a short excitation pulse. This means that the maximum number of e-h pairs which can recombine radiatively $N$, (see Eq. 4.1) is equal to $N_{NC}$, the number of nanocrystals in the illuminated volume. Non-radiative recombination introduces a proportionality factor $\eta$ between these two quantities, which is basically the quantum yield of PL. Since radiative recombination of a single e-h pair results in a single emitted photon, we can combine Eq. (4.2) and Eq. (4.6) and get

$$S_{PL} = \chi N_{PL} = \chi N^* = \chi \eta N_{NC}(1 - e^{-\sigma_{ex} J_{pump}}).$$  \hspace{1cm} (4.12)

In particular, we note that at an infinite pump fluence the above equation gives:

$$S_{PL,max} = \chi \eta N_{NC},$$  \hspace{1cm} (4.13)

while for small excitation fluence we get

$$\left. \frac{dS_{PL}}{dJ_{pump}} \right|_{J_{pump} \to 0} = \chi \eta N_{NC}\sigma_{ex}.$$  \hspace{1cm} (4.14)
Comparison of Eq. 4.7 with the last equation tells us that \( \mu A S_{abs} = \eta N_{NC} \sigma_{ex} \). In the linear regime for an ensemble of NCs we can see that \( \mu = \eta \). In other words, the quantum yield is linked to the parameters as
\[
\eta = \frac{N \sigma_{ex}}{A S_{abs}}. \tag{4.15}
\]

Because knowledge of \( N \) cannot be obtained (just the product \( \chi N \) can be obtained by fitting), only the relative quantum yield can be determined experimentally in this case, and is proportional to the ratio of the fitting parameter \( \sigma_{ex} \) and the measured absorbance signal \( S_{abs} \). However, the saturation \( S_{PL,max} \) is independent of excitation wavelength \( \lambda_{ex} \), showing that \( N \) is a constant not depending on \( \lambda_{ex} \). Thus, plotting the ratio of \( \sigma_{ex} \) and \( S_{abs} \) will give us directly information about the relative quantum yield \( \eta_{rel} \). Applying this analysis to the data collected for Sample #1, and extending the excitation range to 310 nm with a dye laser pumped by a XeCl excimer laser, gives us the results for a relative quantum yield shown in Fig. 4.5. At the start of a cycle in PL, a NC absorbs a photon and an \( e-h \) pair is created. Subsequently the \( e-h \) pair will quickly (\( \sim 1 \) ps [57]) relax toward the bottom of conduction and top of valence bands, respectively. Finally, recombination leads to emission of an IR photon with an energy determined by the NC bandgap. From this it is expected that the total numbers of emitted and absorbed photons are correlated, i.e. \( \eta \) is constant. From Fig. 4.5 it is evident that this is indeed true in the lower range of excitation energies. However, in the figure a clear enhancement is seen for energies above a certain threshold, around \( \sim 3 \) eV (420 nm). This shows that at this energy, \( \eta \) increases due to an additional excitation process. The relevant process is schematically illustrated in part (b) of Fig. 4.5; the excess energy \( \Delta E \) of the “hot” carrier (\( \Delta E = h\nu - E_{NC} \), where \( h\nu \) and \( E_{NC} \) are photon and NC bandgap energies, respectively) is large enough to allow for an Auger process of intra-band relaxation with simultaneous excitation of a neighboring NC, with the condition that it is located inside of the energy transfer range [58]. In result, two NCs can be excited per single absorbed photon. Analyzing the energy diagram in Fig. 4.5, indeed such a process is expected to be allowed for photon energies exceeding the sum of twice the NC bandgap, \( h\nu > 2E_{NC} \approx 3eV \). Thus, when the energy of the incident photon exceeds this threshold, relaxation to the ground state can occur through emission of two photons in the Si NC exciton PL range.

4.2.2 Quantum cutting and multiple exciton generation

This phenomenon, which we termed space-separated quantum cutting (SSQC) bears close resemblance to that of multiple exciton generation (MEG) in which two, or more, \( e-h \) are induced in a single NC upon absorption of a photon. The MEG process for NCs has been proposed theoretically and subsequently
4.2. QUANTUM CUTTING

Figure 4.5: [a] Relative quantum yield of PL for Sample #1 as a function of excitation photon energy. [b] A diagram showing the involved process: (1) Excitation of Si NC with a high energy photon creating a “hot” e-h pair with excess energy. (2) Intra-band Auger process exciting a neighboring NC and removing the excess energy ($h\nu - E_{NC}$). (3) NC luminescence. [c] A schematic illustration of the process in real space: one photon is absorbed by one NC, two photons are emitted by distinct NCs.
experimentally verified for different semiconductor materials [59, 60, 61, 62, 63, 64, 65, 66]. Furthermore, it has been demonstrated for colloidal silicon NCs [50] and more recently also in carbon nanotubes [67]. Lifetimes of multi-excitons in a NC were found to be very short (<100 ps and shorter, depending on material and NC size [54] due to the enhanced Auger recombination and subsequent fast carrier cooling [68]). When compared to bulk semiconductor materials, a much higher efficiency of the MEG process in nanocrystalline environment has been reported, as resulting from an enhanced Coulomb interaction. In the most spectacular case, generation of up to 7 \( e^{-h} \) pairs from absorption of a single highly energetic photon has been found for NCs of PbSe, with a small and direct bandgap [69].

**MEG controversy**

Detailed investigations of MEG process in NCs of different materials revealed controversial results. It turned out that some of the early results on efficient CM could not be reproduced [70] and other were withdrawn [71]. While part of the controversy could be attributed to material differences and, very specifically, to surface conditions [72] and photocharging [73], experimental artifacts could contribute as well. This is illustrative for experimental challenges involved in MEG investigations. In particular, most evidence for the MEG comes from ultrafast dynamics of induced absorption and emission, where picosecond transients need to be resolved and deconvoluted. As shown by the detailed study for a particular case of PbSe NCs [61], great care needs to be taken to eliminate multiphoton absorption and carrier trapping, as both effects may easily lead to great overestimation of the MEG efficiency. In line with that, the later investigations confirmed the MEG effect for NCs, but found much more modest values for multiplication factors and energy thresholds than the earlier reports [61, 71, 74, 75]. In contrast to these, a recent report concluded that the nanocrystalline environment is not at all advantageous for the MEG process [76]. Based on the new measurements of impact ionization in bulk PbS and PbSe, the authors of Ref. [76] argued that efficiency of this process is equal, or even larger, than the corrected results for MEG in NCs of these materials. The accompanying theoretical model explained that the advantageous effect of the quantum confinement on MEG efficiency, due to the increased overlap of electronic wave-functions and enhancement of Coulomb interaction, is fully counterbalanced by the simultaneous reduction of density of (two-exciton) states. Contrary to the earlier discussed work, this new report questioned then the very basis for the interest in MEG in NCs.

While the majority of MEG studies concentrated on NCs of direct bandgap materials, the effect has also been found for colloidal Si NCs [50]. Based on induced absorption measurements performed on relatively large Si NCs, a very significant enhancement of MEG efficiency with respect to bulk Si has been concluded. To this end it is fair to mention that experimental MEG investigations for Si NCs are
considerably more difficult than for direct bandgap materials, in view of important contributions of nonradiative recombination channels. Since these processes are usually very fast, they complicate interpretation of induced absorption dynamics in terms of carrier multiplicity, as carrier trapping and Auger processes are difficult to separate in absorption transients.

**Microscopic mechanism of MEG**

The microscopic origin of MEG is under debate and several possibilities have been put forward. These include:

1. Impact ionization by a hot carrier created as a result of photon absorption \[64, 65\]

2. Coherent superposition of single and multiexciton states \[59\] due to the strong Coulomb interaction of carriers confined in NCs, which should take place when the energy relaxation rate of a single electron-hole pair is lower than both the two-exciton state thermalization rate and the rate of Coulomb coupling between single and two-exciton states.

3. Multiexciton formation via a virtual state \[77, 78\]. This process can be described by second order perturbation theory and here two possible scenarios, with comparable rates, have been proposed. The first one proceeds via a virtual single exciton state. In this case, the direct optical transition from vacuum to a single exciton state is followed by the transition into the final two-exciton state due to Coulomb interaction \[77\]. In the second scenario, the first step is the transition initiated by the Coulomb interaction from vacuum to a bi-exciton state, and the second step is optical intraband transition \[78\].

4. More recent theoretical modeling \[79\] suggests that a prominent role could be played by defects in the bandgap of a NC. While this idea is of general character and not restricted to a particular material, it could be especially important for the case of Si NCs embedded in an oxygen-rich environment of SiO\(_2\), for which oxygen-induced defects are known to appear in the bandgap for sufficiently small NC sizes. In particular, a relation could be sought with the well known SiO\(_2\)-related 420 nm (\(\sim 3\) eV) defect band \[80\].

The processes (2) and (3) can be responsible for MEG without any delay, i.e., in the moment of the photon absorption, and can be effective for production of multiple excitons in a single NC. However, extra excitons occurring in the same NC are recombining on a picosecond time scale \[54\]. The impact ionization process (1) and defect mediated process (4) start with some delay after the absorption and proceed via a real state when the hot electron-hole pair is created by the
absorbed photon with energy exceeding the energy gap. Process (1) is well known for bulk semiconductors, where it can increase the number of photo-excited carriers [25]. One may expect that the impact ionization rate should rise dramatically in the case of NCs due to the strong Coulomb interaction of confined carriers and the decreasing rate of phonon emission caused by the discrete spectrum [64, 65]. Indeed, pseudopotential calculations predict a higher rate of impact ionization in CdSe dots than in bulk material for electrons with excess energies just above the band edge [81]. Preliminary theoretical considerations indicate that impact ionization is a suitable candidate to account for the SSQC phenomenon. The effective dielectric constant governing the Coulomb interaction between carriers in different NCs embedded in SiO$_2$ matrix is considerably smaller than the dielectric constant of Si. Using the Auger recombination rate (the reverse process to the impact ionization) inside the silicon NC calculated before [82], we have got the value of the order of $10^{10} - 10^{11}$ s$^{-1}$ for the rate of the process under consideration for two NCs at a distance of less than 1 nm. This rate is comparable to the energy relaxation rate determined by the Auger process between carriers confined in one silicon NC of 3 nm diameter when there is one exciton per NC [83]. From the NC-NC distance distribution depicted in Fig. 4.6 we conclude that more than 50% of all NCs in the samples investigated here have their closest neighbor at a distance of less than 1 nm from the surface, i.e., sufficiently close to facilitate the proposed energy transfer. For completeness, we recall that the Förster resonant energy transfer (FRET) which was shown to be responsible for long-range energy diffusion in a closely packed CdSe quantum solid [84], has low probability for Si NCs due to the indirect bandgap. Nevertheless, a phonon assisted Förster mechanism might be more probable.
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4.2.3 Conclusion

We have shown how quantum cutting can take place in a system consisting of Si NCs in SiO$_2$. In contrast to the earlier work on MEG, the downconverted energy quanta appear in another NC, from where it can be emitted as a photon. This adds an additional virtue to the MEG process, it considerably increases the excitonic lifetime - from the picosecond range characteristic for multiexcitonic Auger processes up to the microsecond range necessary for radiative recombination in indirect bandgap materials. It also makes the SSQC effect particularly interesting for PV applications, enhancing the “extraction time-window” of photo-generated carriers by several orders of magnitude. Furthermore, the demonstration of the SSQC process for Si is technologically interesting in view of the prominent role of Si and Si-derived materials in electronic, optoelectronic and especially in photovoltaic applications. The use of nanocrystals provides the additionally appealing aspect that the energy levels can be tuned to suit the application by changing the size of the particles [85, 86]. For solar cells it has been shown theoretically that multiple exciton generation [87] and photon down-conversion [88] can increase the efficiency beyond the Shockley-Queisser limit. On the more practical experimental side, the SSQC can be investigated in experiments conducted in microsecond range, considerably more reliable than the ultrafast (sub-)nanosecond spectroscopy applied in all the previous MEG investigations. Therefore, in the light of the aforementioned controversy on the enhancement of MEG in NCs, the SSQC process provides for a good reference.
Carrier multiplication – the generation of two or more e-h pairs following the absorption of a single photon – may lead to improved photovoltaic efficiencies [89] and has been observed in nanocrystals made from a variety of semiconductors, including silicon. However, with a few exceptions [90], the past reports were based on indirect evidence obtained by ultrafast techniques [59, 69, 50, 61]. In this chapter, we present detailed investigations of carrier multiplication in closely spaced silicon nanocrystals by measuring enhancement of the photoluminescence quantum yield. We observe a step-like increase in quantum yield for larger photon energies that is characteristic of carrier multiplication [91]. Modeling suggests that the carrier multiplication is occurring with high efficiency and close to the energy conservation limit. Furthermore, it is also shown that the efficiency of the process decreases upon separation of the nanocrystals.

5.1 Introduction

The Kasha-Vavilov rule [92], which states that the quantum yield of luminescence is independent of the wavelength of the exciting radiation, applies for a large variety of molecules. Although there are some exceptions to this empirical rule, it is certainly fair to state that the PL spectrum usually shows very little dependence on the excitation wavelength. This implies that, for higher excited states, relaxation into the emitting state is considerably more efficient than other channels of non-radiative and radiative recombination. In the first approximation, the same rule applies also to semiconductor NCs, which in many ways can be considered as giant molecules as illustrated, for example, by CdSe/ZnS core/shell quantum dots [93]. More generally, relaxation of “hot” carriers generated by the absorption of
high-energy photons in semiconductor NCs is more complex [19, 79, 94, 95]. It is commonly the case that the photoluminescence quantum yield of NCs decreases for larger photon energies, as more non-radiative pathways related to surface and other trap states become accessible.

5.2 Experimentals

We explored the excitation wavelength dependence of photoluminescence quantum yield (ratio of the number of emitted and absorbed photons) for silicon NCs fabricated using different approaches. One type was prepared by co-sputtering of silicon and SiO$_2$ onto a quartz substrate, followed by annealing at high temperatures [14]. A thin ($\sim 700$ nm) sub-stoichiometric layer of SiO$_{x}$, where $x = 1.60$ and 1.89 for samples A and B, respectively, was annealed in a nitrogen atmosphere for 30 minutes at 1150 °C. This resulted in a distribution of Si NCs in SiO$_2$ with an average size of 4.1 nm (Sample A) and 3.1 nm (Sample B). The second material was composed of porous silicon grains suspended in ultraviolet-grade ethanol, made by electrochemical etching of crystalline silicon. The preparation procedure hereof can be found in Section 2.2.2. The po-Si samples contained small (1-3 nm) closely spaced and possibly interconnected and/or aggregated oxidized silicon NCs of different shapes [31]. The NC size distribution in the “po-Si 1” sample was narrower than in “po-Si 2”, as a result of longer sedimentation and purification steps.

PL of oxidized silicon NCs has been investigated in detail and is known to originate from localized defect states or quantum-confined band-to-band transitions, which show similar spectral and temporal characteristics [96]. It is generally accepted that band-to-band recombination occurs for larger NCs. For smaller ones electronic states due to oxygen-related defects on the surface will dominate photoluminescence, limiting the quantum confinement induced opening of the optical bandgap [17] and the “blue” shift of excitonic emission. Past investigations have shown that transition between these two channels of radiative recombination takes place in a continuous way, with no evidence for a barrier potential at defect levels. In addition to these two main emissions, there is also a contribution from radiative recombination of non-equilibrium carriers [57]; however, its effect on the total photoluminescence quantum yield is minor.

5.3 Results

The experimentally determined dependence of the external photoluminescence quantum yield on excitation photon energy is displayed in Fig. 5.1. Although the absolute values vary for different samples, the similarity in the overall behavior
Figure 5.1: Spectral dependence of PL QY. Results are shown for sample A, sample B, po-Si 1 and po-Si 2. The lower panels show the PL spectra of each sample. (the energy axis is multiplied by either 2 or 3, indicated by $2E_{PL}$ and $3E_{PL}$, respectively). The black dashed lines, indicating the “steps”, serve only as a guide to the eye.

is striking: the initially low and constant value of quantum yield for the lower photon energies is followed by an increase for larger energies. This behavior is unexpected in view of previous remarks, and indicates that a new physical mechanism is being activated upon excitation with higher-energy photons. A very specific common feature observed in the first three panels is a step-like character of the measured increase of quantum yield in the higher energy range. The lower panels in Fig. 5.1, showing corresponding photoluminescence spectra multiplied by two and three, reveal their coincidence with the quantum yield steps. The occurrence and the width of the steps in the upper panels is related to the width of the multiples of photoluminescence spectra and can therefore be naturally explained as resulting from the distribution of nanocrystal sizes (A simulation of this effect will be given in Section 5.4). This is directly illustrated by the more or less continuous character of the quantum yield increase for the po-Si 2 sample, where a broad size distribution and broader photoluminescence spectrum obscure observation of the steps.

5.4 Discussion

The experimentally obtained spectral dependence of the external photoluminescence quantum yield given in Fig. 5.1 is clearly very different from that predicted by the Kasha-Vavilov rule (constant quantum yield), or that expected for nanocrystals (decrease of quantum yield at higher excitation energies). A simi-
lar step-like increase of quantum yield appears as a result of “quantum cutting” in rare-earth ion systems [97, 98], when absorption of a single photon of sufficiently large energy by one type of ion results in subsequent excitation transfer to two (or more) rare-earth ions with lower excitation energy. Such an effect was originally proposed for inorganic crystals by Dexter, where a single photon absorbed by a sensitizer leads to the emission of two half-energy photons by an activator [99]. The step-like behavior has also been reported for carbon nanotubes [67] and assigned to the carrier multiplication process, with a large-energy photon being able to generate multiple free electrons. It is therefore natural to also explain the enhancement of photoluminescence quantum yield found here for silicon nanocrystals in terms of carrier multiplication, similar to what has been observed in NCs of different semiconductor materials [90, 59, 69, 50, 61, 63] including silicon, where absorption of a single photon with a sufficiently large energy may result in generation of multiple electron-hole pairs. We note that it has been argued that the indirect bandgap of silicon should lead to enhancement of the carrier multiplication rate [100]. With carrier multiplication, every time the excess energy of an excitation photon overcomes the threshold of a multiple of the bandgap energy (plus additional activation energy for the process), one more electron-hole pair can be produced, increasing the free carrier population. Because part of the free carrier population undergoes radiative recombination, this will enhance photoluminescence and thus increase its quantum yield. The step-like character of the quantum yield increase can then be seen as the most characteristic fingerprint of that process.

The dependence of the QY of such a system we can model by considering only energy conservation and bandgap energy. In a model system (see Fig. 5.2a) the NCs all have the same bandgap, which means that energetically CM becomes possible when the absorbed energy quanta is at least $2E_G$. The PL spectrum of such a system is shown in Fig. 5.2b, where there is only a peak at the bandgap energy. For CM taking place at energy conservation limit it is important to consider the multiples of the bandgap energy; $2E_G$ and $3E_G$, since for these energies an increase in carrier generation can be expected. For this purpose these peaks are combined in the spectrum shown in Fig. 5.2b, which indicates a CM density of states function which we denote by $\phi_{CM}(h\nu)$. The bottom panel of Fig. 5.2b shows the dependence of the QY as a function of the excitation photon energy determined by:

$$QY(h\nu) = \frac{\int_0^{h\nu} \phi_{CM}(h\nu') I_{PL}(h\nu') d(h\nu')}{I_{PL}(h\nu)}, \quad (5.1)$$

where the denominator is the number of emitting states, i.e. the PL band $I_{PL}(h\nu)$. In this way we get a normalized QY, which is unity for $E_G < E(h\nu) < 2E_G$. Note that for energies $E(h\nu) < E_G$ this value is not defined, since both nominator and denominator are 0 resulting from absence of absorption. The
(a) Energy transfer

(b) Theory single gap

Figure 5.2: (a) Energy diagram showing two NCs with identical bandgap-energy. The green arrow indicates transfer of excess energy to the next NC, thereby exciting a carrier across the bandgap. (b) Top: Schematic PL spectrum of a single energy gap system (red line). The blue line shows multiples of this PL spectrum, indicating the energies where energy transfer is possible. Bottom: Spectral dependence of QY under assumption of energy transfer at conservation limit for this system.

Step-like increase in QY is evident, and also it is obvious that the width of the increasing steps is determined by the PL spectrum. In a realistic NC system there is a distribution of sizes leading to a distribution of bandgap energies. The PL spectrum of a real system is shown in the top panel of Fig. 5.3a, where $I_{PL}(h\nu)$ is shown for sample A. When the same procedure is applied as in the case of a single bandgap system, we again get the CM density of states function $\phi_{CM}(h\nu)$ by combining $I_{PL}(h\nu)$ with multiples of the PL spectrum. $QY(h\nu)$ calculated with Eq. 5.1 is shown in the bottom panel of Fig. 5.3a. While there is still a step-like increase in the QY, it is considerably smoothened by the size distribution.

The results from this analysis are compared to the normalized QY data obtained for sample A in Fig. 5.3b. The similarity in the shape is striking. An even better agreement between the theoretical model and experimental data is obtained when the QY dependence is shifted by 300 meV, which indicates that there is an additional energy necessary to enable CM $\Delta E = 0.3$ eV. This value is about 8 times smaller than for bulk Si.

In 2010 a phenomenological model to describe CM in bulk and NC materials was proposed by Beard et al. [91]. In their analysis the bandgap energy is the...
fundamental unit of energy which is required to produce an electron-hole pair. Furthermore the CM onset energy and efficiency are mutually related. When we apply the model to carrier generation values for bulk Si \(E_g = 1.13 \text{ eV}\) a good agreement is obtained for a multiplication efficiency \(\eta_{EHPM} = 0.6\) (see Fig. 5.4). The results for Si NCs (sample A) can also be described very well within this framework, where the bandgap is determined by the peak of the PL spectrum \(E_g = 1.38 \text{ eV}\), and \(\eta_{EHPM} \approx 0.99\).

Previous reports on carrier multiplication in semiconductor nanocrystals were predominantly based on ultrafast transient absorption measurements, but in the present case it is observed by enhancement of radiative recombination. Because Auger recombination inside these nanocrystals is approximately six orders of magnitude faster than radiative decay, the individual excitations must be separated into different nanocrystals in order to be observed in time-integrated PL measurements, in analogy to the aforementioned quantum cutting process for rare-earth ions [51]. This implies that the proximity of Si NCs is an important parameter. To test this, and to justify our interpretation, we compared quantum yield enhancement in two samples that contained silicon nanocrystals of similar size but different concentrations in order to vary the average distance. As can

Figure 5.3: (a) Top: PL spectrum of sample A which has a distribution of bandgap energies of the individual NCs (red line). The blue line shows multiples of this PL spectrum, indicating the energies where energy transfer is possible. Bottom: Spectral dependence of QY under assumption of energy transfer at conservation limit for this system. (b) Comparison of theoretical QY dependence (red dots), and normalized QY data of sample A (open squares). Blue dots indicate theoretical QY shifted horizontally by 300 meV.
be seen from Fig. 5.5 the slope with which the quantum yield increases is lower for the sample with smaller nanocrystal concentration, indicating the lower efficiency of the carrier multiplication process in this case [91]. To complement this experiment, we also examined the excitation dependence of photoluminescence quantum yield for free-standing colloidal silicon nanocrystals (See Fig. 5.6) (preparation procedure can be found in Section 2.2.3). In contrast to the results depicted in Fig. 5.1, the free-standing colloidal silicon nanocrystals exhibit characteristics typically expected for nanocrystals, with quantum yield actually decreasing at higher energies as opposed to that of the high density samples. This effect originates probably from an increase of non-radiative recombination and carrier trapping effects for higher energies of excitation. We add that a fingerprint of such a reduction can also be noted in the characteristics of sample B, where the decrease is abrogated when quantum yield is enhanced again by the carrier multiplication effect.

For the sake of completeness, we briefly consider alternative explanations for the increase of photoluminescence quantum yield determined in this study. The most obvious possibility is a reduction of non-radiative recombination. This specific process we can rule out for several reasons. First, both the photoluminescence spectra and their transients (within an experimental resolution of 5 ns) for a particular sample have identical characteristics throughout the investigated range of excitation energies. Second, such an interpretation is also improbable in view of the characteristic features of the quantum yield excitation dependence (the step-like behaviour commencing with a threshold value). Third, as mentioned before, for free-standing nanocrystals the opposite trend is observed, with the relative importance of non-radiative pathways increasing with energy, lowering
the quantum yield. Similar arguments also rule out an explanation of quantum yield enhancement in terms of optical activation of “dark” nanocrystals (“blinking”) at larger photon energies [56]. Finally, we might add that recent induced absorption measurements on similar materials confirmed enhanced generation of free carriers at higher excitation energies [101].

To conclude, we comment on the impact of reported findings regarding the potential application of silicon nanocrystals to third-generation photovoltaics, in which

Figure 5.5: Effect of inter-nanocrystal separation. Spectral dependence of PL QY for two samples with same average NC size distribution, but different concentrations. Black and gray dashed lines serve as guides to the eye. Error bars represent experimental accuracy of QY determination for different photon energies.

Figure 5.6: Spectral dependence of PL QY for freestanding colloidal Si NCs. The dashed lines act as a guide to the eye.
5.4. DISCUSSION

Figure 5.7: Comparison of carrier generation yield for bulk Si (taken from Ref. [25]) with values of quantum yield for sample A and po-Si 2 (normalized to unity in the low-photon-energy regime). Thick red and blue semi-transparent lines are added as guide to the eye and can be reproduced very well using the CM modeling developed in Ref. [91]. Standard reference solar spectra AM 1.5 and AM 0 (extraterrestrial) are indicated in green and light green, respectively.

various approaches for overcoming the photon-to-electron conversion limits are explored [89]. Silicon nanocrystals have been studied in the past in relation to their ability to transform short-wavelength photons into a range more beneficial for photovoltaic conversion, and have been shown to increase the internal quantum efficiency of a standard silicon cell [102]. To illustrate the potential of silicon nanocrystals for photovoltaics we compare the current findings with the literature values on carrier multiplication in bulk silicon [25] (Fig. 5.7). For this purpose, the initial efficiency at small photon energies has been set to 1 for all data. The advantageous properties of nanocrystals with respect to bulk are obvious. First, the absolute value of the threshold energy for carrier multiplication for nanocrystals is considerably smaller than that for bulk, even though they have a larger
bandgap. Second, the increase in efficiency is much larger and steeper, reaching a value of 200% for an energy of 3.4 eV, and increasing further for higher energies. To demonstrate potential applications for silicon nanocrystals in photovoltaics we also included the standard reference terrestrial (AM 1.5) and extraterrestrial (AM 0) solar spectra. The onset energy for the mechanism is within the solar spectrum and readily shows the benefits of the use of silicon nanocrystals. Future research will tell whether a similarly higher conversion efficiency can indeed be realized in photovoltaic devices.
Chapter 6

Ensembles and light interaction

In this chapter a study of the photoluminescence spectra for ensembles of silicon nanocrystal and their evolution for different excitation intensities is presented. A combination of size-dependent absorption cross-section and saturation effects in these nanocrystals have a profound effect on the ensemble PL spectrum. Simulations of this effect are shown and compared with experimental data. The presented simulations describe how the distribution of excited nanocrystals changes under different excitation conditions and leads to a spectral shift of the ensemble PL. The influence of excitation properties and its effect on the spectral profile is discussed. Next to this, also the influence of different radiative rates in an ensemble of NCs is addressed.

6.1 Spectral evolution on excitation intensity

6.1.1 Theory and experiment

There is a lot of literature available on the dependence of the bandgap of the Si NCs on the diameter, for an overview hereof see e.g. Ref. [103]. In Section 2.3.3 it was shown that, for the sputtered films, a good fit for the experimental data for the optical gap is given by

\[ E_g(D) = E_{Si} + \frac{1.86}{D^{1.39}}, \]

where \( E_{Si} \) is the bandgap of bulk Si, similar as the theoretical dependence determined in [37, 104]. Rewriting Eq. 6.1 gives the relation between diameter and wavelength:

\[ D(E_g) = \left( \frac{1.86}{E_g - E_{Si}} \right)^{\frac{1}{1.39}}. \]
Also it was shown Section 2.3.3 that the NCs prepared in this way commonly have sizes whose logarithm is normally distributed;

$$N(D) = \frac{1}{D\sigma\sqrt{2\pi}}e^{-\frac{(\ln(D) - \mu)^2}{2\sigma^2}},$$  \hspace{1cm} (6.3)

with $\mu$ and $\sigma$, being the mean and standard deviation, respectively, of the diameter $D$’s natural logarithm. Fig. 6.1 shows results of fits of Eq. 6.3 to the experimentally determined PL data.

In Section 4.1 it was concluded that, under the condition that the excitation pulse is much shorter than the PL lifetime, every NC can emit a single photon only. Multiple excitons localized in the same NC, that have been excited by multi-photon absorption, undergo a fast non-radiative Auger recombination. Finally, only a single exciton remains, which can undergo radiative recombination. The number of excited NCs $N^*$ after an excitation pulse can in this case be described by:

$$N^*(J_{\text{pump}}) = N(1 - e^{-\sigma_{\text{abs}}J_{\text{pump}}}),$$  \hspace{1cm} (6.4)

where $N$ is the number of NCs in the illuminated volume that can emit a photon, $\sigma_{\text{abs}}$ the absorption cross-section, and $J_{\text{pump}}$ the pump fluence. From geometrical considerations it is expected that the $\sigma_{\text{abs}}$ scales with the square of the diameter of the NC, which is theoretically supported by calculations of optical absorption.
6.1. SPECTRAL EVOLUTION ON EXCITATION INTENSITY

Figure 6.2: Simulated spectra obtained from Eq. 6.6 for ratio of pump fluence of 0.01, 0.03, 0.07, 0.3, 0.65, 1.

cross-sections for Si NCs of different sizes [105]. We can now write $\sigma_{\text{abs}} = \zeta D^2$, where $\zeta$ is a proportionality factor. In this case Eq. 6.4 can be written as:

$$N^*(J_{\text{pump}}) = N(1 - e^{-\zeta D^2 J_{\text{pump}}}).$$

(6.5)

We can use now the expression for the distribution of NC sizes from Eq. 6.3 and combine this with Eq. 6.5 to arrive to an expression for the number of excited NCS as a function of excitation pump fluence and their associated bandgap energy:

$$N^*(E_g, J_{\text{pump}}) = N(D(E_g))(1 - e^{-\zeta D(E_g)^2 J_{\text{pump}}}).$$

(6.6)

By converting $E_g$ to wavelength with the relation $\lambda = \frac{hc}{E_g}$ the associated PL spectrum can be obtained. Qualitatively this equation describes how the ratio of excited NCs for different sizes changes upon illumination under different excitation powers. So, under assumption that the quantum efficiency for photoluminescence is identical for all sizes, it shows how the PL spectrum changes with laser power. Larger NCs have a larger absorption cross-section, so will be saturated in emission at smaller pump fluences than the smaller NCs. This means that when the pump fluence is increased even more, the smaller NCs can still increase their contribution to the total (ensemble) emission. As a result, the PL spectrum will shift to shorter wavelengths. Fig. 6.2 presents PL spectra obtained with Eq. 6.6 for 6 different values of pump fluence with ratio’s 0.01, 0.03, 0.07, 0.3, 0.65, 1. While the intensity increases, saturation sets in at longer wavelengths and the peak shifts to shorter wavelengths. A comparison of experimental data of PL and the simulations is shown in Fig. 6.3. We note here that carrier multiplication, known to occur in similar systems [106], has been omitted by using an excitation photon energy below the threshold of 2 times the NC bandgap. For clarity, the normalized spectra are shown. In the simulations the same ratios of excitation fluence are used as in the experiment. The value of $\zeta$ was in this case determined from the saturation behavior at a single wavelength by the method presented.
in Refs. [51, 45]. In this method Eq. 6.4 is fitted to the power-dependent PL intensity to obtain $\sigma_{\text{abs}}$ for a specific wavelength, which is subsequently used to deduce a value for $\zeta$. The simulation models the experimental spectra well; the peak shifts to shorter wavelengths and the shift on the small wavelength side is more pronounced than that for longer wavelengths.

Next to a size-dependent absorption cross-section, there is also a dependence on the decay time [47]. Typically, smaller Si NCs have PL lifetimes in the order of 10 $\mu$s, while for large NCs this increases to $\sim 100$ $\mu$s. This effect leads to red-shift of PL spectra for longer detection times, which is often observed experimentally [107]. For Si NCs, most commonly a stretched exponential decay of PL intensity at a single wavelength is observed:

$$I(E_g, t) = N(E_g) \cdot e^{-\left(\frac{t}{\tau_{\text{PL}}(E_g)}\right)^\beta}.$$  \hspace{1cm} (6.7)

We have used values for $\beta$ and $\tau_{\text{PL}}$ found in Ref. [47] in order to be able to simulate spectra at different times after excitation. Fig. 6.4 shows these results for $t = 0, 50, 100, 150, 200$ and $250$ $\mu$s. A clear shift of the maximum PL intensity in time is accompanying the change of decay, very similar as observed in [107]. In the interpretation of such time-dependent phenomena it is thus essential to remove contributions originating from above “experimental” effects.

### 6.1.2 Discussion

The shift of PL spectra to shorter wavelengths with increasing excitation power has been shown to occur in different types of NC ensembles. Different explanations have been suggested for this behavior [108, 109, 110] and the importance of the absorption cross-section has been noted as well [41, 111]. Although the above proposed framework does not necessarily fully explain the experimentally observed shifts of PL spectra, it is important to account for the strong influence...
of the discussed effects. It should be emphasized that the analysis and simulations done here are based on the condition that the system is excited by a short pulse, with respect to the PL lifetime, and the emerging luminescence is decaying fully in between the pulses. In practice this means that the pulse repetition rate should be small enough to allow for all the excited carriers to return to the ground state. Under continuous excitation, typical for most experimental reports, the characteristics change considerably, as equilibrium conditions are important in this case. The size-dependent decay time could substantially alter the excitation power-dependent emission, and an even larger blueshift can be expected, since the shorter PL lifetime of small NCs allows for more radiative recombinations.

Now the question arises under which experimental conditions PL spectra should be collected in order to get reliable information about the physical parameters of the system. For NCs showing long decay times, like Si, it is possible to excite the entire distribution by a pulsed excitation. After the pulse, all multiple excited carriers in a NC undergo a fast Auger non-radiative recombination, and every NC can, in principle, emit one photon. This would then be the best way to obtain information about the entire ensemble. However, high pump fluences might be necessary to arrive to this situation and non-linear and heating effects can appear and influence PL properties \[112\]. Alternatively, at low powers, where the average amount of absorbed photons per NC \(< 1\) the shape of the PL spectrum will not change for varying power. This would be the best region to do comparative experiments, but limited PL signal might complicate the practical usability. It is also important to note that in this case mostly the large particles contribute to

![Figure 6.4: Simulated spectra for different times after a pulsed excitation of the entire ensemble of NCs, acquired from Eq. 6.7. The spectral dependence of PL decay time, \(\tau_{PL}(E_g)\), has been obtained from Ref. [47] (image)](image-url)

Figure 6.4: Simulated spectra for different times after a pulsed excitation of the entire ensemble of NCs, acquired from Eq. 6.7. The spectral dependence of PL decay time, \(\tau_{PL}(E_g)\), has been obtained from Ref. [47]
CHAPTER 6. ENSEMBLES AND LIGHT INTERACTION

luminescence and a scaling based on absorption cross-section should be employed.

6.1.3 Conclusions

To sum up, it has been shown that PL spectra of typical Si NC ensembles show a relatively strong dependence on the excitation fluence. A shift by 30 nm of the maximum of PL intensity appears between low power excitation and that under saturation conditions. It has been demonstrated that this shift can be modeled by taking into account the differences in absorption for different sizes of NCs. This, and the notion that each Si NC can only emit a single photon after a pulsed excitation, determine the distribution of NCs in the ensemble that is excited and contributes to luminescence. The evolution of this excited state distribution with respect to excitation pump fluence can be modeled fairly well by these simulations. Additional simulations of differences in PL lifetime in the ensemble show spectral narrowing and redshift of peak intensity in time-dependent spectra. We want to stress the importance of excitation conditions on the PL spectra of ensembles of specifically Si NCs, but this can be expanded to all semiconductor NCs, where ensembles and size-dependent absorption are imminent.

6.2 Optical density and excited state distributions

6.2.1 Introduction

For quantitative analysis of different properties, like absorption cross section and multiple exciton generation rate, it is important to know in what excitation regime the experiments are being done. Optically thick systems, i.e. with a short path length of light through the sample, will contain NCs under different excitation conditions depending on their position relative to the surface where light is incident. The influence this effect has on the average amount of photons absorbed per NC, \( \langle NC^* \rangle \), is considered in this paragraph. The consequences for experimental quantities, where this parameter is essential, are discussed.

6.2.2 Distribution of excited NCs

For a random distribution of NCs, the number of NCs that have absorbed integer \( x \) photons after an excitation pulse, \( N_x \), will be determined by a Poisson distribution function:

\[
N_x = P_x N_{NC},
\]

with

\[
P_x = \langle NC^* \rangle^x e^{-\langle NC^* \rangle} \frac{1}{x!},
\]
where $N_{NC}$ is the total number of NCs. For this evaluation it is important to assure that there is a homogeneous absorption and excitation flux throughout the distribution. Furthermore, scattering of light on the NCs is ignored (typical Rayleigh scattering cross-section for visible wavelengths is $\sim 10^{-21}$ cm$^2$, 4-5 orders of magnitude smaller than the absorption cross-section). In this case we get a distribution of excited NCs as shown in Fig. 6.5. From this figure it is apparent that the contribution of multiply excited NCs ($x \geq 2$) becomes considerable at values of $\langle NC^* \rangle = 0.2$. The relative contribution of these NCs is here already 10%, so that a good singly excited NC regime should be found at still smaller values (for example a relative contribution of 1% requires $\langle NC^* \rangle = 0.02$). In studies of CM the multiply excited NCs can give a high apparent multiplication efficiency as multie exciton-like signals are created by absorption of multiple photons. This effect is enhanced by uncertainties in determination of pump fluence and absorption cross section [61, 113].

When we introduce also absorption of the excitation pulse throughout the sample, $\langle NC^* \rangle$ does not correlate linearly anymore with the excitation pump fluence as above. This is a direct result of the difference in excitation flux at different depths of the NC distribution. We can in this case define an average amount of excited NCs at depth $d$:

$$\langle NC^* \rangle (d) = \langle NC^* \rangle (0) \cdot e^{-\alpha d}, \quad (6.10)$$

where $\alpha$ is the absorption coefficient and $\langle NC^* \rangle (0)$ the average amount of excited NCs on the top layer, which can be evaluated, for example, by multiplication of the pump pulse fluence and independently determined absorption cross-section: $\langle NC^* \rangle (0) = J_{pump} \times \sigma_{abs}$. Combining Eqs. (6.9) and (6.10) gives us the excited

![Figure 6.5: The dependence of the excited population as a function $\langle NC^* \rangle$ determined from Eq. (6.9). $P_0$ denotes the unexcited fraction, $P_1$, $P_2$, $P_3$. the single, double and triple excited NCs, respectively, and $P_{ex}$ the total excited fraction determined by 1-$P_0$. The right picture shows the region of $\langle NC^* \rangle$ between 0 and 1.](image-url)
NC distribution at depth $d$:

$$P_x(d) = (\langle NC^* \rangle(0) \cdot e^{-\alpha d}) \cdot \frac{e^{-(NC^*)(0) e^{-\alpha d}}}{x!}, \quad (6.11)$$

which for $\lim \alpha \to 0$ simplifies to Eq. (6.9) again. We can introduce the optical density (OD) to get a more general expression, $\alpha = \text{OD}/l$, where $l$ is the total thickness, which we will set to 1 for simplicity. If we now want to determine the total excited population, we have to integrate contributions at all depths and divide by $l$:

$$P_{ex} = \int_0^l 1 - P_0(d) \, dd = \int_0^1 1 - e^{-(NC^*)(0) e^{-\text{OD} \cdot d}} \, dd, \quad (6.12)$$

which has to be evaluated numerically. Fig. 6.6 shows saturation behavior for different values of OD; the changes for larger absorption values become apparent.

Experimentally it is often easier to determine $\langle NC^* \rangle$, which is given by

$$\langle NC^* \rangle = \frac{J_{\text{pump}}}{N_{NC}} \cdot (1 - e^{-\text{OD}}). \quad (6.13)$$

Values of $\langle NC^* \rangle(0)$ can be deduced by taking this relation and letting the thickness of the illuminated volume go to zero:

$$\langle NC^* \rangle(0) = \lim d \to 0 \frac{J_{\text{pump}} \cdot (1 - e^{-\text{OD} \cdot d})}{N_{NC} \cdot d} = \frac{J_{\text{pump}}}{N_{NC}} \cdot \text{OD}. \quad (6.14)$$

By combining Eqs. 6.13 and 6.14 it is now possible to deduce a relation between $\langle NC^* \rangle(0)$ and $\langle NC^* \rangle$:

$$\langle NC^* \rangle(0) = \langle NC^* \rangle \frac{\text{OD}}{1 - e^{-\text{OD}}}, \quad (6.15)$$
which is only dependent on the OD. By changing the variables in Eq. 6.12 to $\langle NC^* \rangle$ with the above relation we can get the excited population dependence on this parameter. Fig 6.7 shows how the excited population changes as function of $\langle NC^* \rangle$ for different values of OD. It is obvious that the saturation sets in at larger excitation powers for increasing OD, while for small values of $\langle NC^* \rangle$ the dependence is not so much influenced by the value of OD.

For interpretation of saturation data it is thus obvious that the optical density is an important parameter which should be taken into account.
Chapter 7

dynamics of Er$^{3+}$ emission sensitized by silicon nanocrystals

The system of erbium and silicon nanocrystals doped in SiO$_2$ is studied in this chapter. Silicon nanocrystals can function as efficient broadband sensitizers of erbium luminescence in SiO$_2$. Different temporal aspects of luminescence bands associated to silicon nanocrystals and Er$^{3+}$ ions reveal energy exchange between the two species. Furthermore, a temperature-dependent study of the luminescence characteristics shows the occurrence of a defect band, which overlaps with erbium emission complicating the interpretation of photoluminescence characteristics. With this knowledge we show that thermally activated luminescence quenching processes with different activation energies are responsible for de-excitation of emitting centers, either Er$^{3+}$ (60 meV) or defects (90 meV). Similarly as for silicon nanocrystals, the quantum yield of erbium-related luminescence shows an increase at photon energies above a certain threshold. The value of this threshold is found to be lower than for a system with exclusively silicon nanocrystals. This is interpreted as a quantum cutting process, where the down-converted energy is in this case received by Er$^{3+}$ ions.

7.1 Introduction

Optical communication is at the foundation of modern day global interaction. The internet and other broadband services are increasingly demanding an expansion of the current silica-based fiber and optoelectronic technologies. An important goal is to achieve cheap and compact optical components which can be implemented on a large scale, for example, for fiber-to-home solutions. For
this purpose there is an enormous research effort for finding optical materials that can be integrated with silicon chip technology. Optical fibers have a strong wavelength-dependent transmission spectrum and it turns out that around 1.5 μm there is a minimum in attenuation of signal traveling through a silica fiber. Erbium is a rare earth atom for which the energy of the first excited state of the Er\(^{3+}\) charge state coincides with this wavelength (1.5 μm or 0.8 eV). Since the energy levels of rare earth ions, related to transitions within the 4f-manifold, are stable and not much influenced by the host material, they are interesting as light emitters in a wide variety of matrices. The simplest idea for a CMOS compatible Er based emitter is by incorporating Er\(^{3+}\) ions in a Si host. In this structure it turned out that Er\(^{3+}\) can be effectively excited, but the long lifetime of the Er\(^{3+}\) excited state promotes an efficient Auger-like de-excitation mechanism, quenching the emission strongly at temperatures above 150 K \[114\]. Another “easy” solution is by incorporating Er\(^{3+}\) ions in an SiO\(_2\) host. In this case there is no thermal quenching of Er\(^{3+}\) related emission and it is readily observed at room temperature. However, since intra 4f transitions of the Er\(^{3+}\) ions are only weakly-allowed, excitation is severely limited and typical excitation cross sections are of the order of 10\(^{-20}\) cm\(^2\). The system of SiO\(_2\) doped with Er\(^{3+}\) ions and Si NCs combines to a certain extent the high thermal stability of the Er\(^{3+}\) doped SiO\(_2\) with the possibility of inducing emission non-resonantly. This system is studied widely ever since it was found that room temperature photo- and electroluminescence of Er\(^{3+}\) ions could be effectively sensitized with Si quantum dots \[35, 115, 116, 117, 118\]. Upon optical excitation, photons are predominately absorbed by Si NCs by promoting an electron to the conduction band. The carrier lifetime in Si NCs is relatively long, as the indirect bandstructure intrinsic of Si is preserved \[119\], making it possible for a non-radiative recombination of e-h pair to transfer its energy to an Er\(^{3+}\) ion (See Fig. 7.1). In this way it is possible to achieve excitation of Er\(^{3+}\) ions by a non-resonant absorption, allowing for pumping with broadband excitation source, but also increase the (effective) excitation cross-section by approximately 3 orders of magnitude when compared to the resonant excitation \[120\]. However, limitations, such as a relatively small part of Er\(^{3+}\) ions being susceptible to this indirect excitations and loss of optical activity have been reported \[48\], severely hampering the usability of this system.

7.2 Temporal aspects

7.2.1 Microsecond PL dynamics

Investigations of time-resolved (TR) PL in these systems have revealed a lot of information concerning the different excitation, de-excitation and energy transfer processes taking place on different time scales \[58, 121, 122\]. The PL dynamics of Er\(^{3+}\) ions and NCs showed that there is a decay component in the NC-related
7.2. TEMPORAL ASPECTS

Figure 7.1: Schematic illustration of excitation mechanism in a system of Er\(^{3+}\) and Si NCs doped SiO\(_2\). An e-h pair induced in Si NC recombines and energy is transferred to an Er\(^{3+}\) ion in the vicinity, putting it in an excited state. Subsequently Er\(^{3+}\) ion relaxes to 1st excited state (\(^4I_{13/2}\)) and from there it can emit a photon with a wavelength of 1.5 \(\mu\)m.

PL with a characteristic time of \(\tau_{NC1} \approx 1.2\ \mu\)s, which is paralleled with a rise of 1.5 \(\mu\)m emission from Er\(^{3+}\) ions. This is a footprint of the energy transfer process taking place between Si NCs and Er\(^{3+}\) ions. It turned out that an even better agreement between these characteristic times could be found when also the relaxation time from higher excited states of Er\(^{3+}\) is included. The characteristic rise time of 1.5 \(\mu\)m emission is then determined by a two-step process, where energy transfer from Si NCs excites Er\(^{3+}\) into one of the higher excited states and subsequent relaxation takes it to \(^4I_{13/2}\) state, \(\tau_{rise} = \tau_{tr} + \tau_{rel}\) (see Fig. 7.1). F"orster (dipole-dipole) mechanism has been proposed to be responsible for this energy transfer [123]. For longer timescales there are still the “normal” decay dynamics found for Si NCs, due to emission from those NCs that do not transfer energy (\(\tau_{NC2} \approx 10 – 100\ \mu\)s) and for the radiatively decaying Er\(^{3+}\) ions (\(\tau_{Er} \approx 2\ \text{ms}\)).

Next to these time characteristics, there are also mechanisms active on shorter timescales. Typical room temperature 1.5 \(\mu\)m decay shows a time-resolution limited (typically < 10 ns) increase of intensity followed by a fast (< 100 ns) decay [121, 122, 124, 125, 126]. Different mechanisms have been put forward as the physical origin of this process, which are also dependent on sample preparation procedures.

1. For low temperature annealed erbium doped Si-rich SiO\(_2\), it was argued that luminescence centers associated with excess-silicon related defects are responsible for the indirect excitation of Er\(^{3+}\) on nanosecond timescale [126]. In this case there is no fast decay observed.

2. For high temperature annealed samples, it was suggested that fast cooling of hot e-h pairs created in Si NCs is facilitated by an Auger process of
energy transfer to \( \text{Er}^{3+} \) ions, which are then directly excited to the \( ^4I_{13/2} \) state. This is paralleled by a quenching process, where the excited \( \text{Er}^{3+} \) ions relax to the ground state by transferring energy to carriers inside Si NCs. As a result intense Er-related emission appears and quenches within the first microsecond after laser pulse [58].

The \( 2^{nd} \) explanation has been challenged based on observations of a similar fast PL at 1.5 \( \mu \)m in Er-free SiO\(_2\) samples [122, 124, 127]. Therefore it has been postulated that fast PL at 1.5 \( \mu \)m arises from deep trap centers emitting in the visible and IR region [122] or, similarly, from defect centers either in the SiO\(_2\) matrix or at the interface with Si NCs [124, 127]. The purpose of this chapter is to address above mentioned issues and answer two important questions:

1. Is the nanosecond emission at 1.5 \( \mu \)m Er-related?
2. What is the microscopic mechanism responsible for it?

For this goal we have investigated time and temperature dependence of fast emission for different systems containing Si NCs in SiO\(_2\) of which some were Er-doped.

### 7.2.2 Nanosecond PL dynamics

The cooling rate of “hot” carriers inside Si NCs is expected to be dependent on the size of NCs, as phonon bottleneck effect could alter electron-phonon interaction efficiency (see Section 1.3.2). Since the excitation mechanism of \( \text{Er}^{3+} \) ions inferred by intraband transition of confined carriers inside Si NC is in competition with “standard” cooling by phonon emission, it should also be influenced by size changes. The fast PL characteristics of 1.5 \( \mu \)m emission and its possible dependence on NC size would be a fingerprint of this mechanism. For this reason a series of Er-doped SiO\(_2\) co-doped with Si NCs of different sizes has been prepared and studied for their optical response at room temperature (RT) and at 7 K. All samples in this study have been annealed at 1150 or 1200 °C and the average size of NCs, as determined by the relation between PL peak energy and average NC diameter from Ref. [16], was 3.3, 3.8 and 4.7 nm.

Results of PL decay at 1.5 \( \mu \)m for these series can be found in Fig. 7.2. From the left panel we can see at a first glance that the PL decay is quite similar for different sizes of Si NCs. The initial fast peak, occurring with the same temporal structure as the excitation pulse, is followed by a slightly slower decay. From single exponential decay fits of region between 20-200 ns, we get a decay time for all samples of approximately 36 ns, so no differences in fast temporal characteristics are found. This leads to the preliminary conclusion that the initial fast decay is not related to the cooling time of carriers inside NCs, which is not unexpected, since carrier cooling times are predicted to be much shorter than the nanosecond timescale observed here [79]. In the right panel of Fig. 7.2 results are shown for
7.2. TEMPORAL ASPECTS

Figure 7.2: 1.5 µm decay for the first 500 ns after pulsed excitation with excitation wavelength $\lambda_{\text{ex}} = 450 \text{ nm}$. *left panel:* Decay for 3 samples with different size of Si NCs and the same Er$^{3+}$ concentration. *right panel:* Decay for 2 samples with similar Si NC size and different Er$^{3+}$ concentration.

Figure 7.3: Time-resolved spectral dependence of PL for Si NCs doped SiO$_2$ annealed at 1150 °C for sample A (Er-doped) and sample B (Er-free). The results show the normalized PL decay for the first 1000 ns after laser excitation and have been obtained at RT with $\lambda_{\text{ex}} = 450 \text{ nm}$. The broad band for shorter wavelengths originating from Si NCs is observed over the entire time window. The weaker band around 1500 nm observed for sample A for longer times is due to Er$^{3+}$ ions.

samples with two different concentrations of Er$^{3+}$ ions. The larger concentration gives a much more pronounced peak in the first moment of excitation, so during the laser pulse, and after that it decays strongly below the intensity of the lower Er sample (the traces are normalized for longer times). Although the difference in this behavior can have many origins, it offers a strong indication that the fast 1.5 µm emission is somehow related to Er$^{3+}$, and is not only originating from the matrix. Whether this is emission from the Er$^{3+}$ ions or, for example, from defect states introduced by the doping procedure is not determined here.

Additional information about the origin of the emission comes from the spectral
dependence of time resolved emission in the visible and the IR regions in the first $\mu$s after an excitation pulse. 4 different samples have been studied, A and B (both Si4T1150, B co-doped with Er$^{3+}$ with 0.11 at.%) and C and D (both Si64T1200, D co-doped with Er$^{3+}$ with 0.11 at.%), more details of fabrication procedure and composition can be found in section 2.2.1. Results of this study are summarized in Fig. 7.3 for samples A and B and in Fig. 7.4 for samples C and D. For all samples a broad band around 900 nm can be observed, which is related to the emission of Si NCs. With the introduction of Er$^{3+}$ ions i.e. samples A and C, a number of changes can be observed when compared with their Er-free counterparts. There appears a luminescence band around 1.5 $\mu$m that is quite stable in intensity in the 200-1000 ns time window. This band can be related to radiative recombination from the $^4I_{13/2}$ state of Er$^{3+}$, which has a long decay time (typically ms) and is thus not reducing much in the depicted time-frame. Another observation is that with the introduction of Er$^{3+}$ ions the emission of Si NCs is clearly suppressed (not observable for the normalized data), which illustrates the efficient energy transfer from SiNCs to Er$^{3+}$ ions. For the first 200 ns there is a fast decaying broad PL band overlapping with the spectrum around 1.5 $\mu$m, which is particularly clear in Fig. 7.4 for both Er-doped and Er-free samples. The built-up time of this luminescence cannot be resolved and so has to be very fast $\tau < 5$ ns. Other (relatively small) differences between results obtained for the two sets of samples are of lesser significance and can be attributed to variations of sizes and concentration of Si NCs in these materials.

In order to deduce information about the microscopic origin of the fast 1.5 $\mu$m emission and allow for a direct comparison with Ref. [122, 124], the spectral de-
Figure 7.5: Spectral PL intensity integrated over the first 200 ns after laser excitation. The upper panel compares spectra of samples A and B, and the lower panel C and D.

dependence of the PL intensity integrated over the 0-200 ns time window for both sets of samples is shown in Fig. 7.5. The upper panel compares PL signal from Er-doped and Er-free samples annealed at 1150 °C, while the lower panel shows results for the samples annealed at 1200 °C. In both sets the Si NCs-related emission around 900 nm is visible in both samples, while a 1.5 µm emission peak is only seen in samples A and C, i.e. doped with Er³⁺ ions. This peak has features characteristic for emission from the first excited state of Er³⁺ ions in such materials, which indicates that a part of the fast signal observed around 1.5 µm in our materials is Er-related. This behavior is in contrast with results reported in Refs. [122, 124], where no Er-related signal has been found in the first 200 ns.

Now we turn our attention to the broad band observed particularly in samples C and D (Fig. 7.4) at wavelengths longer than 1100 nm, but outside of the range where emission from Er³⁺ could take place. This band has a short decay time constant (τ_{dec} < 100 ns) and therefore its time-integrated intensity is small compared to the other two bands. Similar structures have been observed in the past and were usually identified as recombination at defects [128, 129, 130]. It is likely that the intensity of this band is sample-dependent and that it overlaps with the 1.5 µm Er-related emission. Therefore we have to conclude that there is also a contribution to the fast emission at 1.5 µm, which has a different origin than the intrashell transition of Er³⁺ ions. A natural explanation for the different results
found in this study when compared to other reports can be found in different sample preparation, with the most important distinction being the annealing temperature. In our case high temperature annealing ensured formation of Si NCs, while the lower temperature annealed systems of Refs. [122, 124] contain most likely amorphous nanoparticles. A large difference of corresponding Er$^{3+}$ ions and defect-related emission and their relative intensity can be expected.

7.2.3 PL dynamics for low temperatures

More information about dynamics and their origin can be obtained by going to lower temperatures. This section will discuss results of a study on fast emission of these systems occurring at 1.5 $\mu$m for lower temperatures. Fig. 7.6 shows time-resolved PL intensities detected at 1.5 $\mu$m over a large time window for temperatures in the range of 7-300 K. A few observations are imminent:

- The PL intensity at long times increases when going to lower temperatures. This effect can be seen in time-integrated PL intensity as well, and results from a combination of removal of thermal quenching effects and the narrowing of Er$^{3+}$ PL line, leading to the enhanced collection efficiency.

- The fast decaying component slows down considerably, having a time constant of 36 ns at room temperature and $>1$ $\mu$s at 7 K. In result, observation of the rise of intensity with time constant due to the slow transfer by Förster mechanism $\tau_{\text{rise}}$ (see section 7.2) is obscured at lower temperatures.

- PL intensity of the initial fast component increases approximately 4 times when going from RT to 7 K. This is stronger than the mentioned increase at long times, which is only about 1.8 times.

As explained above, the first effect is well understood, but the other effects require closer inspection in order to make conclusions concerning their origin. PL decay kinetics at 1.5 $\mu$m obtained for different excitation wavelengths are depicted in the left panel of Fig. 7.7. The results are normalized for the initial intensity. While the fast decay kinetics do not change for different excitation photon energies, the slower $\mu$s component shows an increase for shorter wavelengths. The right panel depicts PL decay for an excitation wavelength of 490 nm for different pump fluencies. In this case also fast decay kinetics do not change, but the slow component increases for harder pumping. In Chapter 4 it was shown that emission from Si NCs saturates for larger pump fluencies as strong Auger non-radiative mechanism removes multiple e-h pairs in a single NC and limits in this way the PL intensity. Since the excitation of Er$^{3+}$ ions in this system is mediated by Si NCs, saturation effects can also be expected to limit the energy transfer to these species. In the second column of Table 7.1 the average number of photons absorbed per NC, $\langle \text{NC}^* \rangle$, is determined by $\langle \text{NC}^* \rangle = \sigma_{\text{ex}} \times J_{\text{pump}}$, 
Figure 7.6: PL decay of 1.5 µm emission at temperatures ranging from 7K to room temperature for the first 100 µs after an excitation pulse at 490 nm.

with accompanying ratios in the third column. In the linear regime of excitation power dependence there should be a 1-to-1 relation between this ratio and that of integrated PL intensity (column 4). We see that this is not the case and especially the largest pump fluence shows a large discrepancy with the expected intensity. This effect together with the values of $\langle N_{C^*} \rangle$, indicate that the “slow” Er$^{3+}$ luminescence is saturated for $P_{\text{pump}} = 470 \, \mu$J. The ratios for the fast and the slow component (last column) are taken from the right panel of Fig. 7.7. The “slow” component grows relatively faster, or when we reverse the argument, the “fast” signal has a smaller increase and thus saturates, or quenches, stronger. Similarly, this saturation effect might also explain the differences obtained under pumping with different excitation photon energies (left panel Fig. 7.7). Here the relative intensity of the “slow” component increases for shorter wavelengths, fol-

<table>
<thead>
<tr>
<th>$P_{\text{pump}} (\mu$J)</th>
<th>$\langle N_{C^*} \rangle$</th>
<th>ratio excitation</th>
<th>PL intensity</th>
<th>fast/slow ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>1.5</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>225</td>
<td>4.0</td>
<td>2.7</td>
<td>2.5</td>
<td>0.94</td>
</tr>
<tr>
<td>470</td>
<td>8.3</td>
<td>5.5</td>
<td>3.2</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Table 7.1: Calculated average number of absorbed photons per NC, $\langle N_{C^*} \rangle$, and accompanying ratios for the different pump powers. PL intensity depicts the absolute ratio of integrated PL intensities. The last column indicates the amplitude ratio of the fast and slow component, where the first value is set to unity.
following the trend in absorption cross-section and, for constant pump powers, the increasing excited state population. The above-mentioned difference in characteristics between the two components of the PL decay at 1.5 $\mu$m in this system are difficult to explain by invoking only Er$^{3+}$ based emission. A more detailed study of emission properties for this system is necessary to elucidate its origin.

**Defect band**

Prior work showed that PL spectra of Er-doped SiO$_2$ sensitized with Si NCs at cryogenic temperatures exhibit a broad band that appears around a wavelength of 1.3 $\mu$m [128]. A similar band was also seen in a system where Ge was used instead of Si [129]. In that case it was suggested that a temperature-dependent phonon-assisted Förster-type energy-transfer process from luminescence centers responsible for this band to Er$^{3+}$ ions, was behind the Er excitation. Lowering the temperature resulted in obscuring the Er-related emission by increasing intensity of radiative recombination of the luminescence band which had a comparably long lifetime.

In the materials used in our study we do not observe any PL in the spectral window from 800 to 1600 nm with a lifetime in excess of 10 $\mu$s, except for the Er-related peak with the lifetime $\sim$2 ms. For short timescales however, the broad band arising around 1.3 $\mu$m is very pronounced and overlaps with emission related to $^4I_{13/2} \Rightarrow ^4I_{15/2}$ transitions in the Er$^{3+}$ 4f-manifold. The overlap suggest possibility for a Förster resonant energy transfer from these centers responsible for the broad band, to 1$^\text{st}$ excited state of Er$^{3+}$ ions.

Time-resolved spectra for samples without Er$^{3+}$ doping showed a similar band
7.2. TEMPORAL ASPECTS

situated around 1.3 $\mu$m, which had also strong temperature dependent decay characteristics. Similar radiative transitions have been observed in different materials and were usually identified as recombination at defects [127, 129, 131]. The similarity of this band in very different materials, suggests that the defects are related to a combination of Si and SiO$_2$, and that the high temperature annealing promotes formation of these radiative defects [131].

When PL of Er-doped and non-doped systems of Si NCs in SiO$_2$ matrix are compared it is observed that there is a clear Er-related component in the initial 200 ns after an excitation pulse, both at room temperature and at 7K. A different conclusion was drawn in studies where a lower annealing temperature was used [122, 132], possibly resulting from differences in radiative and non-radiative pathways in these materials.

Two different approaches can be employed to account for the contribution of defect-related emission and to get the “clean” Er-related dynamics. One approach uses PL dynamics at 1.5 $\mu$m from an Er-free sample and which is then subtracted from the PL of an Er-doped sample. A second approach relies on the assumption that the defect-related emission is modified due to the presence of Er$^{3+}$ ions. In this case emission from the defect band close, but not overlapping with Er emission, is used to characterize it and scaled in intensity with the 1.5 $\mu$m emission of the Er-free sample is subtracted from the Er-doped PL dynamics at 1.5 $\mu$m. It is essential that the dynamics for the defect-related emission does not vary for both wavelengths, which was concluded for the Er-free sample. Both methods confirm that there exists a “fast” nanosecond component for the entire 7-300K temperature range, which is originating from Er$^{3+}$ ions. The model proposed in Ref. [121], where interband transitions of carriers in the Si NCs transfer energy to the Er$^{3+}$ ions exciting them directly to the $^4I_{13/2}$ state, followed by fast de-excitation by the reverse process, could account for such a fast feature. If the transition involved does not match the energy conservation requirements, this process must be phonon-assisted, which will manifest itself by a strong temperature dependence of the associated time constants. However, in such a case this process should be dependent on excitation photon energy, which is not observed – Fig. 7.7. Another explanation of the fast Er-related emission involves Er$^{3+}$ ions inside the Si NCs, or trapped at the boundary with the matrix. These are susceptible to an instantaneous excitation directly into the first excited state via absorption of photons with sufficient energy leading to simultaneous excitation of Er$^{3+}$ ion and creation of an $e$-$h$ pair in a NC [121], which is a non-resonant process [133]. These Er$^{3+}$ ions can also induce a donor center, as a result of which they will efficiently non-radiatively de-excite, analogous to what happens in bulk Si:Er [134].

Previous studies have shown that information about the microscopic mechanisms of Er$^{3+}$ luminescence can be obtained by analysis of the temperature dependent
quenching of its intensity [135, 136, 137]. Activation energies determined from fits of PL quenching profiles with an Arrhenius equation are $\sim 60$ meV for the band at 1.5 $\mu$m and approximately 90 meV at 1.4 $\mu$m in the Er-doped sample and correspond to processes responsible for de-excitation of $\text{Er}^{3+}$. We note that in this case the contribution of defect emission at 1.5 $\mu$m emission has been removed before analysis. This is reasonable, as PL quenching in the Er-free sample has an activation energy of $\sim 95$ meV, i.e. very similar as that of the defect-related level in the Er-doped sample. This suggests that different centers are responsible for the thermal quenching of luminescence of different bands, indicating their different origin. An Er-related trap level with ionization energy of $\sim 60$ meV [138, 139] seems to be responsible for excitation of $\text{Er}^{3+}$ ions to the first excited state, with the reverse process de-exciting it to the ground state, whereas a defect-related luminescence band is quenched by a thermally activated process with an energy of $\sim 90$ meV.

On basis of a comparative time-resolved PL study on Er-free and Er-doped materials with high quality crystalline Si NCs at different temperatures, we conclude that there exists an Er-originating fast PL band appearing at a wavelength of 1.5 $\mu$m instantaneously after laser excitation and characterized by a temperature dependent sub-$\mu$s decay time. The occurrence of a PL band in Er-free sample shows very similar characteristics as the 1.5 $\mu$m of $\text{Er}^{3+}$, but in a much larger spectral window. This band is generally assigned to defects in the Si NC/SiO$_2$ interface superimposed on the Er-related emission. Different contributions to the excitation of $\text{Er}^{3+}$ ions have been considered and thermally activated luminescence quenching shows that processes with different activation energies are responsible for de-excitation of emitting centers, whether $\text{Er}^{3+}$ (60 meV) or defects (90 meV).

### 7.3 PL QY considerations for $\text{Er}^{3+}$

The luminescence from $\text{Er}^{3+}$ ions sensitized by Si NCs originates from single dopants, where emission of interest takes mainly place from $^4I_{13/2}$ state. Here we neglect emission from higher excited states, since relatively quick intra-$f$ shell relaxation competes with it, reducing its contribution to below 0.1% of the total number of photons. Effectively this system can then be represented by the two-level model introduced in Section 4.1.3 and a similar mathematical treatment can be applied. The rate equation (Eq. 4.1) then will assume the form:

$$\frac{dN^*_{\text{Er}}}{dt} = \sigma_{\text{Er}} \phi (N_{\text{Er}} - N^*_{\text{Er}}) - \frac{N^*_{\text{Er}}}{\tau_{\text{E}r}},$$

(7.1)

where $N_{\text{Er}}$ is the maximum number of $\text{Er}^{3+}$ ions which can be excited, $N^*_{\text{Er}}$ the number of excited $\text{Er}^{3+}$ ions, $\sigma_{\text{Er}}$ the effective excitation cross section of $\text{Er}^{3+}$ ions, $\phi$ the laser flux and $\tau_{\text{E}r}$ the radiative lifetime of the $^4I_{13/2}$ state. Since the radiative lifetime $\tau_{\text{E}r} \approx 2$ ms is much longer than the laser pulse, we can assume
that no recombination occurs during the laser pulse and at the end of the pulse the number of excited Er$^{3+}$ ions is given by:

$$N_{Er}^* = N_{Er}(1 - e^{-\sigma_{Er} J_{pump}}),$$

(7.2)

where $J_{pump}$ is the number of photons per cm$^2$ per pulse. Following the analysis of Section 4.1.3, we arrive to a similar expression as Eq. 4.8:

$$\chi \mu A S_{abs} \propto \sigma_{Er},$$

(7.3)

where $\chi$ is a parameter depending on experimental factors, $\mu$ the PL efficiency, $A$ the illuminated area and $S_{abs}$ the absorbed fraction of excitation light. As noted in Section 4.2, each emitting species, in this case Er$^3$, can only emit a single photon after an excitation pulse. This notion allows us to use the treatment of (Eqs. 4.12-4.15) and finally arrive at:

$$\eta = \frac{N_{Er} \sigma_{Er}}{A S_{abs}}$$

(7.4)

In this way determination of the ratio of $\sigma_{Er}$ and $S_{abs}$ gives the relative quantum yield of the Er-related PL.

### 7.4 Er$^{3+}$ quantum cutting

Following the excitation model illustrated in Fig. 7.1, a constant QY of the Er-related PL is expected for different excitation photon energies; a single absorbed photon excites an Er$^{3+}$ ion via a Si NC with a certain efficiency, similar as in the case of NCs (Section 4.2).

Fig. 7.8 shows the experimentally determined quantum yield of the Er-related PL. Each data point in this figure represents the ratio of the effective PL excitation cross-section to the fraction of absorbed photons for a particular wavelength of the incoming light. In each case, the PL excitation cross-section was determined from the slope of the plot of PL intensity versus laser pump fluence, $J_{pump}$, in the linear region. In this way, the effective excitation cross-section of Er$^{3+}$ emission at different wavelengths can be compared. The wavelength dependence of the fraction of the incident light that is absorbed by the sample was measured in a separate experiment. The correlation between the number of absorbed and emitted photons expected for the single-photon generation process of Fig. 7.1 is indeed found for the lower range of excitation energies, where the QY is constant. However, a clear enhancement is seen for energies above a certain threshold of $\sim 2.6$ eV (480 nm). For these energies, the efficiency of the energy transfer to Er$^{3+}$ increases indicating that a different excitation mechanism becomes activated. The process is schematically illustrated in Fig 7.8b; the excess energy $\Delta E$ of the “hot” carrier ($\Delta E = h\nu - E_{NC}$, where $h\nu$ and $E_{NC}$ are photon and NC
Figure 7.8: (a) Relative quantum yield of Er-related PL (1.5 μm) as a function of excitation energy. The quantum yield is determined here as the ratio of the effective cross-section of Er PL and the absorbed fraction of incident photons. The error bars reflect the uncertainty in the value of the power of the laser, (10%), expressed as the standard deviation (determined separately). (b) Diagram of the process involved: 1, excitation of the Si NC with a high energy photon; 2, intraband process exciting an Er$^{3+}$ ion, and removing excess energy; 3, erbium-related luminescence. (c) Schematic of the process, showing one photon absorbed by one NC, and two photons emitted by two distinct Er$^{3+}$ ions.
Figure 7.9: Dependence of Er-related PL intensity on the excitation pump pulse fluence $J_{\text{pump}}$, for different excitation wavelengths in the range 450-600 nm. Note that the saturation level is independent of excitation wavelength

bandgap energies, respectively) allows for an Auger process, wherein the carrier undergoes intraband relaxation by transferring the energy to an Er$^{3+}$ ion, and putting it in an excited state. In this case two Er$^{3+}$ ions can be excited upon absorption of a single photon by a NC, with the second excitation resulting from the conventional band-to-band recombination process, as indicated in the figure. The minimum energy necessary for such a “double” process to occur is given by the sum of the excited state of Er$^{3+}$ (0.8 eV) and the silicon NC bandgap ($\sim$1.5 eV), thus $\sim$2.3 eV. Similar as in the case of Si NCs, it is important to note that the saturation level of Er PL intensity is independent of excitation wavelength (see Fig. 7.9) and that the decay kinetics are also the same. A change in lifetime of the luminescence could be camouflaging a possible change in number of emitters, which would undermine the analysis, which was based upon assumption of a fixed maximum amount of optically active Er$^{3+}$ ions. Even more, the change of lifetime could be responsible for a change in quantum yield, since the integrated PL intensity will also change. To check this possibility, measurements of the temporal development of the Er-related PL for two different excitation wavelengths have been performed, for photon energies below and above the threshold. From the results depicted in Fig. 7.10 we conclude that the decay times are identical for both excitation regimes. Therefore, together with the notion that the PL saturation level is the same for the different excitation wavelengths, we can exclude that the observed change in quantum yield could appear due to an alteration of Er$^{3+}$ lifetime.

The additional excitation mechanism possible for above threshold photon energies shown in Fig. 7.8b, requires proximity of the energy receiving species, in this
case $\text{Er}^{3+}$ ions. For the intraband transitions exciting the $\text{Er}^{3+}$ ions it has been shown that mostly higher multipole contributions should be important for the energy transfer [121]. This notion implies that the intraband mechanism is more strongly dependent on the separation between the energy exchanging species, than the interband recombination related energy transfer. Changing the average distance between Si NCs and $\text{Er}^{3+}$ ions would in this case would alter the total efficiency of the excitation process. For larger distances one can expect the “fast” process to have a smaller relative contribution to the total PL signal.

In order to provide further insight into the excitation mechanism, we extend the investigation of PL quantum yield to a material which has similar properties as the above studied system (size of NCs, bandgap, crystalline quality, Er-concentration), but a different average distance between the energy receiving species (Si NCs) and the energy emitting species ($\text{Er}^{3+}$). This is obtained by fabrication of a similar sample with smaller concentration of Si NCs of $[\text{NC}] = 2.1 \times 10^{18} \text{ cm}^{-3}$ as opposed to $[\text{NC}] = 4.1 \times 10^{18} \text{ cm}^{-3}$ of the former one. A simulation based on an analysis of a system of “point” particles whose centers are randomly distributed, originally developed by Hertz [140], of the distance distribution between Si NCs and $\text{Er}^{3+}$ ions in the two samples can be found in Fig. 7.11a.

The spectral dependence of the relative quantum yield of Er PL for both samples is depicted in Fig. 7.11b. We note that both dependences show a constant value for the low photon energy region, characteristic for a single photon generation process. The value of the relative QY is normalized for small photon energies, to
enable direct comparison. It is obvious that the increase in efficiency for larger energies is much more prominent in the sample where the average distance between Si NCs and Er\(^{3+}\) ions is smaller, as was anticipated. This observation does not allow to explain the nature of the underlying mechanism, but it provides direct support for an distance dependent energy transfer process between spatially separated centers.
Chapter 8

P–B co-doped silicon nanocrystals

In a ultimate attempt to bring the photon energy range for carrier multiplication down even more, a study is performed on B and P doped silicon nanocrystals. It is shown that luminescence in this case occurs from donor-acceptor pair recombinations and has a photon energy that is below the bulk silicon bandgap. Determination of photoluminescence quantum yield is complicated in these systems and different solutions on how to circumvent that are presented. Finally, an outlook of the research, presenting a possible road map for future investigations is given.

8.1 Introduction

Electronic states in semiconductors can be described by band theory of solids. For silicon the electronic structure consists in the simplest approximation of the occupied states that form the valence band and empty states the conduction band. The Fermi energy is approximately in the center of the bandgap and at room temperature there are practically no thermally excited carriers in the conduction band. One important reason that silicon is so successful in (micro)electronic technology is that its electrical transport properties can be very well controlled by impurity doping. n-type doping can be obtained by introducing group V elements, which form shallow donor states just below the conduction band. Similarly p-type doping is done by introducing group III elements, giving an acceptor level close to the valence band. The energetic positions of these levels allow for their easy population at room temperature, thereby strongly chaning electronic properties.
CHAPTER 8. P–B CO-DOPED SILICON NANOCRYSTALS

Similar considerations opened a large research field concerning the influence of P and B doping in Si NCs [141, 142, 143]. Since there are only a small number of constituent atoms, already a single dopant strongly affects the optical and electronic properties of a Si NC [144, 145]. In general, the presence of a dopant is disastrous for emission of Si NCs, as the carrier introduced by it will induce a strong Auger interaction with photo-excited carriers. However small concentrations of P-doping were observed to actually increase luminescence intensity, which was attributed to passivation of dangling bonds [146, 147]. The Auger quenching of emission could be avoided in compensated NCs simultaneously doped with n- and p-type impurities. Although effective doping of NCs is generally very difficult, resulting from effects like self-purification [148], statistical distributions of dopants and size dependence of doping efficiency [149], co-doping of B and P in Si NCs has been shown to be favorable, as calculated formation energies are smaller than for undoped or single-doped NCs [145]. Moreover, it was found both theoretically [144], and experimentally [150], that codoping effectively reduces the “optical” bandgap with respect to that of undoped NCs, and that emission shifts to energies below bandgap of bulk Si. The location of the doping centers is very important for the properties of the NCs, however determination hereof is experimentally very difficult. Theoretical modeling [151] shows that boron favors locations around the center of a NC, while phosphorus is preferentially found on surface sites. The latter has also been confirmed experimentally [152] and is possibly related to presence of dangling bonds [146, 147]. These results show the possibility to tune the optical properties of Si NCs by impurity-based engineering.

The ability to change the electronic structure and lower the bandgap can be beneficial for cooperative effects like carrier multiplication for photovoltaic conversion. NCs are widely studied for their ability to generate multiple excitons upon absorption of a single photon (see Chapter 5). The beneficial properties of NCs in terms of their more efficient CM ability are tempered, since their increased bandgap energies limit the part of the solar spectrum that can be converted. Si has a bandgap that is close to the optimum for a single junction solar cell, as determined by the Shockley-Quisser limit [1]. For NCs the bandgap becomes larger and, although it increases the photovoltage, it lowers the photocurrent – even when the effect of CM is taken into account. Detailed calculations show that the maximum power conversion efficiency for a solar cell with optimal CM can be obtained with a bandgap around 0.8 eV [87]. Codoped Si NCs might offer the ability to shift the emission toward this value and, similarly, also bring down the energy threshold for CM.
8.2 Spectra and decay times

Fig. 8.1 shows normalized PL spectra for the sample series M5 (see Section 2.2.1 for specific parameters). The three samples in this series have similar deposition compositions and annealing procedure, but different level of phosphorus and boron doping (no doping, 1.1% or 2.2% doping). The undoped sample shows emission around an energy of 1.42 eV, associated with recombination of quantum confined excitons. The introduction of P and B doping shifts the PL peak intensity to smaller values - see Fig. 8.1. The highest doping level gives a peak of emission around 1.0 eV, and at the same time the integrated PL intensity becomes smaller (not indicated in the figure). This decrease is generally assumed to arise from the inhomogeneity in the distribution of dopants throughout the NCs, where those that are not precisely compensated, i.e., with no equal numbers of P and B dopants, will have a strong Auger quenching of emission [53]. The emission at energies below that of bulk Si bandgap is suggesting that it originates from transitions between donor and acceptor states, influenced also by the actual number of dopants present in a NC.

Further information about this mechanism could possibly be deduced from PL decay kinetics. Fig. 8.2 depicts spectral dependence of decay times from the same series of samples. For the undoped sample, it can be seen that at large photon

![Image of normalized PL spectra](image)

Figure 8.1: Normalized PL spectra of B and P co-doped Si NCs in SiO$_2$ of multilayer series M5, (see Section 2.2.1 for sample parameters), with different doping concentrations. Peaks of PL intensity for different samples are indicated by arrows. The dotted line shows the bulk Si bandgap.
energies there is a relatively short decay time, which increases for smaller ener-
gies. This behavior is typical for emission from quantum confined carriers in the
size dispersed ensemble; smaller photon energies are originating from larger NCs,
where quantum confinement effects are smaller, and quasi-direct (in k-space)
transitions are less probable. It can also be observed that for a fixed emission
energy, doping reduces the lifetime of PL, probably as these dopants also intro-
duce non-radiative recombination pathways. On the small photon energy side,
typically below the bulk Si energy gap of 1.15 eV, the decay times are more or less
constant. This suggests that the mechanism behind this emission is not related to
size distribution of NCs anymore, but purely to the dopants. From the empirical
relation between size and emission energy for undoped Si NCs (see Section
2.3.3) it is possible to estimate the size of NCs from PL peak. We note that this rela-
tion is obtained for samples having a single layer of Si NCs. The multi-layered
samples in this study might have a slightly different relation, but the trend will
be the same. The sizes of series 3 of the samples have been determined from the
PL peak intensity in this way. The PL peak of the 1.1% and 2.2% doped samples
are separately determined and the combined results hereof are shown in Fig.
8.3. While the undoped samples have a strong size dependence of the position of the
emission peak, this is not the case for both doped samples. This insensitivity of
the PL maximum on the NC size is again indicative for a different mechanism
behind their luminescence, and shows that its origin can be explained by donor-
acceptor recombination, as opposed to the confined free excitons in the undoped
samples [153].

Figure 8.2: PL lifetime at different photon energies for multilayer series M5.
8.3 Photoluminescence quantum yield

The previous section showed that P and B doped Si NCs have the properties which are predicted by theory. Emission takes place at energies smaller than the bulk Si bandgap, and the dynamic and structural characteristics hereof strongly suggest that this emission is related to recombination of donor-acceptor pairs. As mentioned in the introductory paragraph, a smaller bandgap than that of bulk Si is desirable for use of carrier multiplication effects in photovoltaics. Emission from these states below the bulk Si bandgap indicates that they might also be involved in CM effect. A study of the photoluminescence quantum yield, similar as in Chapter 5, is needed in order to determine if such an effect occurs, and if the onset threshold is indeed shifted to smaller photon energies.

Due to experimental limitations of the setup used in prior chapters, it was not possible to obtain reliable values of the absolute PL QY for the doped samples in the course of this research project. The infrared emission falls outside the effective range of the silicon charge-coupled device, so use of a different technique and/or detector is imminent. The first, and possibly the simplest, approach is to determine a relative quantum yield for a broad spectral range. This could be done by the same method as that introduced in Section 4.2, where the excitation and absorption cross-sections of the Si NCs and the ratio hereof are determined. An improved determination of the relative PL QY can be obtained with a similar setup as that in Fig. 3.1, where an integrating sphere is used in order to remove
effects that scattering, and differences in optical constants of the material might introduce. In this case, however, it is necessary to complement the setup with a detector capable of capturing emission up to around 1500 nm. A combination of a low cut-off filter and a liquid-nitrogen cooled germanium photo-diode combined with a lock-in amplifier could be readily employed. The photo-diode only detects the intensity of the emitted luminescence of the NCs, and absorption will still be determined in the same way as described in Chapter 5, where the difference in excitation intensity is obtained by comparison with a reference sample. The step toward determination of absolute PL QY will require that luminescence is also spectrally resolved. This can be done by adding a monochromator before the photo-diode, and scan the different wavelengths, but, since this procedure is quite time-consuming, it is preferable to replace the photo-diode by a linear detector. In this way it should be possible to determine the PL QY over a broad wavelength range. The experimental effort in that direction is already going on at the time when this thesis is written.
Chapter 9

Outlook

A fundamental understanding of light-matter interactions in nanocrystal systems is an essential and necessary condition for deployment of their full application potential. The discovery of quantum cutting/carrier multiplication in closely packed ensembles of silicon nanocrystals is an example for the validity of this statement, as the “fundamental knowledge” was clearly insufficient to predict this effect to occur. Fortunately, it was not missed in the experiment and subsequent study produced a wealth of information about fundamental properties of different types of silicon nanostructures, of which a part can be found throughout the past pages. Of course, when the number of answers rise, so does the number of new questions (even more). It is now most important to find out what the opportunities are, and in which direction to go from here?

The optical quantum cutting effect with silicon nanocrystal has been shown to occur in many systems where the mutual distances are small. It takes place not only between Si NCs. Also Er$^{3+}$ ions can serve as a receptor of the down-sized energy quanta. The high internal and also external efficiency of the process has been demonstrated explicitly, and the possibility to tune effective range to smaller photon energies by introducing dopants opens new possibilities.

For application of quantum cutting with Si NCs in photovoltaics there are still some important hurdles that need to be overcome. In a down-conversion scheme, where high energy photons of the spectrum are divided in multiple smaller photons, it is imminent that the absolute efficiency of PL is increased to enable quantum yields above 100%. Optimized growth schemes and surface passivations need to be developed to get high optical activity and remove problems that are inherent of ensembles of nanoparticles.

Decreasing the effective energies of Si NCs by introduction of dopants could lower the threshold for QC/CM and, in this way, enable its effectiveness over a broader range of the solar spectrum. Here a pitfall is the statistical nature of the dopant
distribution throughout the nanocrystals, as not fully compensated nanocrystals will act as non-radiative recombination centers, and a controllable way of introducing the dopants needs to be developed. This is possibly not too far away [154]. Finally, there is the possibility of extracting carriers directly from the NCs, which could circumvent the necessity of high optical activity. Generation of multiple carriers has been achieved experimentally [101], but direct extraction not yet. Non-conductive matrixes are strongly limiting this. Therefore specially tailored matrices for nanocrystals and/or concepts like mini-band formation to promote carrier transport could be explored. A lot of progress has been made already on the study of photovoltaic effect in some other inorganic nanocrystals, and demonstration of almost 6% efficient quantum-dot based solar cell shows that its application is no longer just a scientific peculiarity [155].
Appendix A

Validation of experimental procedure

A.1 Luminescence standard

The experimental scheme to determine absolute QY of PL is generally considered to yield more reliable results than the often used comparative method, where relative QY of PL is calibrated against a “standard”, since it circumvents occurrence of artifacts introduced by scattering and spectral differences in refractive indices. The investigated samples were independently measured in two different laboratories (WZI and ChU), with three distinct excitation sources: a pulsed tunable OPO laser system, a Xenon lamp, and a set of LEDs. In every measurement the samples were excited in low-flux regime, with the average number of absorbed photons per NC being well below 0.1, so that multiphoton absorption by a single NC was excluded. Every setup was calibrated for its spectral response with deuterium- and tungsten-based light sources. The validity of the used method and performance of the systems was tested with standard fluorescence sample of Rhodamine 6G in ethanol, which has an external QY of 0.94 [156]. The results of these tests can be seen in Fig. A.1 for the OPO and LED pumped systems, where the corrected differential spectra are shown. In both cases the QY is given by the ratio of the area of PL (right side) and that of the excitation light (left side). Results for both systems show good agreement with the literature value, a maximum relative error for QY of ~5% has been established.
APPENDIX A. VALIDATION OF EXPERIMENTAL PROCEDURE

A.2 PL QY determined by comparative method

The principle of this method is to find the ratio between the number of emitted photons and number of absorbed photons which can be converted to an absolute QY using a measurement of a well known emission standard under identical conditions. In these experiments the properties of po-Si powders dispersed in ethanol and Rhodamine 6G in ethanol were compared. PL spectra (excitation and emission) were acquired using a fluorescence spectrometer Horiba Jobin-Yvon Fluoromax 3 and Fluorolog 3 in a right angle configuration, where the samples were contained in 1×1 cm quartz cuvettes. Absorption spectra were measured with a double beam spectrometer Specord 250 using a clean solvent as a reference sample. In order to correctly account for differences in the spectral shape between po-Si and Rhodamine 6G, the PLE spectra were not measured directly. Instead, the measured luminescence spectra were corrected and integrated for each excitation wavelength. The final equation for calculation of the relative quantum yield has the form:

$$\eta(\lambda_{ex}) = \text{Const.} \sum_{n=1,...,k} \frac{I_R^n(\lambda_{em})C_R(\lambda_{em})n^2(\lambda_{em})e^{-\alpha_{S+A}d_2}\lambda_{em}}{I_S^n(\lambda_{ex})C_S(\lambda_{ex})e^{-\alpha_{S+A}(\lambda_{ex})d_1}[1 - e^{-\alpha_A(\lambda_{ex})d_A}]\lambda_{ex}},$$

(A.1)

where the relative quantum yield for each spectral step is calculated using steps equal to the spectral bandwidth set by the multichannel detector, see Fig. A.2. In Eq. (A.1) the labels are:

- \(\eta\) ... quantum yield [unit]
- \(\lambda_{ex}, \lambda_{em}\) ... wavelength of excitation and emission [nm]
- \(I_R(\lambda_{ex}), I_S(\lambda_{em})\) ... signals at detectors R and S [mV] resp. [counts]

Figure A.1: Test experiment performed on Rhodamine 6G suspended in ethanol on system with OPO excitation (left) and LED excitation (right).
A.2. PL QY DETERMINED BY COMPARATIVE METHOD

- \( C_R(\lambda_{ex}), C_S(\lambda_{em}) \) ... spectral response correction for signals R and S \([\text{W/m}^2/\text{nm}/\text{mV}]\) resp. \([\text{W/m}^2/\text{nm}/\text{counts}]\)
- \( \alpha_{S+A}(\lambda), \alpha_A(\lambda) \) ... absorption coefficient, including losses by scattering, or only absorption \([\text{cm}^{-1}]\)
- \( n(\lambda) \) ... relative refractive index of sample (for low concentration dispersed NCs or diluted dye this is given by the refraction index of solvent) [unit]
- \( d_1, d_2, d_A \) ... distances between the input cuvette edge and the edge of detected volume, between center of detected volume and the output cuvette edge, and the length of detected volume [cm] (See Fig. A.2)

The relative QY of a standard sample (R6G ethanol solution) must be measured under identical conditions and calculated using the same equation. The R6G absolute quantum yield was considered to be 94 % in ethanol under 488 nm excitation [156]. The absolute external quantum yield of investigated po-Si suspension is obtained by dividing its relative QY by the relative QY of R6G and by 0.94. The summary of the experimental results is given in Fig. A.3.

Figure A.2: Illustration of the experimental conditions under which fluorescence spectra were obtained. (a) Schematics of the experiment indicating the relevant distances for sample cuvette and detector position. (b) Indication of the k-steps of the detection spectrometer slit over the luminescence spectrum. The bandwidth is equal to the step length.
Figure A.3: **Top panel:** Corrected PL spectra of the po-Si sample for different excitation wavelengths indicated on the left-hand side. The PL band around 680 nm dominates, while there is a negligible contribution from blue and ultraviolet regions. The red dots indicate the integrated PL signal as function of excitation photon energy and the dashed blue line indicates the absorption spectrum corrected for scattering. **Bottom panel:** Comparison of the spectral dependence of the absolute QY of the po-Si sample measured using the integrating sphere and by calibration of relative PL QY to that of Rhodamine 6G. Qualitatively there is a good agreement of absolute external QY.
Bibliography


Summary

This thesis presents the PhD promotion research based on the project “photon cutting with Si nanocrystals for smart photovoltaics” carried out at the van der Waals–Zeeman Institute at the University of Amsterdam in the period 2008-2012. It comprises an elaborate study of light-matter interactions in silicon-based nanostructured materials with the aim to develop new concepts and materials that could increase the efficiency of photovoltaic conversion.

The first chapter starts by recalling the importance of silicon in modern society, with the current available state-of-the-art micro-electronic technology being primarily based on this element. Physical limitations of the bulk material for optical applications are presented, and possible solutions that could improve these are discussed. The effect of two promising techniques – the use of nanostructured silicon, and rare-earth doping – have been elaborately studied throughout this research. Next, effects that are emerging in nanostructured materials, with focus on silicon, and how these change the optical properties, as well as carrier dynamics, are described. In the last paragraph there is a short description concerning the establishment and structure of this thesis.

In Chapter 2, details on the employed instrumentation and experimental techniques are discussed. Firstly, the various instruments used for optical spectroscopy are elaborated upon. Secondly, details about the sputtering technique used for sample preparation are given and, thirdly, characterization of the samples by different techniques, as well as simulations of material properties, are discussed.

The quantum yield of photoluminescence is an important parameter of the studied optically active materials. Chapter 3 describes the exact terminology which is employed, followed by the experimental details that have been considered and the conditions necessary for a reliable determination of this parameter. Furthermore, the setup is introduced together with the method used for the determination of the absolute photoluminescence quantum yield. Different origins of error in this determination procedure are considered, and their contributions are estimated. Finally the procedure for calibration, and optimization hereof, is discussed.
Chapter 4 presents a photoluminescence excitation study of silicon nanocrystals embedded in a SiO$_2$ matrix. It is shown that upon short-pulsed excitation, the time-integrated photoluminescence saturates at a level, independent of excitation wavelength – by which the excitation cross-section are highly influenced – and number of generated electron-hole pairs per nanocrystal. It is explicitly shown that saturation is achieved when every nanocrystal has absorbed at least one photon. This sets a natural limit for photoluminescence intensity from an ensemble of silicon nanocrystals excited by a laser pulse with a duration much shorter than the radiative lifetime. Next, a study of the relative quantum yield of photoluminescence for different excitation wavelengths is shown. From this it is concluded that for excitation photon energies exceeding a certain threshold, there arises a additional excitation mechanism increasing the overall excitation efficiency. This is explained in terms of redistribution of the absorbed photon energy between multiple adjacent proximal nanocrystals, generating spatially separated electron-hole pairs. Effectively, this mechanism cuts the energy of the incoming photon. This effect resembles the multiple exciton generation process, where multiple electron-hole pairs are generated in one nanocrystal upon absorption of a single photon. Different physical mechanisms are discussed that might underly the cutting process, as well as the beneficial properties for possible applications.

In Chapter 5 more detailed investigations of the carrier multiplication effect in closely spaced silicon nanocrystals were performed by measuring the absolute quantum yield of photoluminescence. A typical step-like increase in quantum yield for larger photon energies that is characteristic for carrier multiplication is observed in two different types of nanocrystal systems, produced either by sputtering (bottom-up) or made from porous silicon (top down). Modeling suggests that the carrier multiplication is occurring with high efficiency and close to the energy conservation limit. It is also shown that the efficiency decreases upon nanocrystal separation, completely vanishing in a system of free-standing nanocrystals.

Chapter 6 describes a study of the photoluminescence spectra for ensembles of silicon nanocrystals and their evolution for different excitation intensities. Simulations show that the different excitation conditions affect the spectral structure, resulting from a combination of a size-dependent absorption cross-section and the saturation effect shown to occur in the previous Chapter. For larger optical densities there will be a large gradient in excitation conditions dependent on the position of the nanocrystals relative to the surface of light incidence. The influence this effect has on the excited state distributions and consequences for the experimental results are discussed.

Chapter 7 discusses the system of erbium and silicon nanocrystals doped in SiO$_2$. In such structures, silicon nanocrystals can function as efficient broadband sensitizers of erbium luminescence. Different temporal aspects of luminescence bands
associated with silicon nanocrystals and Er$^{3+}$ ions reveal energy exchange between the two species. Furthermore, a temperature-dependent study of the luminescence characteristics shows the occurrence of a defect band, which partly overlaps with erbium emission, complicating the interpretation of photoluminescence characteristics. With this knowledge we could show that thermally activated luminescence quenching processes with different activation energies are responsible for de-excitation of emitting centers, either Er$^{3+}$ (60 meV) or defects (90 meV). Similarly as for silicon nanocrystals, the quantum yield of erbium-related luminescence shows an increase at photon energies above a certain threshold, with a threshold value being lower than for a system with exclusively silicon nanocrystals. This is interpreted as a quantum cutting process, where the down-converted energy is in this case received by Er$^{3+}$ ions.

In a ultimate attempt to reduce the photon energy range for carrier multiplication, a study is performed on B and P doped silicon nanocrystals, which is presented in Chapter 8. It is shown that luminescence in these systems occurs from donor-acceptor recombinations and has a photon energy that is below the bulk silicon bandgap energy. Determination of photoluminescence quantum yield is complicated in these systems and different solutions to circumvent that are presented.

Finally, an outlook of the research, presenting a possible road map for the future, is given in Chapter 9.
Samenvatting

In dit proefschrift wordt het onderzoek uit het project “photon cutting with Si nanocrystals for smart photovoltaics” gepresenteerd. Dit is uitgevoerd in de periode 2008-2012 aan het Van der Waals–Zeeman Instituut aan de Universiteit van Amsterdam. Het omvat een uitgebreide studie van de interactie tussen licht en silicium nanostructuren, waarbij het ontwikkelen van nieuwe concepten en materialen die het rendement van zonnecellen kunnen verhogen de belangrijkste doelen zijn.

In het eerste hoofdstuk wordt het belang van silicium in de huidige maatschappij belicht, waarin het grootste gedeelte van de hoogwaardige micro-elektronische technologie gebaseerd is op dit element. De fysieke beperkingen van bulk silicium voor optische toepassingen worden besproken samen met mogelijke oplossingen om deze te verbeteren. Het effect van twee veelbelovende technieken, het gebruik van nanogestructureerd silicium en doping met zeldzame-aard ionen, is uitvoerig bestudeerd in dit onderzoek. Vervolgens worden effecten die optreden in nanogestructureerde materialen besproken, waarbij de nadruk wordt gelegd op silicium, en hoe deze de optische eigenschappen veranderen. Tenslotte wordt in de laatste paragraaf kort de structuur en totstandkoming van dit proefschrift beschreven.

Details omtrent de gebruikte apparatuur en experimentele technieken worden besproken in Hoofdstuk 2. Als eerste wordt er ingegaan op de instrumentatie die gebruikt is voor de optische spectroscopie. Vervolgens worden details besproken van de sputtertechniek die gebruikt is voor het fabriceren van samples. Tenslotte wordt er ingegaan op de karakterisatie van de samples waarbij gebruik is gemaakt van verschillende technieken, alsmede simulaties van de materiaaleigenschappen. De kwantumefficiëntie van fotoluminiscentie is een belangrijke parameter van de onderzochte optische materialen. Hoofdstuk 3 beschrijft de exacte terminologie die hierbij gebruikt wordt, en ook de belangrijkste voorwaarden die nodig zijn voor een betrouwbare bepaling van deze grootheid. De opstelling die hiervoor gebruikt wordt en verschillende bronnen van fouten in de bepaling hiervan worden vervolgens besproken. Uiteindelijk wordt de procedure van de kalibratie en
SAMENVATTING

de optimalisatie hiervan geïntroduceerd.

In Hoofdstuk 4 wordt er een fotoluminescentie excitatie studie gepresenteerd van silicium nanokristallen in een SiO$_2$ matrix. Hierin wordt gedemonstreerd dat, voor korte excitatiepulsen, de geïntegreerde intensiteit van de luminescentie saturert op een niveau dat onafhankelijk is van de excitatie-golflengte en het aantal gegenereerde elektron-gat paren per nanokristal. Deze verzadiging wordt bereikt wanneer alle nanokristallen minstens een foton hebben geabsorbeerd, waardoor er dus een natuurlijke limiet is aan de maximale luminescentie-intensiteit van deze nanokristallen. Vervolgens wordt de relatieve kwantumefficiëntie van fotoluminescentie bepaald als functie van excitatie-golflengte. Hieruit wordt geconcludeerd dat er een extra excitatie-mechanisme mogelijk is voor excitatie-foton-energieën boven een bepaalde drempelwaarde, waardoor de totale efficiëntie verhoogt. Dit wordt verklaard door een herverdeling van de geabsorbeerde energie over verschillende naburige, gescheiden, nanokristallen. Hierbij wordt de inkomende foton energie effectief “gesplitst”, gelijk aan een zogenaamd ladingervermenigvuldigings-effect. Vervolgens worden er verschillende fysische mechanismen die verantwoordelijk zouden kunnen zijn voor dit splitsen besproken. Tenslotte worden de gunstige eigenschappen hiervan voor mogelijke toepassingen genoemd.

Het bovengenoemde ladingervermenigvuldigings-effect dat optreed in de silicium nanokristallen wordt in meer detail bestudeerd in Hoofdstuk 5 door middel van metingen van de absolute kwantumefficiëntie. Een typische stappsgewijze toename van deze efficiëntie wordt in twee verschillende systemen geobserveerd; de ene geproduceerd door sputteren (bottom-up) en de ander van poreus silicium (top-down). Door middel van modelering wordt er aangetoond dat de ladingervermenigvuldiging met hoge efficiëntie plaats vindt, dicht bij de energetische limiet. Tevens blijkt dat de efficiëntie van het effect omlaag gaat wanneer de nanokristallen zich verder uit elkaar bevinden, waarbij het volledig verdwijnt in een systeem van vrijstaande nanokristallen.

De invloed van excitatie condities op de fotoluminescentie spectra van ensembles silicium nanokristallen en de invloed van excitatie-intensiteit wordt beschreven in Hoofdstuk 6. Simulaties laten zien hoe het emissiespectrum verandert als gevolg van een combinatie van een golflengte-afhankelijke absorptiedoorsnede en het verzadigingseffect dat genoemd d in het voorgaande hoofdstuk. Voor hoge optische dichtheden is er een groot verschil in excitatie-omstandigheden die afhankelijk is van de positie van de nanokristallen ten opzichte van oppervlak waar het licht invalt. De invloed die dit effect heeft op distributies van geëxciteerde nanokristallen en gevolgen voor experimentele resultaten worden verder besproken.

In Hoofdstuk 7 wordt het systeem bestaande uit erbium atomen en silicium nanokristallen in een SiO$_2$ matrix besproken. In deze structuren fungeren de
silicium nanokristallen als efficiënte breedband sensibilisatoren van erbium luminescentie. Verschillende tijdsafhankelijke aspecten van luminescentie banden die geobserveerd worden in deze materialen laten zien dat er een energie overdracht is van de nanokristallen naar de Er$^{3+}$ionen. Verder onthult een temperatuursafhankelijke studie het optreden van een additionele luminescentieband die gedeeltelijk overlap heeft met de emissie van Er$^{3+}$. Deze emmisieband wordt geassocieerd met defecten en compliceert de interpretatie van fotoluminescentie eigenschappen. We laten zien dat processen met verschillende verschillende activatie-energieën verantwoordelijk zijn voor thermische geactiveerde vermindering van luminescentie-intensiteit. Deze worden gerelateerd aan Er$^{3+}$(60 meV) en defecten (90 meV). Net zoals bij de silicium nanokristallen vindt er in kwantum efficiëntie van de Er$^{3+}$ionen in deze systemen een toename plaats voor foton energie groter dan een bepaalde drempelwaarde, welke lager is dan in het geval van alleen nanokristallen. Dit wordt geïnterpreteerd als een kwantumsplitsingproces, waarbij de Er$^{3+}$ionen de ontvanger zijn van de omlaag geconverteerde energie.

In een ultieme poging om het bereik van fotonenergieën voor ladingsvermenigvuldiging met behulp van silicium nanokristallen omlaag te brengen is er onderzoek gedaan aan silicium nanokristallen die gedoteerd zijn met boron en fosfor atomen. De resultaten hiervan zijn beschreven in Hoofdstuk 8. Luminescentie in deze systemen treedt op door middel van donor-acceptor recombinaties, waarbij de fotonenergie onder die van bulk silicium ligt. Het bepalen van de kwantum efficiëntie van fotoluminescentie in deze materialen is erg ingewikkeld en verschillende oplossingen om deze te omzeilen worden gepresenteerd. Tot slot wordt er in Hoofdstuk 9 een mogelijke route voor de toekomst van dit onderzoek gepresenteerd.
Scientific resumé

Grants and awards

- “Personal” Toptalent Grant “Photon cutting with silicon nanocrystals for smart photovoltaics” (€180.000,-) The Netherlands Organisation for Scientific Research (NWO).

- EMRS/Elsevier Graduate Student Award; awarded for the best contribution to the E-MRS Spring Meeting 2008.


Publications

Most important papers (in order of author’s choice)


• “Fast dynamics of 1.5 \( \mu \text{m} \) photoluminescence in Er-doped SiO\(_2\) sensitized with Si nanocrystals” D. Timmerman, S. Saeed and T. Gregorkiewicz, *Optical Materials* **33**, 1091-1093 (2011).

• “Using Si and Si nanocrystals for the 1.5 \( \mu \text{m} \) emission form Er\(^{3+}\) ions” D. Timmerman, S. Saeed and T. Gregorkiewicz, (accepted for publication in Physica Status Solidi C)

• “On the powerdependent spectral shift of photoluminescence from ensembles of silicon nanocrystals” D. Timmerman and T. Gregorkiewicz, (under submission)

• “Tuning the bandgap of Si NCs: the effect of B and P co-doping on luminescence” D. Timmerman, A. Akkerman and T. Gregorkiewicz, (under submission)

Other papers

• “Dynamics and microscopic origin of fast 1.5 \( \mu \text{m} \) emission in Er-doped SiO\(_2\) sensitized with Si nanocrystals” S. Saeed, D. Timmerman and T. Gregorkiewicz, *Phys. Rev. B* **83**, 155323 (2011).


Popular


Oral presentations

International meetings

- Invited “Radiative recombination from carriers generated by carrier multiplication generation in silicon nanocrystals” EMRS Fall Meeting, Warsaw, Poland, 09/2011
- “Tuning the bandgap of Si NCs: the effect of B and P co-doping on luminescence” EMRS, Strasbourg, France, 05/2012
- “General character of long living carriers created by efficient multiple exciton generation in silicon nanocrystals” MRS, San Francisco, USA, 04/2011
- “Increasing quantum efficiency from multiexciton generation in Si nanocrystals” EMRS, Strasbourg, France, 05/2010
- “Saturation of luminescence from Si nanocrystals embedded in SiO$_2$” MRS, Boston, USA, 12/2009
- “On fast and slow PL from Er ions sensitized with Si nanocrystals” IBedM, Tossa de Mar, Spain, 10/2009
- “Efficiency limits of photoluminescence from silicon nanocrystals” SIBET 2009, Manchester, United Kingdom, 06/2009
- “Space-separated multiexciton generation in Si nanocrystals” EMRS, Strasbourg, France, 05/2008
- “Energy threshold in excitation of erbium by Si-nanocrystals” EMRS, Strasbourg, France, 05/2007

National meetings

- “Essential enhancement of carrier multiplication in Si nanocrystals” Physics@FOM, Veldhoven, The Netherlands, 01/2011
- “Space-separated quantum cutting with Si nanocrystals” Physics@FOM, Veldhoven, The Netherlands, 01/2008
• **Invited** “Absorption and generation of light with silicon nanocrystals in SiO$_2$” *Physics in Amsterdam, Sciencepark Amsterdam, The Netherlands, 04/2008*
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