Different nanocrystal systems for carrier multiplication
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Chapter 3

Photoluminescence quantum yield of silicon nanocrystals

We investigate the PL QY for co-sputtered solid state dispersions of Si nanocrystals in SiO$_2$ with different size and density, and conclude that the absolute value of the PL QY shows a varied dependence on the excitation energy. Physical mechanisms influencing the PL QY at different excitation energy ranges are considered. Based on the experimental evidence, we propose a generalized description of the excitation dependence of PL QY of Si nanocrystals in SiO$_2$, and conclude on the important role of impact excitation by hot carriers and parasitic absorption at high and low excitation energy ranges, respectively.

3.1 Introduction

Silicon nanocrystals (Si NCs) combine attractive properties of bulk silicon with the enhanced optical activity. This makes them promising for potential applications in optoelectronics, photonics and PV [76]. For these purposes, ensembles of Si NCs are considered and their high PL QY is an essential parameter for photon emission and conversion applications. Consequently, improvement of the PL QY has become a topic of intense research. Optical properties of Si NCs are influenced by a combination of QC and the surface condition, and therefore depend on the NC size [77]. Indeed, the PL energy, absorption cross-section as well as radiative and nonradiative recombination rates, vary strongly with the NC diameter [16] and the optimal Si NC size, with the highest PL QY upon a particular excitation energy, has recently been established for colloidal Si NCs [78] and their solid state dispersions in SiO$_2$ [79]. In general, the optical properties of solid-state dispersions of Si NCs are determined by those of individual NCs and by cooperative processes. These include an energy transfer and exciton diffusion between Si NCs of different characteristics (bright and dark NCs) [80, 81, 23], MEG by hot carriers [82], sharing of excitation energy between proximal NCs [72, 83, 84], and energy exchange with defects [16, 85], among others. The strength of the cooperative processes and their effect on the optical properties of a NC ensemble depend on the characteristics of the individual NCs themselves as well as on the ensemble properties, such as NC density and proximity [86], confining potential of the embedding matrix [87] and...
3.2 Exploratory study: the role of the excess silicon concentration

In preparation of Si NCs by the thermal annealing of SiO$_x$ layers of sub-stoichiometric SiO$_2$, the amount of excess silicon concentration plays a very important role. Therefore it can be expected that this parameter will have essential influence on the optical properties of Si NC structures, and specially on the PL QY - its absolute value and excitation dependence. This hypothesis has been tested in an exploratory study.

3.2.1 Samples

Two multilayer samples, prepared from substoichiometric silicon oxide layers by annealing at 1150 °C, were used to investigate the influence of Si concentration. Significant reduction of PL QY and a very specific change of its excitation energy dependence upon variation of silicon excess are concluded from the experimental data. For this experiment, 2 multilayer samples were produced by the radio-frequency cosputtering method. All the details of this method and the setup and method for the relevant measurements are shown in section 3.3. The two samples were prepared with 10 % and 30 % silicon excess concentration.

3.2.2 Results and discussion

The left panel of figure 3.1 shows the normalized PL spectra of the two samples upon excitation energy of 3.1 eV. With 10% of excess Si, a part of the PL spectrum is in the VIS range, with the peak at around 1.56 eV (the purple curve). For the sample with the three times higher Si excess (the dark cyan curve), a clear redshift of the PL spectrum can be seen clearly, implying larger sizes of the Si NCs. From

its quality, etc. [81]. The cooperative processes typically involve an energy barrier for their activation, and therefore will change with the excitation energy. On the other hand, it is well known that the Kasha-Vavilov rule [88], which states that the PL QY is independent of the excitation energy, is frequently violated for colloidal semiconductor NCs [89, 90], since carriers photo-generated higher in the conduction/valence bands experience an increased probability of capturing at defect states and/or escape to the outside of a NC, leading to its ionization [83] and a temporal loss of optical activity. In result, the PL QY of NCs decreases typically at short pump wavelengths.

In this study, we investigate the PL QY for Si NC layers and find that it varies strongly in different samples. We investigate and discuss possible physical mechanisms influencing the PL QY at different excitation energies and conclude on an important role of impact excitation and parasitic absorption.
the PL spectra, the average diameters of Si NCs in both samples are determined as 2.7 nm and 5.0 nm for 10\% and 30\% Si excess, respectively [91]. The red spectral shift observed in the left panel of figure 3.1 for the sample with the larger Si excess is in agreement with previous reports [22, 92]. As can be inferred from the PL

![Figure 3.1: Left: normalized PL spectra at the peak of the two samples upon excitation of 3.1 eV, the redshift can be seen as result of extra silicon excess; this implies that the extra amount of Si leads to formation of larger Si NCs (2.7 nm and 5.0 nm, for 10 \% and 30 \% Si excess, respectively) with a smaller bandgap. Right: relative absorption (dashed curves) and PL QY (markers) for the two samples, the larger Si excess leads to an increase of absorption and degradation of PL QY. Also the excitation dependence of PL QY changes dramatically when the Si excess is tripled. The large uncertainty of PL QY values is due to statistical and systematic errors [75], and to fluctuation of the excitation intensity. The error bars of PL QY for the sample with the higher Si excess are almost invisible in this scale, whereas they are large for the lower Si excess; this is due to the large difference of the optical densities of both samples.]

spectra in the left panel of figure 3.1, the higher Si excess results in production of larger Si NCs, as indeed can be expected. The most important point of our findings, on which we focus, is that the excess silicon does not only change the value of the PL QY but also its spectral dependence, see the right panel of figure 3.1. With
increasing the excitation energy, PL QY rises initially with a similar rate for both investigated samples until 2.2 - 2.75 eV, and then strongly diverges depending on the Si excess. In particular, the PL QY at the highest excitation energy degrades nearly threefold as a consequence of the higher Si excess. In order to explain this behavior, we consider the following processes:

- We discuss first the reasons for the growth of PL QY. The relative contributions of SiNCs with different sizes to the total absorption can be estimated by the slopes of the size dependent absorption cross sections, see figure 3 in reference [93]. As can be directly concluded, at lower excitation energies, below approximately 2.7 eV, the contribution of small NCs to the total PL is minor, but increases quickly as the excitation energy grows above this value. In result, the relative PL contribution of smaller SiNCs, which usually have higher emission efficiency [16], gradually rises; this might lead to the initial enhancement of the total PL QY. For excitation above approximately 3 eV, the absorption cross section of SiNCs becomes practically size-independent, and the relative contributions of different sizes remain identical. Another possibility to account for the initial increase of PL QY in the low excitation range would be presence of parasitic absorption channels, e.g. at defect-related levels in the bandgap, which does not contribute to the excitonic emission. The relative contribution of the effect could be dominant at low excitation energies, and gradually diminish at the higher energies, as the core absorption by the NCs themselves increases. Any further increase of PL QY in that range is most directly explained by the SSQC process, whose rate is strongly increasing at higher excitation energies.[82] - see section 3.3 for the detailed discussion.

- We mention the general reasons for reduction of PL QY which commonly appear as the excitation energy is increased. We note the process of exciton diffusion, which transfers the energy from smaller to larger NCs, whose PL QY is lower and the probability of being dark (not emitting) [80] is higher. This could lower the overall PL QY in the high energy range. In addition, PL efficiency at high excitation energy typically suffers from the enhanced possibilities for trapping of hot carriers at defects.

- The final PL QY will be influenced by the above mentioned processes which operate in parallel. We conclude that for the lower Si excess sample, with smaller Si NC sizes, the detrimental processes are not efficient and the SSQC dominates. In result, PL QY grows sharply and increases up to 15 times over the investigated excitation energy range. In contrast, with the higher Si excess, the larger SiNCs clearly promote the quenching processes, hampering any increase of PL QY at higher excitation energy. We can further speculate that for this sample also the SSQC process might be less efficient, due to, e.g.,
larger separation between bigger NCs and their generally lower PL QY. From the experimentally obtained data we conclude that for the sample with 30 % Si excess the processes increasing and degrading PL QY apparently become comparable in magnitude above the excitation energy of 3 eV, and PL QY stabilizes. Further investigations elucidating the effects of different sample parameters on excitation dependence of PL QY in more detail are described in the next section.

3.3 Investigation of excitation energy dependence of photoluminescence quantum yield in the Si nanocrystal layers

3.3.1 Sample preparation

The samples used in this study were produced by a co-sputtering method in the form of multilayer structures (ML), featuring multiple stacks (up to 100) of 3.5 nm thin active layers of Si NCs separated by SiO$_2$ barriers. In this process, two sputtering guns, with Si and SiO$_2$ targets, are used. By operating both guns simultaneously, a Si-rich substoichiometric SiO$_x$ active layer can be grown, while solely the gun with silicon dioxide is applied to develop a barrier layer of pure SiO$_2$. The atomic composition of the active layer can be tuned by adjusting the power of the guns, and the layer thickness is controlled by the exposure time. For the samples investigated in this study, the silicon excess of 15%, 25% and 30% was used in the active layer. The barrier thickness between two adjacent active layers was set at 5 nm to avoid exciton diffusion between these layers [94]. Extensive past research [95, 96] has shown that, in contrast to thick homogeneous layers of Si NCs in SiO$_2$, ML structures allow for a better size control and therefore yield ensembles with a more narrow size distribution.

The sputtered structures were subsequently annealed in N$_2$ ambient at 1150 °C, 1200 °C and 1250 °C to separate Si and SiO$_2$ and to create the Si NCs. As has been concluded, generally a higher Si excess and a higher annealing temperature result in formation of larger NCs, the latter being related to an increasing diffusion coefficient [97, 27]. The particular values of excess silicon concentration and annealing temperatures were selected to produce Si NCs of good crystalline quality and emissivity. In total 9 samples were prepared by a combination of 3 levels of Si excess and 3 annealing temperatures. Due to different initial Si excess and annealing temperatures, the Si/SiO$_2$ segregation process proceeds differently, resulting in a variety of size distributions of Si NCs in individual structures which are typically characterized by a log-normal size distribution [98]. The relation between the size
Figure 3.2: PL spectra of the samples upon an excitation energy of 3.1 eV. The shape of PL spectra follows the log-normal NC size distribution.

Table 3.1: Parameters of 9 ML samples prepared with different Si excess and annealing temperature. The average NC diameters and forthcoming NC densities are estimated from their PL spectra and the amount of excess Si. The errors bars of NC diameters are calculated based on the supporting information of previous research [79]. The last column shows the peak position of the ensemble PL spectrum.
3.3. Investigation of excitation energy dependence of photoluminescence quantum yield in the Si nanocrystal layers

NC size in an ensemble and its maximum of the PL spectrum has been established [92]. Here we have used this relation to determine the average NC size within the produced samples. While this structural characterization of the NCs is indirect and not as accurate as, e.g., by (HR) TEM measurements, it is nevertheless based on extensive previous reports [22, 99, 100] of this kind and sufficient for the purpose of this study which aims at investigation of general trends of the PL QY excitation dependence. Table 3.1 summarizes the preparation parameters, average NC size, density and the peak energy position of the PL spectra for all the samples - see figure 3.2 and reference [79] for further details.

3.3.2 Experimental methods

For the purpose of this study, the linear absorption, PL, PL excitation (PLE) spectra, and PL QY were measured at room temperature in the excitation energy range from 2.15 to 4.5 eV. PL and absorption spectra have been obtained using the same set up as for the PL QY measurements. All of the above optical characterization techniques have contributed to the conclusions of this study. From the PL spectra we retrieve the optical bandgap and the average size. The PLE was crucial to establish the impact of parasitic absorption on the PL QY values for the low excitation energies. Lastly, the linear absorption was used to determine the PL QY and to evaluate its error. The PL QY measurements were performed using low intensity excitation by an L2273 Hamamatsu xenon lamp (150 W) coupled to a Solar MSA130 double grating monochromator. Any directional emission and/or reflections were homogenized by making use of an integrating sphere with a diameter of 7.5 cm. For the detection we used a Solar M266 monochromator coupled to a Hamamatsu S7031-1108S CCD. The system response in the whole detection range has been calibrated by using a Newport halogen-tungsten lamp. The pumping power was adjusted to achieve a low excitation flux, so that each NC absorbs not more than a single photon (the linear absorption regime), see 3.2. The relative linear absorption was calculated from the formula:

\[ \text{ABS} = \frac{N_{\text{sub}} - N_{\text{sam}}}{N_{\text{sub}}} = \frac{N_{\text{abs}}}{N_{\text{sub}}} \]  

(3.1)

where, \( N_{\text{sub}} \) and \( N_{\text{sam}} \) are the numbers of collected photons of the not absorbed excitation beam as the substrate and the sample are placed in the integrating sphere, respectively. \( N_{\text{abs}} \) stands for number of absorbed photons. In a separate measurement, absorption by a sputtered layer of similar thickness but of pure SiO\(_2\) was tested to be negligible. In that way, the absorption of Si NCs only has been extracted.

3.3.3 Experimental results

The absolute and normalized PL QY as function of the excitation in the 2.15 - 4.5 eV range for all the samples are given in figure 3.3. The error bars of the PL QY
values are calculated according to the method described before [101]. Here we will compare the results for different materials and discuss their differences and general trends.

Figure 3.3: a): Excitation dependence of the PL QY in the 2.05 - 4.44 eV excitation range. b): The PL QY normalized at an excitation of 2.7 eV. The different dependences of the PL QY in the excitation range between 2.7 and 3.5 eV is clearly observed.

In many aspects semiconductor NCs behave as large molecules and can be treated as such. Consequently, as already mentioned in the introductory section, one can expect that they will follow the Kasha-Vavilov rule. The experimental results show that this certainly is not the case for the Si NC ensembles investigated here, with none of the 9 samples adhering to this rule. This is illustrated in figure 3.4 which shows the PL QY as function of the excitation energy for 3 samples, showing characteristics that are typical for all the layers. In the low energy range, the PL QY for all the samples exhibits an initial increase with the excitation energy. For the higher excitation energies, above 2.5 - 2.7 eV, the behavior diverges between the samples: while some exhibit continuous increase (sample #1, #2, #3, #4, and #5) over the whole investigated range, for other (samples #7, and #8) the PL QY attains a more or less constant value, or decreases again for the highest energies (samples #6 and #9) - see figure 3.3 for details of all samples. We recall that similar PL excitation dependences of Si NCs PL QY have been observed before. In particular, the initial rise at lower energies has been reported by Valenta et al. [94] for structures similar as used in this study, as well as in some earlier studies on porous Si [102, 103]. Both continuous and step-like increase have been reported by Timmerman et al. [84] for colloidal Si NCs prepared from porous Si and for thick layers of Si NCs dispersed in SiO₂ prepared by co-sputtering and high temperature
3.3. Investigation of excitation energy dependence of photoluminescence quantum yield in the Si nanocrystal layers

Figure 3.4: Excitation energy dependence of the PL QY of 3 samples (#1, #7 and #9), illustrating the three different types of behavior observed in this study. The dashed lines at the excitation energies of $E_{\text{exc}} = 2.7$ eV and $3.5$ eV separate the three excitation energy ranges as used in the discussion.

Annealing. Also the degradation of the PL QY upon high-energy excitation has been observed previously for colloidal PbS [89] and Si NCs [90], among others. Such a diverse and material-dependent behavior indicates presence of different mechanisms which simultaneously influence the PL QY in the investigated samples. The possible negative factors, which can lower the PL QY, might include parasitic absorption of defect states in NCs and/or in the matrix, excitation diffusion to quenching sites [16], photo-charging [83], efficient AR [104], activation of hot-carrier trapping at defect sites [15] and/or alternative channels of non-radiative relaxation of highly energetic carriers. Whereas on the positive side, for the smaller NCs (where the radiative recombination can better compete with the nonradiative channels than in the larger ones [16]), whose relative contribution to PL changes with excitation energy (see discussion later on), and radiative recombination of multiple excitons generated by II, known as SSQC [72, 84, 105], could lead to a PL QY enhancement. The individual contributions of these processes could result in complex dependencies, as indeed observed in this study.

In order to discuss in detail the possible role of the individual process, we divide the broad investigated range of excitation energies into 3 subregions, as indicated in figure 3.4 by the vertical lines: low, with $E_{\text{exc}} < 2.7$ eV, intermediate, with $2.7$ eV < $E_{\text{exc}} < 3.5$ eV, and high, with $E_{\text{exc}} > 3.5$ eV. An important point in our discussion is the SSQC process, and in that case 3.5 eV marks the threshold energy beyond which
this process should have been completed for all the NC sizes investigated here, as will be discussed later.

3.3.4 Discussion

3.3.4.1 Low excitation energies $E_{\text{exc}} < 2.7$ eV

For the low excitation energies $E_{\text{exc}} < 2.7$ eV, the PL QY shows constant, positive gradients for all the investigated samples, i.e., increases with pump energy. We note that in this range eventual PL QY increase via SSQC is not possible [72, 84, 15], since this process requires energies of twice the bandgap energy, so $E_{\text{exc}} > 2E_g + \Delta$ (where $E_g$ and $\Delta$ are the NC bandgap and the activation energy, respectively, with $\Delta \approx 0.3$ eV [84]). Taking into account that the smallest average bandgap energy for Si NC layers investigated here is 1.25 eV, this sets the SSQC threshold excitation energy at $E_{\text{exc}} > 2.8$ eV, thus excluding its contribution in this range. Therefore, we limit our discussion to the two remaining possibilities for the PL QY increase, namely (i) change of PL QY with NC size, and (ii) parasitic absorption in the sample.

- One might expect that a change of the PL QY of a NC ensemble could appear due to the size-dependent excitation cross-section [93]. In that case, the relative contribution of smaller NCs, whose absorption sets in at a higher energy will grow with the excitation energy. Since smaller Si NCs have typically larger PL QYs than the bigger ones [78, 79], this could be accompanied by a simultaneous increase of the PL QY of the ensemble. Nevertheless, this plausible and frequently considered possibility is not supported by the current experimental results. According to the volcano plot [78, 79], the PL QY of Si NCs increases with decreasing size (as the radiative recombination rate grows due to QC), reaches a maximum around $d \approx 4$ nm, and then decreases again, as the quality of the Si/SiO$_2$ interface deteriorates due to the high curvature [78, 40]. Since the average size of the Si NCs in samples #1 and #2 is already smaller than the maximum of the volcano plot, the increased participation of the smaller NCs for those two samples should result in a smaller, or perhaps even negative gradient of their PL QY. This is not observed, with sample #1 showing even the steepest rise of the PL QY of all the investigated materials – see figure 3.5.

- The possibility that absorption by some unspecified sub-bandgap defect states might be of importance for optical properties of Si NCs at low excitation energies has been postulated before [94, 102]. If sizeable, it could play a dominant role for the PL QY in the low energy range, where absorption by Si NCs is inefficient. Its relative contribution would be fading away at higher
3.3. Investigation of excitation energy dependence of photoluminescence quantum yield in the Si nanocrystal layers

Figure 3.5: Relation between the absorption gain $G_{\text{ABS}}$ and the PL QY gain $G_{\text{QY}}$ in the low excitation energy range $E_{\text{exc}} < 2.7$ eV. The extrapolation (shaded trace) indicates that the QY gain vanishes ($G_{\text{QY}} = 1$) for the high absorption gain range. The blue circle corresponds to the absorption gain of pure bulk silicon ($G_{\text{ABS}} \approx 4$) [106] and the blue shaded trace to the gain that can be expected for core absorption of Si NCs [107], with no parasitic component.

As can be seen, the bigger initial QY gain $G_{\text{QY}}$ takes place for samples with a small absorption increase $G_{\text{ABS}}$. We note that the small $G_{\text{ABS}}$ (significantly below the value of $G_{\text{ABS}} \approx 4$ [106] characteristic for pure bulk Si with no additional absorption) is by itself indicative of a large parasitic absorption.
Moreover, when extrapolated (the shadowed trace) toward the high absorption gain which can be expected for the pure Si NC-related absorption ($G_{ABS} > 4$, depending on NC size [107]), the QY gain vanishes, $G_{QY} \approx 1$, meaning that the QY should be constant within this excitation energy range - see figure 3.5, consistent with the presence of parasitic absorption in investigated samples.

Therefore we conclude that the initial increase of the PL QY, in the low excitation energy range, can be well accounted for by parasitic absorption, unrelated to the excitonic emission of Si NCs. In future investigations, this effect could be minimized by using well-passivated materials [40], containing Si NCs of high crystalline quality. Moreover, a high NC density should be preferred, for which the total absorption would be dominated by contribution from NCs; nevertheless, taking into account the large total Si/SiO$_2$ interface area of these materials, some degree of parasitic absorption seems unavoidable.

### 3.3.4.2 Intermediate excitation energies $2.7 \text{ eV} < E_{exc} < 3.5 \text{ eV}$

In this range, the absorption by Si NCs is sufficiently strong and dominates over any additional parasitic component. Therefore, according to Kasha-Valville rule, the PL QY can be expected to remain constant. That is indeed the case for samples #2, #6 and #8, while all the other investigated layers show either a moderate decrease (#9) or a pronounced increase towards higher excitation energies (#1, #3, #4, #5 and #7) - see figure 3.3 for the complete overview of the PL QY dependences for all of the samples. This raises a question whether the stable level observed for samples #2, #6 and #8 represents their true PL QY value, or results from an (accidental) active equilibrium between processes leading to decrease and increase of their PL QY. While the decrease of PL QY at high excitation energies is commonly observed due to the enhanced probability of trapping and/or nonradiative recombination, the increase is unusual, and more difficult to account for. One possible candidate process which could result in an increase of the PL QY is reduction of the so-called blinking [108]. Blinking is a temporary loss of optical activity, and is a characteristic property of all quantum emitters. Its statistics and physical origin for semiconductor NCs, including Si NCs, have been investigated in the past [108, 109]; obviously, any reduction of the off periods, would manifest itself as an increase of their PL QY. However, while no clear consensus on the microscopic mechanism responsible for the blinking phenomenon has been reached, past experimental evidence shows that in CdSe/ZnS, the increased pumping energy commonly boosts the blinking, increasing the off periods and quenching the PL QY rather than enhancing it [110]. The same situation might occur also for Si NCs. Consequently, the blinking of Si NCs can only contribute towards reduction of the PL QY, and not to its enhancement.

As already indicated, a process which has been shown in the past to increase the PL QY of Si NCs is SSQC [84] — a variant of CM where the additional e-h pairs...
3.3. **Investigation of excitation energy dependence of photoluminescence quantum yield in the Si nanocrystal layers**

recombine radiatively, by separating into neighboring NCs. Naturally, this process requires hot carriers of sufficiently high excess energy. The maximum theoretically available enhancement of the PL QY by the SSQC for a particular material can be modeled by integrating multiples of its PL spectrum [105, 111]. Since the absolute vertical scale in such an estimation cannot be set, for the sake of comparison we scale it to the value obtained at an excitation energy where (i) the effect of parasitic absorption on the PL QY can be ignored (or above \( E_{\text{exc}} \geq 2.5 \text{ eV} \) for all the samples investigated here) and (ii) any contribution of SSQC can be excluded, so for \( E_{\text{exc}} < 2E_g \). In figure 3.6 such an estimation is compared with the experimental results for sample #3, as normalized for the excitation energy of 2.65 eV (similar comparisons for other samples for which a clear enhancement of the PL QY in the \( E_{\text{exc}} > 2.7 \text{ eV} \) range has been found - #1, #4 and #5 - are also shown in figure 3.7). We conclude

![Figure 3.6](image_url)

**Figure 3.6:** The excitation energy dependence of the PL QY for sample #3 showing a very pronounced increase. The dashed line illustrates the development of the maximum available enhancement modeled from the PL spectrum, scaled to an excitation energy where we expect the effect of both parasitic absorption and eventual SSQC to be negligible - see text for further explanation. Note that the NC ensemble of this sample is very similar to that of sample A from reference [84] except for its ML structure.
Figure 3.7: The excitation energy dependence of the PL QY for samples #1, #3, #4 and #5. The markers show the experimentally derived PL QY values and the corresponding error bars, the dashed curves represent the maximal possible PL QY increase due to the SSQC effect.

that for these samples, the SSQC process could account for the experimentally observed increase of the PL QY, in the high excitation energy range. We stress that the broken lines in figure 3.6 and 3.7 do not represent theoretical modeling but merely a very crude estimation of the maximal PL QY boost by the SSQC effect, based on the assumption of a particular energy loss and a 100 % (maximal) efficiency. Concerning the explanation of the PL QY increase as arising due to the SSQC process, a few additional remarks can be made:

- As mentioned, the PL-based estimation procedure gives the possible upper limit for the PL QY enhancement by SSQC and its amplitude is arbitrary; therefore it provides only a guidance on how the PL QY could evolve with the excitation energy, if governed by the SSQC process.

- For sample #1, the onset of the SSQC-related enhancement seems to be blurred by the particularly strong parasitic absorption - see the relevant ab-
3.3. Investigation of excitation energy dependence of photoluminescence quantum yield in the Si nanocrystal layers

3.3.4.3 High excitation energies $E_{\text{exc}} > 3.5$ eV

Finally, we discuss the PL QY for the highest excitation energy range $E_{\text{exc}} > 3.5$ eV. From the experimental results we conclude that in that case very different behaviors are found: for sample #1, #2, #3, #4 and #5 the PL QY continues to increase further in a similar manner, which we assign to the continuation of SSQC. In contrast,
the PL QY for the other samples is either more or less stable - samples #7 and #8, or even decreases again at the highest energies - samples #6 and #9. This we assign to efficient trapping which apparently takes place in these materials and overcomes any increase which might appear due to SSQC, or perhaps even prevents the SSQC process. Degradation of the PL QY at high excitation energies has been reported before for colloidal NCs [89] and is naturally explained by the enhanced probability of trapping and/or nonradiative recombination for carriers excited higher into the bands. In the particular case of Si NCs embedded in SiO$_2$, we recall that the energy difference between the bottom of the conduction bands of Si NC and SiO$_2$ is approximately 3 eV, depending on the NC size. That implies that the chance for carrier trapping in the matrix increases dramatically in the high energy excitation range, as the hot carrier is approaching SiO$_2$ states close to the NC surface.

3.3.5 Additional remarks

3.3.5.1 Special points in Brillouin zone

For completeness, we comment on the role of the so-called special points of the Brillouin zone in the excitation dependence of the PL QY. A possible relation between the slight enhancement of the PL QY in Si NCs in vicinity of the direct bandgap $\Gamma_{25} \rightarrow \Gamma_{15}$ transition of Si ($\sim 3.4$ eV) has been originally suggested for porous Si [102] and then repeated for Si NCs in oxynitride [94], but a physical reason why such a relation should appear was not clear. To this end, we have the following remarks:

- Firstly, we recall that due to the required simultaneous conservation of both energy and momentum, the SSQC process should be particularly efficient for some excitation energies, corresponding to specific points in the band structure of the Si [112]. A similar situation has also been postulated for PbSe NCs, for which the MEG was found to be especially efficient in the vicinity of the $\Sigma$ point of the Brillouin zone [113]. In that way the enhanced PL QY in the energy range of the special points would evidence the onset of the SSQC, whose positive contribution to the overall PL QY could subsequently be suppressed by the negative effect of, e.g., increased carrier trapping simultaneously promoted by the high excitation energy [94].

- In the present study, no general correlation of PL QY characteristics with any specific energy values has been found.

- While the experiment suggests that the $\Gamma_{25} \rightarrow \Gamma_{15}$ transition should down-shift upon QC [12], the theoretical modeling of this effect, and even the degree to which it can be identified for Si NCs, is a matter of debate between different theoretical approaches [114]. In any case, the variation of the $\Gamma_{25} \rightarrow \Gamma_{15}$...
3.3. Investigation of excitation energy dependence of photoluminescence quantum yield in the Si nanocrystal layers

transition energy with the NC size makes its correlation with the PL QY dependence dubious.

- It should be noted that a strong parasitic absorption might mask the true onset of the SSQC-induced increase of the PL QY, as discussed in section 3.3.4.2.

We conclude that the results of the present study do not support a relation of PL QY characteristics with any specific points within the (bulk) Si band structure, even if those remain preserved in the band structure of Si NCs [115].

3.3.5.2 Relation between the PL QY gain and the average NC size

The final analysis focuses on the role of the average NC size; although it is not the only parameter characterizing the investigated Si NC layers, it turns out to be important in relation to the PL QY. From the experimental findings of this study, we conclude that not only different samples have different PL QY, but also attain maximum emission efficiency at different excitation energies. The crystallinity of the NCs and the quality of the matrix will impact the PL QY of individual NCs - at all excitation energies - as well as its possible enhancement due to SSQC.

Figure 3.9: (a) PL QY gain between two excitation energies of 2.4E₂ and 3.2E₂ versus the NC size. The red horizontal line separates the net positive from the net negative G\textsuperscript{eff,SSQC}; the shadowed area represents dependence trend with the error margin. (b) the same G\textsuperscript{eff,SSQC} versus the estimated NC density. In the latter case a wider spread, depicted as the shaded range, is observed.

For further discussion of the SSQC effect, we introduce the PL QY gain G\textsuperscript{eff,SSQC} using the so-called reduced energy scale [15], with the excitation energy scaled to the optical bandgap. We define the effective PL QY gain G\textsuperscript{eff,SSQC} for a given sample
as the ratio between its PL QY values for excitation energies at 2.4E\(_g\) and 3.2 E\(_g\), so in the range where, following our reasoning, the SSQC could be the dominant positive factor influencing the PL QY: \(G^{\text{eff}}_{\text{SSQC}} = QY_{3.2E_g}\). In the left panel of figure 3.9, we plot the \(G^{\text{eff}}_{\text{SSQC}}\) as function of the average NC diameter. The horizontal red line demarcates the materials with the positive and the negative gradient of the PL QY. While the data are somewhat scattered, we conclude that the positive contribution is the strongest for the smallest NCs, while for the largest ones negative effects dominate, leading to the net decrease of the PL QY as function of the excitation energy. In seems plausible to attribute that to the fact that large NCs will be, in general, more isolated thus making the SSQC process less likely. On the other hand, we note that the size of the NCs and their density in the investigated materials are correlated – see figure 3.10; therefore the \(G^{\text{eff}}_{\text{SSQC}}\) shows also some correlation with the NC density, albeit with a larger scatter – see figure 3.9b. Based on our results,

![Figure 3.10](image)

**Figure 3.10:** *Estimated NC density as a function of the NC diameter for several annealing temperatures. The shadowed area shows the deviation of the dataset.*

we note that the critical NC diameter separating materials for which the positive effect of SSQC and the negative effects dominate the ensemble PL QY development at higher excitation energies is around 6 nm. We conclude on a general trend, with SSQC dominating for smaller NCs (produced with a lower excess Si and therefore embedded in an SiO\(_2\) matrix of a possibly higher overall quality), and with the efficient hot-carrier trapping reducing the PL QY at high excitation energies (in layers developed with the high Si excess and containing large NCs).

In order to illustrate this general trend, we compare in figure 3.11 the excitation
3.3. Investigation of excitation energy dependence of photoluminescence quantum yield in the Si nanocrystal layers

Figure 3.11: The PL QY values, normalized to the value at the excitation energy of $E_{\text{exc}} = 3.1$ eV, of samples #5 and #7, with the same average diameter, but prepared with different Si excess and annealing temperature; a different behavior is observed in the low and the high excitation energy ranges. The inset: the absolute values of PL QY for the two samples.

dependence of PL QY for samples #5 and #7. These samples feature the same average NC size but have been prepared from SiO$_x$ layers with different stoichiometry and annealed at different temperatures; therefore, while the average NC size is identical for both materials, their other parameters differ. For clarity, both curves have been normalized at $E_{\text{exc}} = 3.1$ eV. Since sample #7 has been prepared with a higher excess Si, the lower overall optical quality can be expected. That is readily confirmed by the data: sample #7 shows a steeper PL QY increase in the low excitation energy range, which we assign to its larger parasitic absorption, and does not feature the SSQC enhancement in the high energy range, which can then be attributed to an efficient nonradiative recombination of hot carriers, generated upon absorption of high-energy photons.

As discussed in the past [82], the efficiency of the SSQC process proceeding by impact excitation in the neighboring Si NCs depends on their coupling; for a particular excitation energy and a NC size, that is influenced by their proximity and the embedding matrix. The variety of samples investigated in this study allows to test that. In figure 3.12 we compare the excitation dependence of the PL QY for
Figure 3.12: Comparison of the excitation energy dependence of the PL QY for samples #2 and #4 - normalized at $E_{\text{exc}} = 3.1$ eV (main panel) and absolute (in the inset). Both samples feature a similar level of parasitic absorption and the nearly identical average NC size. As compared to sample #4, sample #2 corresponds to the larger PL QY error bars because of its lower linear absorption [101].

samples #2 and #4. The average NC size in both materials is very similar, (3.8 nm and 4.1 nm, respectively) and so are their PL spectra. As can be seen, the relative enhancement of the PL QY with the excitation energy in a denser dispersion (#4) is bigger, in line with the expectations for the SSQC process. Inspecting figure 3.12 several comments can be made:

- Sample #2 is developed from material with a lower Si excess annealed at a higher temperature than sample #4; therefore we can expect the better crystal quality of the Si NCs, which should result in a generally more efficient PL [23]. This is confirmed by the experiment, with PL QY of sample #2 exceeding that of sample #4 over the whole investigated range of excitation energies (see the inset).

- While the total absorption of sample #4 is higher due to the larger Si excess, the degree of parasitic absorption is similar for both materials - see figure 3.5. Consequently, following the earlier discussed mechanism, the initial growth of their PL QY, in the low energy range, should be similar. The PL QY
3.3. Investigation of excitation energy dependence of photoluminescence quantum yield in the Si nanocrystal layers

of sample #2 stabilizes for excitation energies $E_{\text{exc}} > 2.5$ eV at the level of approximately 13%. For sample #4 the PL QY at this energy is 4%, which should then correspond to the intrinsic PL QY level of this material, without SSQC.

- At higher energies, further development of the PL QY is quite different for the two samples: the PL QY of sample #4 increases sharply with some indications of a step-like behavior, fitting quite well with the appropriately scaled dependence for efficient SSQC. The PL QY of sample #2 is almost stable, increasing only slightly for the highest pump energies. This can be expected: on one side the higher density of the NCs increases the probability of SSQC in sample #4 with respect to #2, thus explaining the stronger increase of the PL QY. On the other side, the efficient hot carrier trapping, degrading the PL QY in the high energy range, appears for the investigated samples only for the largest Si excess, and the biggest NC sizes, and so should not affect the PL QY of sample #2; in result, this sample follows most closely the Kasha-Vavilov rule.

3.3.6 Conclusions

Figure 3.13: The excitation energy dependence of the optimal NC diameter (i.e. corresponding to the highest PL QY). In the inset, typical volcano plots for exemplary excitation energies of $E_{\text{exc}} = 2.50$ eV and $E_{\text{exc}} = 4.44$ eV.

We conclude that the proposed microscopic mechanisms provide an adequate
description of the experimental findings, and allow for a reasonable description of
the excitation dependence of the PL QY in the investigated range of materials.
For future application of Si NCs, e.g., for photon conversion, the absolute value of
PL QY is an essential parameter. With an eye on reaching the maximum emissivity,
past investigations concentrated on optimization of the Si NC size [78, 23, 39], estab-
lishing the so-called volcano plot [78]. The current study shows that the excitation
energy dependence of the PL QY is of essential importance for photon converter
application. Therefore the past investigations can be extended developing volcano
plot for every excitation energy separately. From these results we conclude that for
conversion of highly energetic photons smaller NCs are preferred, while in the NIR
range larger ones, with a diameter around $d > 4$ nm, show a better performance – see figure 3.13 for details.

3.3.7 Summary

By investigating a variety of Si NCs-in-SiO$_2$ layers we unravel the behavior of their
PL QY as a function of the excitation energy. We find that the PL QY of a particular sample is determined by competition of different mechanisms operating in parallel. Their individual contributions, decreasing or increasing the total PL QY, are strongly dependent on sample parameters, with an important role of the average NC size, and vary strongly with the excitation energy. Hence, this work gives a comprehension of the complex behavior of the PL QY and marks the difficulty in its interpretation, hereby serving as an essential framework for all of those working on the PL QY of (low absorption) nanoparticles.