Excitation efficiency and saturation dynamics of near-infrared emission from Si nanocrystals embedded in a SiO₂-matrix

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Abstract. We have investigated photoluminescence (PL) and linear and induced absorption of Si nanocrystals (NCs) in a SiO₂ matrix. By measuring PL intensity dependence on the excitation photon fluence, we conclude that (i) the excitation wavelength independent saturation level is reached when on average a single photon is absorbed per NC, and (ii) excitation cross-section is proportional to the linear absorption only in the low-energy range; for higher energy it increases faster than absorption, thus indicating more efficient excitation which appears due to space-separated quantum cutting (SSQC). In order to shed more light on the mechanism behind the SSQC, we have compared spectral and temporal characteristics of induced absorption for excitation wavelengths below and above the SSQC threshold. These were found to be very similar, thus indicating that the SSQC process is most likely very fast, possibly taking place already during photon absorption by NCs.

1. Introduction

1.1. Si nanocrystals
Light generation in bulk Si is very inefficient. Its indirect bandgap leads to very long radiative lifetimes of excited electron-hole pairs and consequent domination of nonradiative recombination channels. In Si nanocrystals (NCs), radiative recombination is enhanced due to quantum confinement effect which relaxes the $k$-conservation rule. Furthermore, the energy structure of Si NCs can be altered by changing their size; decreasing the size of NCs will increase both the bandgap and the spacing between the discrete energy levels. Therefore a solid-state dispersion of Si-NCs in SiO₂ matrix is an interesting material system whose optical properties can be tuned over a large energy range.

1.2. Cooperative carrier generation processes
One more consequence which can be expected due to the quantum confinement-induced level discretization is suppression of phonon cooling of excited carriers – the effect known as the phonon bottleneck. Competing cooling processes can in this case play a more prominent role. One of these is the inverse Auger recombination, where a high-energy electron/hole generates an electron-hole pair. This effect of impact excitation is well-known in bulk semiconductors [1], where it has low probability. It has been reported to take place also in different types of semiconductor NCs – PbS, PbSe, InAs and CdSe [2–4], and, recently, in a colloidal suspension of Si NCs [5]. In case of NCs, such a process results in generation of two (or more) electron-hole pairs in a NC upon absorption of a single photon.
of sufficient energy and is termed multiple exciton generation (MEG) or carrier multiplication (CM). The lifetime of multiple excitons in a single NC is very short (~ps), as wavefunction overlap in confined environment leads to strong carrier-carrier interactions and efficient Auger recombination. Consequently, regardless of how many excitons are generated within a NC, only one of them – the “last” remaining electron-hole pair – will have a sufficiently long lifetime to allow for its radiative recombination.

Recently, we have shown that in closely packed ensembles of Si NCs, a variation of the MEG process appears, in which a hot carrier cools by generating an electron-hole pair in a neighboring NC – the process termed space-separated quantum cutting (SSQC) [6]. In this case, the two electron-hole pairs formed by absorption of a single high-energy photon are localized in different NCs. Therefore their mutual interaction is strongly reduced, thus increasing their lifetimes and enhancing chance for radiative recombination and emission of two photons.

1.3. Carrier dynamics in Si nanocrystals

Presently occurrence of MEG is indirectly inferred from dynamics of free carrier absorption under (extremely) low power excitation, so as to exclude the possibility of multi-photon absorption within a single NC. In order to understand physical mechanisms of cooperative carrier generation processes, detailed knowledge of carrier dynamics in nanocrystalline environment is imperative. This is presently not the case; while in bulk Si these processes have been thoroughly investigated and satisfactory understanding has been obtained, carrier relaxation and recombination in NCs is still poorly known. Very specifically, this concerns the afore-mentioned suppression of the phonon-bottleneck effect. As a result, the debate on the MEG process continues [7]. Here the existing reports claim that the generation of the multiple carriers is very fast and either proceeds instantaneously during the absorption process itself [8] or during the first ~100 fs after photon absorption [9]. Consequently, different scenarios are considered, in which the high-energy photon either transfers its energy directly to two separate carriers by formation of a virtual state or creates a “hot” exciton whose cooling takes place via efficient impact excitation of another carrier. In case of Si NCs, yet additional complication to this process is introduced by indirect nature of the bandgap. It is fair to say that the actual mechanism of the generation of the multiple carriers by a single photon is still not understood. Elucidation of this process constitutes the major motivation of this study.

2. Experimental

2.1. Samples

The reported investigations have been performed on thin films (~micrometer) of Si NCs embedded in a matrix of SiO₂. These have been prepared by a radio-frequency co-sputtering method. SiO₂ and Si targets were simultaneously sputtered on a fused quartz substrate. Post annealing in N₂ ambient at 1100°C was subsequently conducted in order to segregate this substoichiometric mixture into Si NCs and SiO₂. In this method, size of Si NCs can be tuned by varying the amount of silicon during sputtering and, to certain extent, by the annealing temperature. The actual size of the produced samples was determined by high resolution transmission electron microscopy. The results presented in this report have been obtained for Si NCs of 3.1 nm diameter with a size distribution of ~14%.

2.2. Experimental setups

In this study photoluminescence (PL) and linear and (time-resolved) induced absorption (IA) have been investigated.

The setup used for PL measurements consisted of a tunable optical parametric oscillator pumped by the third harmonic of a pulsed Nd:YAG laser (354 nm) operating at a repetition rate of 10 Hz and with a pulse length of 5 ns. The PL spectra were resolved with a Jobin-Yvon TRIAX 320 monochromator and detected with a Hamamatsu R5509-72 photomultiplier. The illuminated area of the sample was
kept constant by use of a pinhole, in order to get a flat profile of the laser beam and to ensure identical excitation spot in all measurements.

The induced absorption experiment was performed using a femtosecond pump-probe configuration, implemented with two Ti:Sapphire pumped OPAs for a tunable pumping wavelength. The excitation pulse was split in a primary pump pulse and a secondary probe exploring properties of the excited state. The probe pulse was passed though a white light convertor and mechanically delayed in respect to the primary pulse by means of an optical delay line thus allowing for time-resolved investigations. The detected induced absorption signal $I_{\text{detection}}$ was then corrected as follows: $I_{\text{detection}} = (I_{\text{pump+probe}} - I_{\text{probe}})/I_{\text{probe}}$, with $I_{\text{pump+probe}}$ and $I_{\text{probe}}$ corresponding to absorptions of the probe beam under and without the influence of the pump, respectively. Experimental resolution was ~200 fs.

The linear absorption of the samples was determined with a Varian-50 UV-VIS spectrophotometer, for wavelengths between 200-1100 nm.

All the measurements discussed in this report were obtained at room temperature.

![Figure 1](image1.png)

**Figure 1.** Intensity dependence of NC-related PL on the number of pump photons per pulse (fluence) for different excitation wavelengths. The slope of the initial part, related to the excitation cross-section, becomes steeper for shorter wavelengths, while the saturation level remains identical.

![Figure 2](image2.png)

**Figure 2.** Relative quantum efficiency (see text for explanation) as function of the excitation photon energy. The quantum efficiency is constant up to photon energy of ~ 3 eV and the increases, indicating a second excitation mechanism. The dashed line acts as a guide to the eye. The arrows mark excitation wavelengths used in IA experiments. In the inset, PL spectrum of the NCs under study.

3. Experimental results

3.1. Excitonic photoluminescence

In the initial experiments, we have investigated intensity of PL due to exciton recombination. Figure 1 shows the results as obtained for different excitation wavelengths ranging from 354 to 650 nm. It can be concluded that (i) the saturation level is independent of excitation wavelength while (ii) the actual photon fluence at which PL intensity saturates decreases for shorter excitation wavelengths. The latter effect indicates increase of the excitation cross-section of exciton-related PL, which can be determined from the initial slope of intensity dependence, in the linear regime. In order to check whether this effect can be attributed to the wavelength dependence of absorption cross-section of Si NCs, the absorbance of the sample has been independently measured in a separate experiment. In figure 2 we
plot the ratio of the excitation cross-section and absorbance, termed the relative quantum efficiency, as a function of quantum energy of the incoming photons. As can be seen, this parameter remains constant for low quantum energies until a threshold value of $E_X \approx 3$ eV, and shows strong increase for more energetic photons.

3.2. Induced absorption

Induced absorption measurements have been performed at two pump wavelengths of $\lambda_{\text{pump}} = 500$ nm (2.5 eV) and $\lambda_{\text{pump}} = 345$ nm (3.6 eV), i.e. below and above the energy threshold value $E_X$ for the quantum efficiency increase, as indicated with arrows in figure 2. Figure 3 illustrates the spectral dependence of the induced absorption as obtained with a fixed delay of $\Delta t = 20$ ps for the visible and the infrared probe range at both pump settings. At both pumping wavelengths, the photon fluxes have been chosen such as to assure low and equal average number of electron-hole pair per NC: $<N_{e-h}>345$ nm $\approx <N_{e-h}>500$ nm $< 1$.

![Figure 3. IA results for 345 nm and 500 nm pumping for a time delay of 20 ps between pump and probe pulses. Two probe ranges are shown: (a) the visible (380-800 nm) and (b) NIR (900-1300 nm). Excitation conditions are such that $<N_{e-h}>345$ nm $\approx <N_{e-h}>500$ nm $< 1$. Only minor differences appear.](image)

Also dynamics of IA have been measured under the same experimental conditions, i.e. for $\lambda_{\text{pump}} = 345$ nm and $\lambda_{\text{pump}} = 500$ nm and the visible and near-IR probe ranges. The results are depicted in figure 4 for the time window of the first 200 ps after the pump pulse. As can be seen, apart for the intensity difference which can be inferred from figure 3, the measured IA dynamics are quite similar for both pump values.

4. Discussion

The investigated PL emission – see the spectrum depicted in the inset to figure 2 – originates from exciton recombination in Si NCs. Therefore saturation of this PL band points to the limited number of excitons participating in that emission. Since there appear to be no fundamental limits to generation of electron-hole pairs in NCs as the incoming photon flux increases, the fact that PL intensity saturates clearly indicates that only a limited number of generated excitons can recombine radiatively. Moreover, that number seems to be independent of the photon energy, while it is well known that absorption probability of photons increases with their quantum energy. (We also note that the number of illuminated NCs is kept constant by a pinhole). Such a situation is indeed to be expected since, as discussed in the introduction, multiple excitons localized in the same NC undergo very efficient nonradiative recombination. Therefore, when excitation exposure is shorter than the radiative recombination, only a single photon might be emitted by excited NC regardless of the actual number of electron-hole pairs which have been generated in it. Since in the present case laser pulses of $\sim 5$ ns are
used while the exciton radiative recombination time is in the microsecond range, this PL intensity limitation indeed can be expected. In order to investigate that, we have estimated the amount of NCs that have been excited after a laser pulse over the excitation power range using a Poissonian distribution

\[ N_x = N_{NC} \times \frac{<NC^*>^x}{x!} e^{-<NC^*>}, \]

where \( x \) – indicates the number of photons absorbed per NC, \(<NC^*>\) is the average number of photons absorbed per NC, and \( N_{NC} \) is the amount of NCs in the illuminated volume. We have also verified that kinetics of PL did not depend on the excitation wavelength. Taken together, these results show that the saturation of the PL signal sets in at the moment that almost all of the NCs have absorbed at least one photon. This implies that each NC contributes a maximum of one photon to the PL signal, confirming validity of the earlier presented reasoning.

**Figure 4.** Normalized IA dynamics for 345 nm and 500 nm pumping for two different probing wavelengths of 530 nm (a) and 1200 nm (b). Temporal dependence appears to be independent of pump energy.

In contrast to the saturation level, the excitation cross-section of excitonic PL clearly increases for shorter wavelengths. This is to be expected, since absorption cross-section of bulk Si for higher energy photons is larger and the same can be expected also for Si NCs. However, the results depicted in figure 2 clearly show that this effect accounts for the increase of excitation cross-section in the low photon energy range: the relative quantum efficiency, which simply reflects the number-of-photons-in to the number-of-photons-out ratio, is indeed constant but only until the threshold value of \( E_X \approx 3 \text{ eV} \), thus reflecting linear relation between the two. For photon energy larger than \( \sim 3 \text{ eV} \) the quantum efficiency increases. This effect indicates onset of a different excitation mechanism which starts to operate in parallel to the standard one. It has been assigned to the quantum cutting process in which an additional exciton can be generated at the expense of kinetic energy of a hot carrier [6]. As can be seen, the efficiency of this new process increases steeply with photon energy: for the shortest wavelength used in the current study, the total quantum efficiency is almost tripled in comparison with that attained by the “standard” excitation process. This illustrates the potential of the SSQC process of multiple carrier generation and gives good prospects for its photovoltaic, and possibly also photonic, applications.

As discussed in the introductory section, one can expect that IA could shed light on the microscopic mechanism behind the SSQC effect. This is based on the past experience in other materials, where practically all the information available on MEG has been obtained from IA investigations [2–5, 7]. We therefore compare results of IA experiments performed under conditions which do not allow for the SSQC process (\( \lambda_{pump} = 500 \text{ nm}, \ h\nu < E_X \)) with these for which the SSQC process can be expected (\( \lambda_{pump} = 345 \text{ nm}, \ h\nu > E_X \)). We note that in both cases the excitation fluence
has been chosen so as to assure equal and small number of electron-hole pairs to be excited per NC<br/>&lt;NC†&gt; < 1, in order to assure that absorption of multiple photons by a single NC, which could<br/preclude observation of SSQC related effects, can be excluded.

Figure 3 presents the IA spectra as obtained with the two excitation wavelengths for the visible<br/>(figure 3a) and the infrared (figure 3b) probe ranges. In general, bands in an absorption spectrum are<br/usually related to specific transitions. In the current case, these could be intra-band transitions and, for<br/sufficiently large pump quantum energies, transitions from NC- to SiO₂-related levels. Different<br/excitation photon energies should enable absorption in different excited state levels. Consequently, the<br/IA spectrum is likely to change depending on pump wavelength. As can be concluded, some<br/differences can only be seen in the visible, while the spectra obtained for the infrared are identical. On<br/the other hand, some structure in absorption spectrum can appear due to interference caused by<br/internal reflections within the optically active layer. Such interference “fringes” have indeed been<br/observed in the linear absorption spectrum of the investigated samples in the visible. Therefore we<br/conclude that IA spectra are quite similar under sub- and sup-threshold pumping which indicates<br/ultrafast cooling of carriers within their bands: regardless of their original energies defined by different<br/pumping wavelengths, within the rise time of the signal the carriers cool to the (lowest) state from<br/which similar absorptions are enabled by the probe.

From the above observation, an important conclusion can be drawn. The similarity of IA spectra<br/measured for different excitation photon energies implies cooling on a time scale similar to (or faster<br/than) the setup resolution (~200 fs). This in spite of the theoretically predicted retardation of phonon-assisted energy dissipation in the quantum confined regime. This conclusion is also confirmed when<br/IA transients taken under the two pumping conditions are compared – see figure 4: transients for<br/different pump photon energies reveal identical dynamical behavior and also similar amplitude. This<br/implies that the same relaxation and recombination processes are observed, leading to an identical<br/initial situation for absorption probing.

5. Conclusions
In the presented study, we conclude on the very fast (< 200 fs) thermalization of carriers excited by<br/photon absorption in Si nanocrystals. This implies that the SSQC process inferred from excitation<br/cross-section of excitonic PL is likely to occur on a similar time scale, or faster. This gives preference<br/to theoretical models which suggest the MEG process to take place during photon absorption. Nevertheless, it is only fair to mention that the above interpretation of experimental results should be<br/considered very critically; current conclusions on the ultrafast carrier cooling should be verified using<br/other experimental approaches.

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