Optical spectroscopy of carrier dynamics in semiconductor nanostructures

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Chapter 3

Thermally stimulated exciton emission in Si nanocrystals

Increasing temperature is known to quench the excitonic emission of bulk Si, which is due to thermally induced dissociation of excitons. Here, we demonstrate that the effect of temperature on the excitonic emission reverses for quantum-confined Si nanocrystals. Through laser-induced heating of Si nanocrystals embedded in SiO$_2$, we achieve an above threefold (>300%) increase of the radiative (photon) emission rate. We theoretically model the observed enhancement in terms of a thermally stimulated effect, taking into account the massive phonon production under intense illumination. These results unravel one more important advantage of Si nanostructures, illustrating that their optical properties can be influenced by temperature. They also provide an important insight into the mechanisms of energy conversion and dissipation in ensembles of Si nanocrystals in solid matrices. On the practical impact side, the radiative rate enhancement under strong continuous wave optical pumping is closely relevant to the possible application of Si nanocrystals for spectral conversion layers in concentrator photovoltaics.

3.1 Introduction

Silicon is currently the most important semiconductor material for electronic and photovoltaic applications. However, its light absorption and emission rates are low compared to direct bandgap materials. The optical properties of Si can be improved using nanostructures, where quantum confinement effects play a role resulting in, among others, opening up of the indirect bandgap and an increase of the radiative recombination rate[9, 28, 51, 52, 53]. At the same time, laser heating during optical excitation is strongly enhanced in nanostructures compared to bulk[54]. Phonon production and heating of NCs appears due to: (i) cooling of hot carriers generated by above-bandgap excitation, (ii) emission during indirect bandgap recombination to compensate for the momentum mismatch and/or (iii) non-radiative AR of multiple electron-hole pairs appearing in a single Si NC[15, 55]. The latter process sets the upper emissivity limit of a single photon per NC. In this study, we investigate the effect of heating on the excitonic emission of Si NCs embedded in an SiO$_2$ matrix and we demonstrate an effective threefold enhancement of their radiative recombination rate. This result represents the proof-of-principle demonstration that purposeful phonon management can be used to manipulate the optical properties of Si NCs and in that way increase the optical faculty of Si.

3.2 Experimentals

3.2.1 Materials

For the purpose of this study, samples of closely packed Si NCs embedded in an SiO$_2$ matrix have been fabricated by two different preparation methods, namely radio-frequency co-sputtering and plasma enhanced chemical vapor deposition (PECVD). The samples prepared by radio-frequency co-sputtering Si and SiO$_2$ on a quartz substrate, followed by thermal annealing in N$_2$ gas at 1150°C, have a multilayer (ML) structure of in total 100 bilayers, each consisting of a 5nm passive SiO$_2$ and a 3.5nm active layer containing the Si NCs (see Ref. [56] for further details). For comparison, and to create a general picture
which is not linked to a particular fabrication method, also a set of samples grown by PECVD was investigated. These samples were deposited as alternating layers of Si-rich silicon oxynitride (SRON; SiO$_x$N$_y$) and stoichiometric SiO$_2$ on fused silica substrates, followed by annealing in high-purity N$_2$ gas at 1150°C and in H$_2$ gas at 500°C. The PECVD ML samples all have stoichiometry parameters (x and y), which are nearly identical, and contain each 40 bilayers of 4.5nm SRON and an SiO$_2$ spacer thicknesses of 1, 1.6, 2.2 and 2.8nm, for samples ML1 to ML4, respectively (see Refs [57] and [58] for further details). The PL spectra of these four ML PECVD samples can be found in Fig. 3.1(b) of Ref. [57].

3.2.2 Experimental techniques

3.2.2.1 Photoluminescence

The time-integrated PL spectra of the co-sputtered samples are obtained under 405nm continuous wave (cw) excitation (Mitsubishi ML320G2-11) in an inverted microscope setup (Zeiss Axio Observer.Z1) with an objective (Zeiss LD EC Epiplan-Neofluar 100×/0.75 DIC). Part of the sample is selected using a slit and the PL is detected using a liquid N$_2$-cooled charge-coupled device (CCD, Princeton Instruments PyLoN: 1340×400B) coupled to a spectrometer (Princeton Instrument Acton SP2300). Replacing the slit and the grating with a mirror allowed us to resolve the beam shape and the intensity profile of the beam incident on the sample. The laser power is adjusted by using a set of neutral-density filters and a Glan-Thompson polarizer.

The power dependence of the PL of the PECVD samples was studied using a home-built microspectroscopy based on an inverted optical microscope (Olympus IX-71) with an objective lens (100×/0.8). Excitation was provided by either a 405nm cw diode laser (Omicron LDM405.120.CWA.L) or the 355nm output of a frequency-tripled diode-pumped Nd:YAG laser (CNI Optoelectronics MRL-F-355, repetition rate of 4kHz and pulse width of ~6ns) coupled to the objective in the epifluorescence configuration. The PL from the excitation spot was imaged on the entrance slit of a 30cm imaging spectrometer (Acton SpectraPro SP-2358i) with a back-illuminated liquid N$_2$-cooled CCD (Princeton Instruments SPEC-10:400B) as a detector.

An important advantage of these two imaging spectroscopy arrangements is that the detected area can be precisely controlled, avoiding averaging effects that take place when the whole excitation spot is detected (as in a standard PL setup). Moreover, the spot size is kept constant for the different excitation powers; this is significant, since the (possible) temperature rise produced by the laser illumination is dependent on the spot size[59].

3.2.2.2 Transient induced absorption

The IA experiments were performed with an ultrafast pump-probe setup comprising of a Ti:sapphire regenerative amplifier (pulse width of ~100fs), running at a repetition rate of 1kHz (Spectra-Physics). The fundamental output beam at 800nm was split into two paths. The first path was directed into an optical parametric amplifier (TOPAS, LightConversion) to generate a tunable pump beam ranging from the UV to the NIR, while the second path was focused onto a sapphire crystal to produce the white-light supercontinuum (850-1600nm, 0.78-1.46eV) as a probe. The transmitted probe beam was detected by a pair of coupled high-speed multichannel detector arrays coupled to a high-speed data acquisition system (HELIOS, Ultrafast Systems). The IA signal, $I_{IA}$, (also sometimes referred to as the IA differential absorbance, $\Delta A$) is determined as:

$$I_{IA} = \Delta A = A_{ON} - A_{OFF} = \log_{10} \left( \frac{I_0}{I_{T,ON}} \right) - \log_{10} \left( \frac{I_0}{I_{T,OFF}} \right) = \log_{10} \left( \frac{I_{0}/I_{T,ON}}{I_{0}/I_{T,OFF}} \right) = \log_{10} \left( \frac{I_{T,OFF}}{I_{T,ON}} \right),$$

(3.1)
where $A_{ON}$ ($A_{OFF}$) and $I_{T,ON}$ ($I_{T,OFF}$) are the absorbance and transmitted probe fluence with the pump laser on (off) and $I_0$ is the incident probe light on the sample.

### 3.2.2.3 Raman spectroscopy

Raman spectroscopy measurements are performed with a Renishaw inVia Micro-Raman microscope. The Raman spectra were measured under 514nm (2.41eV) cw laser excitation (Ar-ion laser). The intensity of the laser power could be varied by switching between filters having various transmissions (e.g. 1, 5, 10 and 50%).

### 3.3 Results and discussion

#### 3.3.1 Flux-dependent photoluminescence properties

In general, the PL intensity in the low-power regime, when none of the NCs has absorbed more than a single photon, is proportional to the number of absorbed photons and is therefore roughly linear with respect to the excitation pump flux (or fluence in case of pulsed excitation). For a higher flux, the PL growth rate decreases toward zero when multiple excitons appear in a single NC. Calculations for spherical Si NCs show AR times to be in the range of 0.01 to 1ns for NCs of similar sizes as investigated in this study ($d_{NC} \approx 2.5-7nm$)[60]. Since the radiative lifetime is much longer ($\approx 500\mu s$), the significantly faster non-radiative AR process removes all excess carriers so that only a single electron-hole pair per NC will recombine radiatively. Thus, the AR of multiple excitons sets the upper limit for the number of emitted photons, independent of the number of absorbed photons and the excitation photon energy[15]. On the other hand, the number of phonons that can be generated within a NC does not have a limit and grows with the increasing number of absorbed photons. However, the experimental evidence does not confirm that simple model. For all the investigated Si NCs embedded in an SiO$_2$ matrix (see Section 3.2.1 for more details on the investigated samples), we observe that, under 405nm (3.06eV) cw excitation, the PL intensity, $I_{PL}$, follows at low flux initially a linear dependence: $I_{PL} \propto \varphi^a$ with $a=1$, where $\varphi$ is the excitation photon flux and $a$ the growth rate. Above a certain threshold value of the excitation pump flux, the PL intensity growth rate decreases to a sublinear power dependence ($I_{PL} \propto \varphi^a$ with $0 < a < 1$; high flux). Complete saturation ($I_{PL} \propto \varphi^a$ with $a=0$; high flux) is never achieved, even for the highest excitation photon flux used in this study, for which multiple photons are absorbed per NC (see Fig. 3.1(a) for an exemplary dataset obtained under cw excitation). Moreover, the increase of PL intensity above the expected saturation point is accompanied by a blueshift of the PL spectrum over (almost) the whole investigated flux range (see Fig. 3.1(b)). Both the experimentally observed increase of the PL intensity with the pump power as well as the accompanying blueshift of the PL spectrum depicted in Fig. 3.1, show clearly two distinct regimes. This result violates the generally accepted model of excitonic PL in Si NCs, where efficient AR leads to the near-instant (picosecond timescale) quenching of multiple excitons localized in the same NC, so that a maximum of only a single electron-hole pair per NC can contribute to PL[61]. Under assumptions of fast AR, the dependence of the PL intensity, $I_{PL}$, on the flux $\varphi$ reads[62]:

$$I_{PL} = \frac{\eta \sigma \varphi}{1 + \sigma \varphi \tau_{rad}},$$  \hspace{1cm} (3.2)

where $\sigma$ is the optical absorption cross section at the pump wavelength, $\tau_{rad}$ is the time constant of radiative recombination and $\eta$ is the internal QY, which is defined as $\eta = \frac{\tau_{nrad}}{\tau_{rad} + \tau_{nrad}} = \frac{\Gamma_{nrad}}{\Gamma_{rad} + \Gamma_{nrad}}$, where $\tau_{rad}$ ($\Gamma_{rad}$) and $\tau_{nrad}$ ($\Gamma_{nrad}$) are the radiative and non-radiative recombination time constants (rates), respectively. Thus at a high flux, the PL intensity should saturate at $\eta/\tau_{rad}$ - clearly at variance with the experimental results. Also the pump photon flux dependence of the PL peak position shows two distinct ranges. The PL band blueshifts with the pump flux, but the rate of this shift clearly slows down in the high-flux excitation range. The blue spectral shift at low powers is commonly attributed to the NC
size dependence of the absorption cross section,[61], so that the size distribution of excited NCs changes under different excitation flux. Large NCs have a larger absorption cross section[62] (see also Fig. 2.1) and will therefore saturate at a lower excitation photon flux than the smaller NCs. This results in a blueshift of the PL spectrum. At even higher excitation photon flux, when all the NCs are saturated regardless of their size, the PL spectrum will not shift any more due to the size-dependent absorption cross section. However, experimentally we observe that at high flux (with more than one exciton per NC) the PL spectrum does not stabilize, but continues to blueshift, albeit at a lower rate.

![Figure 3.1: Typical flux dependence of the photoluminescence intensity for a Si nanocrystals in SiO₂ sample under 405nm (3.06eV) continuous wave excitation. (a) The PL intensity (of a co-sputtered sample, λ_{det}=870nm, E_{det}=1.43eV) over more than four orders of magnitude of the excitation pump flux, in a double logarithmic representation. The gray solid curve corresponds to the behavior expected on the basis of a simple model with an efficient AR (Eq. 3.2). (b) The excitonic PL peak position as function of the excitation photon flux for the same sample as in panel (a).]

3.3.2 Sample temperature

In order to explain the microscopic origin of the experimental findings of this study, we consider the effect of the high excitation photon flux on the sample temperature, since the experimental observations indicate that at a high flux the sample temperature increases. At a high excitation photon flux, many photons are absorbed by a single NC and most of the deposited energy is dissipated as heat, increasing the NC temperature. We note that under the highest flux used in this study, more than 100 photons are absorbed by a single NC within the exciton lifetime. Under the assumption of efficient AR and thus the “effective” presence of a single exciton per NC only, there will be more than 300eV of energy converted into heat in every NC within the exciton lifetime, of approximately 100µs. This readily explains the permanent damage of the investigated material and the initial irreversible decrease of the PL intensity, which can be inflicted by an extreme excitation flux (see Fig. 3.4). (At this point it is important to note that the necessary precautions have been taken so that all the results, which are presented here, are obtained under conditions where no permanent change/damage to samples occurs, and are fully reproducible on the same sample, which can be cycled multiple times (see Fig. 3.4).) As a matter of fact, the situation is similar to that of freestanding Si particles whose temperature was shown to rise up to ~1350K under cw intense laser illumination[63, 64, 65, 66, 67, 68, 69] (see also Chapter 5). In addition, vibrational lifetimes can alter significantly in nanostructures, leading to phonon localization and trapping, promoting even further temperature increase[70]. The sample temperature can be conveniently estimated from Raman measurements[63, 64, 65, 66, 67] (see also Chapter 5). However, in the present case, unlike in the recalled studies, the relatively strong excitonic PL precludes direct observation, and intensity comparison, of the
Stokes and anti-Stokes Raman modes (see Fig. 3.5), necessary for temperature estimation. In order to verify sample heating as a possible origin of the additional PL, we have compared the flux dependence of the PL intensity under 405nm (3.06eV) cw and 355nm (3.49eV) pulsed excitation. As shown in Fig. 3.2(a), in the latter case complete saturation of the PL intensity is observed. Since the Si NCs can dissipate energy between two consecutive pulses under the pulsed excitation, the photons are predominantly emitted not during the laser illumination but when the sample is cooling down significantly; this result supports then our notion that the additional growth of the PL intensity under strong cw pumping could be related to the temperature increase of the sample. This is further confirmed by experiments on a series of structures featuring single Si NCs layers intercalated by spacers of pure SiO$_2$ (see Fig. 3.7 for a schematic illustration). As can be seen in Fig. 3.2(b), the PL intensity saturation sets in as the spacer thickness increases. For ensembles of closely spaced Si NCs, one can expect that the thermal properties of Si NC ensembles depend sensitively on the NC spacer thickness. For thinner spacers, more energy is absorbed and dissipated in a smaller volume of the ML structure leading to stronger heating and a larger temperature increase (see Fig. 3.2(c) for a schematic illustration). In Fig. 3.2(b) the normalized PL intensity is shown for a set of ML samples produced by PECVD with different spacer thicknesses but almost identical NC size distributions; the smaller the spacer thickness, the larger the temperature increase and the stronger the PL saturation. Thus, all these measurements are consistent with our hypothesis that sample heating is responsible for the additional PL.

The PL intensity can continue to grow above the expected saturation point, if either the radiative rate increases or the non-radiative rate decreases (see Eq. 3.2). The latter typically increases with temperature, due to the enhancement of multiphonon recombination (larger phonon availability)[71]. Therefore, the persistent increase of the PL intensity above the expected saturation point indicates an enhancement of the radiative rate.

### 3.3.3 Effect of temperature on the radiative recombination rate

We now theoretically consider the effect of the temperature increase on the radiative excitonic emission in Si NCs. The radiative recombination in bulk Si is assisted by phonons. The recombination rate, $\Gamma_{\text{rad}}$, can be presented as[72]:

$$\Gamma_{\text{rad}} = \frac{1}{\tau_{\text{rad}}} = \frac{g_{\text{eh}}(T)}{\tau_{\text{rad}}^0} \coth\left(\frac{\hbar \Omega}{2T}\right).$$

Here, $\tau_{\text{rad}}^0$ is the radiative recombination lifetime at zero temperature, taken neglecting the Coulomb interaction between electrons and holes, and $g_{\text{eh}}$ is the effective Sommerfeld factor. The average optical phonon number, $\coth(\hbar \Omega/(2T)) \equiv 2N+1$ with $N=1/(\exp(\hbar \Omega/T)-1)$, where $\hbar \Omega \sim 60\text{meV} \sim 700\text{K}$ is the characteristic optical phonon energy of Si, accounts for the sum of Stokes and anti-Stokes processes. It is close to unity at room temperature ($N \ll 1$) and increases at higher temperatures due to the growth of the average optical phonon number resulting in (i) stimulation of the Stokes processes ($\sim N+1$) and (ii) emergence of anti-Stokes processes with phonon absorption ($\sim N$). However, the total radiative rate in the bulk decreases with temperature because of the Sommerfeld factor $g_{\text{eh}}(T)$ in Eq. 3.3[72, 73]. The Sommerfeld factor describes the modification of the radiative rate due to Coulomb attraction between electrons and holes. For hot carriers, the Coulomb interaction becomes relatively weak as compared to the kinetic energy, the effective electron-hole distance increases, and the radiative recombination is quenched. In NCs the temperature dependence of the radiative rate differs strongly from the bulk and the rate can increase with temperature. Namely, for the considered sizes of the NCs, the recombination remains phonon-assisted[74]. However, the Coulomb interaction becomes weaker than the quantum confinement, since the sizes of the considered Si NCs are smaller than the bulk exciton radius $a_B \sim 4.4\text{nm}[75]$. As a result, the change of the Sommerfeld factor can be neglected. The radiative rate is then solely determined by the phonon population, $1/\tau_{\text{rad}} = \coth(\hbar \Omega/(2T))$ and should increase with temperature. The increase of the radiative rate becomes substantial for temperatures comparable with the optical phonon energy, $\hbar \Omega \sim 700\text{K}$.
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Figure 3.2: Evidence for laser-induced heating under continuous wave excitation. (a) Power dependence of the PL intensity ($\lambda_{\text{det}}=915\text{nm}$, $E_{\text{det}}=1.36\text{eV}$) of a ML sample (PECVD) with a spacer thickness of 1.6nm (ML2) under 405nm (3.06eV) cw (red up-triangles) and 532nm (3.49eV) pulsed (blue up-triangles) excitation, depicted in a double logarithmic representation. The results for the cw excitation are scaled to maximally overlay at low powers with the data obtained under pulsed excitation. (b) Normalized PL intensity ($\lambda_{\text{det}}=915\text{nm}$, $E_{\text{det}}=1.36\text{eV}$) versus excitation photon flux for the ML samples (PECVD) with spacer thicknesses of 1 (squares, ML1), 1.6 (up-triangles, ML2), 2.2 (down-triangles, ML3) and 2.8nm (diamonds, ML4) under 405nm cw excitation (scaled to maximally overlay the below-saturation points), in a double logarithmic representation. (c) Schematic illustration (not to scale) of the discussed processes for samples with different spacer layer thicknesses (right and left column) and under low (top row) and high (bottom row) excitation photon flux. With increasing incident photon flux (purple arrows), the photon emission (magenta wavy arrows) as well as the phonon generation rate (dark green zigzag arrows) increases (indicated by the thickness of the symbols), while the phonon density increases for thinner spacers. Under low excitation photon flux, the phonon generation rate is low and the spacer thickness-dependent phonon density does not lead to a strong enough temperature enhancement, such that the radiative emission rate, $\Gamma_{\text{rad}}$, is not significantly influenced. Therefore the below-saturation points in panel (b) are independent of the spacer thickness. The increase of the radiative rate becomes substantial at high temperatures, when the phonon density is high. Thus, at high flux, the phonon density, which is dependent on the spacer thickness, is an important parameter which governs the enhancement of the radiative emission rate. This can also be seen in panel (b), where stronger saturation (lower radiative emission rate) occurs for thicker spacers (lower phonon density).
In order to estimate whether such a strong heating of the NC layers is plausible, we have considered the balance between the absorption of the laser power and the heat escape through the layer boundary. Our analysis of the heat equation\cite{76} in the film geometry is described in more detail in the Section 3.5.2. The temperature of the sputtered layer with the thickness $L \sim 1 \mu m$ has been evaluated as $T \sim 300K + P_{abs} \xi / (2\pi k L)$, where $P_{abs}$ is the absorbed laser power, $k$ is the heat conductivity and $\xi = \ln(k L / (2\alpha R^2)) / 2$ is the dimensionless factor of the order of unity, depending on the excitation spot radius $R$ and the heat transfer through the film boundary $\alpha$. In crystalline Si and SiO$_2$ the heat conductivity coefficients are equal to $k \sim 140 W/(m \cdot K)$ and $k \sim 1 W/(m \cdot K)$, respectively. This value leads to a relatively weak temperature increase of the order of $\sim 100K$ at the highest investigated flux under 405nm cw excitation. However, it has been shown in, among others, Refs \cite{77} and \cite{78} that the heat conductivity becomes more than 10 times lower in thin SiO$_2$ films with the thickness of the order of microns, compared to bulk SiO$_2$. In the samples investigated in this study, the effective heat conductivity should be mostly determined by SiO$_2$, since its volume fraction in the studied samples exceeds 75%. Thus, we can reasonably assume a fivefold suppression of the heat conductivity in the considered sputtered ML structures, where each active and passive layer has a thickness below 10nm, $k \sim 0.3 W/(m \cdot K)$. As a result, we arrive to a temperature of $\sim 1000K$ and a radiative rate increase of $\sim 3$ times, which is in a quantitative agreement with our experimental findings. For a given heat conductivity, this temperature increase reduces with the total thickness of the sputtered ML film and is therefore suppressed for thicker spacers between the NC layers, again in good agreement with the experimental results in Fig. 3.2(b). We also note that in the proposed description, we take into account carrier interactions with optical phonons only. Possible contributions from acoustic phonons, with lower characteristic energies, will lead to the rate enhancement even at lower temperatures. Thus, our results should be considered as an estimation of the lowest possible radiative rate enhancement.

The laser-induced heating of the sample and the related presence of phonons have a pronounced effect on the PL spectrum as well. At low temperature, the exciton recombination involves predominantly the release of phonons, resulting in a spectrally red-shifted PL spectrum compared to the exciton energy (Stokes replica). At higher temperatures, also radiative recombination accompanied by phonon absorption (anti-Stokes emission) appears, resulting in an effective blueshift of the PL spectrum at high excitation photon flux. This effect is indeed experimentally observed (see the persistent blueshift of the PL spectrum above the expected saturation point in Fig. 3.1(b)). The appearance of the blueshift for the high-flux regime cannot be explained by the NC size-dependent absorption cross section, as discussed earlier, and provides the most direct support for the proposed interpretation of the additional emission in terms of its thermal stimulation.

### 3.3.4 Alternative mechanisms

For completeness, we will now discuss alternatives for the possible origin of the continuation of the PL intensity increase and the blueshift of the PL spectrum above the saturation point. One possibility of the additional PL at high pumping flux is the excited-state emission, as proposed by G. Faraci et al. to explain the giant superlinearly increasing PL intensity in crystalline Si grains of about 100nm size\cite{64}. The necessary condition in that case is that the radiative rate is significantly larger and/or the AR rate reduces for hot compared to ground-state excitons. However, it is well established that the phonon-assisted radiative recombination rates are nearly identical for low-lying excited states, since the matrix elements of the interaction between carriers and optical phonons are not strongly modified at low excitation energies.

Another way to generate additional photons above the saturation level predicted by the commonly accepted model is to allow radiative recombination from two (biexciton) or more electron-hole pairs in a single NC, as proposed by, among others, D. Kovalev et al.\cite{62} and F. Pevere et al.\cite{79}. Our additional analysis indicates, however, that the biexciton model cannot explain the observed PL intensity enhancement. Applying the biexciton model to our data, requires values of $\sim 100-400$ns for the non-
radiative lifetime of the biexciton. This is controlled by the AR process, as mentioned before (see Section 3.5.3 for further details and a corresponding fit to our data). Although AR times of an order of a nanosecond have been occasionally proposed by theory in the past\[60, 80\], and more recently for NCs with certain “resonance” dimensions\[81\], they are much different from some obtained in more recent calculations\[20\] and, most important, are at variance with multiple experimental data\[32, 35, 82, 83, 84\]. To establish the AR time in our sample, we have carefully measured it using a femtosecond pump-probe technique. The NCs were excited by 500nm (2.48eV) photons and a NIR continuum (850-1600nm, 0.78-1.46eV) was used as a probe pulse. Following the procedure introduced by Klimov et al.\[12\], we have cautiously measured transient IA dynamics for several excitation intensities of the pump, as shown in Fig. 3.3. From this data, we conclude that the biexciton lifetime for our ML sample is shorter than 100ps, in agreement with previous reports\[32, 35, 82, 83, 84\] and recent calculations\[20\]. This value is much smaller than the AR time necessary in order to explain the experimentally observed PL intensity enhancement within the framework of the biexciton model. Therefore, we exclude that biexciton emission is responsible for the PL intensity enhancement observed in this study.

![ transient induced absorption dynamics for several excitation photon fluences. Normalized transient IA dynamics of the same sample as depicted in Fig. 3.1 under 500nm (2.48eV) excitation measured at probe wavelengths near 1250nm (0.99eV, obtained by integrating the signal from 1200 to 1300nm) for pump pulse fluences of 0.4 (diamonds), 1.6 (down-triangles), 3.0 (up-triangles), 6.0 (squares) and 12.0mW (circles). Transients are normalized to an equal number of absorbed photons. ]

### 3.4 Conclusions

In conclusion, we have demonstrated that the radiative rate of exciton recombination in Si NCs can be effectively enhanced by temperature increase. In particular, a threefold enhancement has been demonstrated upon laser-induced heating in ML structures of Si NCs embedded in SiO\(_2\). Future research will
have to test the limits of this effect and tell whether a purposeful phonon management in Si nanostructures can yield radiative recombination rates with application potential. For example, the insulation of the NCs or the use of a matrix with a better or worse thermal conductivity can affect the radiative lifetime and also lower the onset of the radiative rate enhancement. Moreover, the possibility of phonon injection should be investigated to increase the radiative rate without inducing damage to the sample due to heat generation. The present study therefore identifies an important new advantage of Si NCs and shows that dedicated phonon management on the nanoscale could offer a possible avenue to enhance the optical faculty of Si, toward the much desired Si photonics. Moreover, since the photon fluxes under which the observed increase of the radiative emission rate takes place are comparable to those in concentrator photovoltaics, the current findings could also be relevant for the use of Si NCs in future generations of solar cells.

### 3.5 Supporting information

#### 3.5.1 Supporting figures

![Figure 3.4: Photoluminescence intensity as function of illumination time. When the sample is exposed to the highest excitation photon flux ($\lambda_{\text{exc}}=405\text{nm}, E_{\text{exc}}=3.06\text{eV}$) used in this study, the PL intensity decreases toward a constant value within 100s. This value remains constant and is reproduced after the laser is blocked for 15min, indicating that the decrease of the PL intensity is permanent, so irreversible. In order to exclude this effect, in this study we have always laser-illuminated the sample for several minutes before each measurement, until the PL intensity stabilized, and during the measurement itself we have checked the reproducibility of the data by ramping in laser power back and forth. All the results reported here are obtained under conditions where no permanent change to the samples occurred and are reproducible on the same sample.](image-url)
Figure 3.5: **Raman spectra under 514nm (2.4eV) continuous wave excitation.** (a) Raman spectrum of the ML film with Si NCs (same sample as used for the results depicted in Fig. 3.1 and Fig. 3.3) for a broad detection window showing the PL from the Si NCs. (b) Raman spectrum of bulk Si (dashed gray) and the Si NCs sample (black) zoomed into a narrow detection window ranging from 450 to 600cm\(^{-1}\). The first order Si-Si peak is clearly visible for the Si wafer, but is hidden underneath the PL from the Si NCs, preventing the estimation of the local temperature of the ML.

Figure 3.6: **Flux dependence of the photoluminescence intensity for a Si nanocrystals in SiO\(_2\) sample under 405nm (3.06eV) continuous wave excitation.** (a) The PL intensity of the same sample as depicted in Fig. 3.1 at \(\lambda_{\text{det}}=750\) (\(E_{\text{det}}=1.65\text{eV}\), red), \(\lambda_{\text{det}}=800\) (\(E_{\text{det}}=1.55\text{eV}\), violet) and \(\lambda_{\text{det}}=850\)nm (\(E_{\text{det}}=1.46\text{eV}\), blue) as function of the excitation photon flux, depicted in a double logarithmic representation. The curves have been scaled vertically to overlap at the low flux. (b) Two PL spectra of the sample depicted in Fig. 3.1 at relatively low (blue) and high (red) excitation fluxes.
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3.5.2 Theoretical evaluation of the temperature of the multilayer film

Our goal is to estimate the temperature increase, \( T' \), of the ML film with Si NCs, shown in Fig. 3.7, due to the cw laser illumination. To this end, we solve the heat transport equation\[76\]:

\[
\text{div} \ k(z) \ \text{grad} \ T'(\rho, z) = -Q(\rho, z)
\]

with \( k(z) = \begin{cases} 
0, & z < 0 \\
\kappa, & 0 < z < L \\
0, & \text{otherwise}
\end{cases} \), \( \angle 3.4 \)

with the boundary condition:

\[-k \frac{dT'}{dz} = \alpha T', \]

both at the upper and lower boundaries of the film, \( z=0 \) and \( z=L \). Here, \( \alpha \) is the heat transfer coefficient through the boundary. We assume, a homogeneous heat source with the radius \( R \),

\[ Q(\rho, z) = \begin{cases} 
Q, & 0 < z < L, \rho < R \\
0, & \text{otherwise}
\end{cases} \], \( \angle 3.6 \)

with the heat volume density \( Q = \frac{P}{\pi R^2} \) and \( P \) being the absorbed power. The homogeneous approximation is valid since the film thickness is smaller than the light absorption length. This is verified by the measured optical density, that is equal to \( \sim 0.16 \) for the highest flux.

The system of Eqs 3.4 to 3.6 can be solved using the Green function of the heat equation,

\[
\text{div} \ k(z) \ \text{grad} \ G(\rho - \rho', z, z') = \delta(\rho - \rho'),
\]

that is found by means of the Fourier expansion along the coordinates \( x \) and \( y \):

\[
G = \int \int \frac{d_2q}{(2\pi)^2} \frac{1}{2q} e^{iq(\rho - \rho')} g_q(z)
\]

\( \angle 3.8 \)

with \( g_q(z) = e^{-q|z-z'|} + 2A \cosh q(z-L/2), 0 < z < L. \)

The coefficient \( A \) is determined from the boundary conditions as:

\[
A = \frac{(kq - \alpha)e^{-q(L/2-z')}}{2[\alpha \cosh(qL/2) + kq \sinh(qL/2)]}.
\]

\( \angle 3.9 \)

The temperature reads:

\[
T'(r) = \int d^3r' G(\rho - \rho', z, z') Q(\rho, z').
\]

\( \angle 3.10 \)

Substituting the Green function, we find the temperature in the center of the spot as:

\[
T'(z,\rho = 0) = \frac{QR}{k} \int_0^\infty dq \frac{J_1(qR)}{q^2} F(q)
\]

\( \angle 3.11 \)

with \( F(q) = 1 - \frac{\alpha \cosh(q(z-L/2))}{\alpha \cosh(qL/2) + kq \sinh(qL/2)} \).

Next, we present an approximate analytical estimation of the integral taking into account that the pump spot radius \( R=5\mu m \) is much larger than the film thickness \( L\sim 0.85\mu m \). The expression under the integral in Eq. 3.11 has two factors, the form factor containing the Bessel function and the factor \( F(q) \) depending on the heat transfer coefficient. We expand the first factor in the series over the small parameter \( qR \) and assume that the heat conductivity is weak, \( F(q)\approx 1 \). This yields the following integral for the temperature:

\[
T' = \frac{QR^2}{2k} \int \frac{dq}{q},
\]

\( \angle 3.12 \)
Figure 3.7: Sketch of the film with Si nanocrystals under the focused laser illumination. The optically active layer, on top of an SiO₂ substrate with heat conductivity \( k_{\text{sub}} \), has a ML structure with thickness \( L \) and a heat conductivity \( k_{\text{film}} \). It is exposed to a laser beam with a pump spot radius \( R \). That diverges at both lower and upper limits. The integral can be made convergent by introducing the cutoffs at \( q=0 \) and \( q=\infty \) by comparing it with the exact integral (Eq. 3.11), that is regular both at \( q=0 \) and \( q=\infty \). The upper cutoff in Eq. 3.12 is at \( q_{\text{max}} \sim 1/R \), where the Bessel function starts decaying. The lower cutoff in Eq. 3.12 is at the wave vector \( q_{\text{min}}=\sqrt{2\alpha/kL} \), where the factor \( F(q) \) becomes small. As a result, the temperature can be estimated as:

\[
T' = \frac{QR^2}{2k} \frac{2\xi}{\pi kL},
\]

(3.13)

with the dimensionless coefficient:

\[
\xi = \ln \frac{q_{\text{max}}}{q_{\text{min}}} = \frac{1}{2} \ln \left( \frac{kL}{2\alpha R^2} \right).
\]

(3.14)

The exact value of the heat transfer coefficient \( \alpha \) at the film boundaries is not known since it depends on the microscopic structure of the sputtered MLs. We perform the numerical estimation using the values typical for the radiative transfer, \( \alpha \sim \sigma T^3 \), where \( \sigma=5.7 \times 10^{-8} \text{W/(m}^2\text{K})^4 \) is the Stefan-Boltzmann constant. For \( T=1000 \text{K} \), we obtain \( \alpha \sim 60 \text{W/(m}^2\text{K}) \). Using the value \( \alpha=100 \text{W/(m}^2\text{K}) \) and \( k \sim 0.3 \text{W/(m} \cdot \text{K}) \) we arrive at \( T' \sim 1000 \text{K} \) in Eq. 3.13, in agreement with the numerical evaluation of the integral (Eq. 3.11).

### 3.5.3 Determination of the biexciton lifetime

In general, a NC can be either in a ground or excited state containing one, two or more excited electron-hole pairs (excitons). Let us consider a universal model with \((n+1)\) states (where \( n \) is the maximum number of excitons in a NC). An electron-hole pair is created by the absorption of a photon and recombines with a characteristic lifetime, either radiatively or non-radiatively. A schematic diagram of this in the case of a three-state system is given in the inset of Fig. 3.8. The rate equation for the probability \( P_i \) to have \( i \geq 0 \) excitons in a single NC is of the form:

\[
\frac{dP_i}{dt} = \sigma \varphi (P_{i-1} - P_i) + \frac{P_{i+1}}{\tau_{i+1}} - \frac{P_i}{\tau_i},
\]

(3.15)

where \( \sigma \) is the absorption cross section, \( \varphi \) the excitation photon flux, \( \tau_i \) is the effective lifetime of the \( i \)th exciton, \( P_{-1}=0 \) and \( P_{\text{tot}}=\sum P_i=1 \). One approach to solving this in the steady-state case is the following.

In steady state we have \( \frac{dP_i}{dt}=0 \) and we can write Eq. 3.15 as the homogenous system:

\[
0 = MP,
\]

(3.16)
where \( P = P_0, \ldots, P_n \) and \( M \) are \( n \times n \) matrices containing \( \pm \sigma \varphi \) and \( \pm \frac{1}{\tau_1} \) at the appropriate positions. The general solution for an \( n \)-state system is:

\[
\begin{cases}
  P_0 = \frac{1}{\Delta} \\
  P_i = \prod_{k=1}^{i} \sigma \tau_k \varphi / \Delta & 1 \leq i \leq n
\end{cases}
\]

with \( \Delta = 1 + \prod_{i=1}^{n} (\prod_{k=1}^{i} \sigma \tau_k \varphi) \). The effective lifetime is:

\[
\frac{1}{\tau_i} = \frac{1}{\tau_{i,rad}} + \frac{1}{\tau_{i,nrad}},
\]

where \( \tau_{i,rad} \) and \( \tau_{i,nrad} \) are the radiative and non-radiative lifetimes, respectively. The PL intensity (average number of total emitted photons per second) from an \( n \)-state system is given by:

\[
I_{PL} = N^* \sum_{i=1}^{n} \frac{P_i}{\tau_{i,rad}},
\]

where \( N^* \) is the number of emitting NCs. It is also convenient to define:

\[
\varphi_i = (\sigma \tau_i)^{-1}.
\]

When we do not allow radiative recombination of higher states (more than one electron-hole pair in a single NC), the PL intensity under cw excitation is given by:

\[
I_{PL,2} = A_2 \frac{\varphi^2}{1 + \varphi / \varphi_1},
\]

where \( A_2 \) is a proportionality factor. This is the generally accepted model, where the PL intensity saturates completely as only a single exciton state gives photon emission. Since we do not observe such a complete saturation, it is evident that the observed excitation photon flux dependence of the PL intensity cannot be fitted by this equation.

Allowing for radiative recombination of biexcitons (i.e. two electron-hole pairs in a single NC), where there are four pathways for an electron and hole of the two electron-hole pairs to recombine, and we therefore assume \( \tau_{2,rad} = \frac{\tau_{1,rad}^4}{4} \), leads us to the following formula for the PL intensity:

\[
I_{PL,3} = A_3 \frac{\varphi + 4\varphi^2 / \varphi_1}{1 + \varphi / \varphi_1 + \varphi^2 / (\varphi_1 \varphi_2)},
\]

where \( A_3 \) is a proportionality constant. This formula allows us to fit the power-dependent PL intensity data. From the fit we can determine the recombination time of biexcitons. Using the value of \( \rho = \frac{\varphi_2}{\varphi_1} = \frac{\tau_2}{\tau_1} \sim 490 \) for the sample depicted in Fig. 3.1 together with the effective lifetime of the exciton (\( \tau_1 \sim 130 \mu s \)), which we have determined from the experimentally measured PL decay dynamics, we arrive to a value of \( \sim 265\mu s \) for the effective lifetime of the biexciton. The radiative biexciton lifetime is in the microseconds range, since \( \tau_{2,rad} = \frac{\tau_{1,rad}^4}{4} \), where \( \eta_1 \) is the quantum efficiency of the exciton, which has a value between 0 and 1. Using this information together with Eq. 3.18, we can approximate \( \tau_2 \sim \tau_{2,rad} \). Therefore, we can assume that the method probes the non-radiative lifetime of the biexciton, which is usually directly linked to the AR time. This leads to a value of \( \sim 265\mu s \) for the AR time of the sample depicted in Fig. 3.1. Similar values are found for other samples. Thus, applying the biexciton model to our data, we arrive to values of more than 100ns for the non-radiative lifetime of the biexciton.
Figure 3.8: Typical flux dependence of the photoluminescence intensity for a Si nanocrystals in SiO$_2$ sample under 405nm (3.06eV) cw excitation with a fit to the biexciton model. The PL intensity ($\lambda_{det}=870\text{nm}$, $E_{det}=1.43\text{eV}$) over more than four orders of magnitude of the excitation pump flux in a double logarithmic representation with a fit to Eq. 3.22 (gray curve) of the same sample as depicted in Fig. 3.1. A schematic diagram of three-state system is shown in the inset, as described by Eq. 3.15.