Anomalous temperature dependence of the the spin-flip thermalization time between the dark and bright exciton states in silicon nanocrystals

Brian Julsgaard, Ying-Wei Lu, Peter Balling, and Arne Nylandsted Larsen
Dept. of Physics and Astronomy, University of Aarhus, Ny Munkegade 120, DK-8000 Aarhus C, Denmark.
(Dated: September 10, 2009)

Silicon nanocrystals are studied by time-resolved fluorescence spectroscopy. After laser excitation the bright and dark exciton ground state levels are populated at random, but subsequently the decay curves reveal a thermalization between these levels. The characteristic thermalization time is found to be approximately 100 ns for temperatures below 100 K and surprisingly increases for higher temperatures. The decay curves are analyzed using a simple two-state model for the bright and dark exciton ground states.

Since the discovery of light emission from porous silicon, the structural and optical properties of nanostructured silicon has been studied extensively. In particular, the electron-hole exchange interaction is responsible for splitting the exciton ground state into bright (radiative recombination dipole allowed) and dark (almost dipole forbidden) states, which was demonstrated by time-resolved fluorescence measurements for various temperatures while assuming the bright and dark state populations to be in thermal equilibrium. However, the spin-flip mechanism behind this thermalization has not yet been studied for silicon nanocrystals (NCs). In this letter we demonstrate that the spin-flip process can be seen directly in the luminescence decay curves, and we measure the characteristic time scale for the thermalization versus temperature.

A sample of silicon NCs was prepared by magnetron sputtering, annealed at 1100°C for 1 hour in N₂ (2 Bar), and subsequently passivated at 500°C for 1 hour in 95% N₂ + 5% H₂ (2.4 Bar). By co-sputtering Si and SiO₂ on a Si-wafer an approximately 300 nm thick layer of SiO₂ was achieved with x = 1.60±0.05 determined by Rutherford backscattering spectrometry (corresponding to a silicon excess concentration of 25±5%). The room-temperature luminescence spectrum (late-time spectra in Fig. 1(c)) is peaked at 787 nm, being consistent with previously reported results for ~ 2 nm diameter NCs (when considering the differences between magnetron sputtering and plasma-enhanced chemical vapor deposition).

The experimental setup is shown in Fig. 1(a). A frequency-doubled Ti:Sapphire femtosecond laser delivers pulses at 400 nm with a repetition rate of 1 kHz and excites the NC sample, which is contained in a closed-cycle cryostat. The luminescence is spectrally filtered by a monochromator (Δλ = 2.5 nm) and detected by a silicon avalanche photo-diode (APD). A reference detector enables correction for variations in pump power. The sample emits light in two main bands, see Fig. 1(c). At early times the luminescence is centered around 550 nm and decays on a time scale of 1.5 ns independent on emission wavelength and temperature. For this reason, the long-wavelength tail of the early-time band can be identified and subtracted from the late-time band, which is centered in the range of 750-800 nm. We attribute the late-time emission to the exciton recombination in the NCs while the early-time luminescence closely resembles the emission from oxygen-related defects. Support to this picture is also given by the fact that the late-time emission center energy varies with temperature in a way not very different from the bulk silicon bandgap variation (Fig. 1(d)), while the early-time band center energy is independent on temperature. In the following we focus on the late-time band only, and the early-time contribution has been subtracted from all the data shown in Fig. 1.

The ground state of the quantum confined exciton is...
split into two (double-degenerate) states, a bright state, $|B\rangle$, and a dark state, $|D\rangle$ (Fig. 1(b)). The bright state can recombine radiatively via a $\Delta J = 1$ transition, while the dark state is ideally radiatively forbidden ($\Delta J = 2$). The selection rules do not apply strictly, but we expect a small ratio, $R = \Gamma_{D,\text{rad}}/\Gamma_{B,\text{rad}}$, between the radiative decay channels from the exciton states.

The simple model of Fig. 1(b) has previously been applied successfully to other semiconductor NCs, and is described by the rate equations:

$$\frac{\partial \rho_B}{\partial t} = -(\Gamma_B + \Gamma_{BD})\rho_B + \Gamma_{DB}\rho_D,$$

$$\frac{\partial \rho_D}{\partial t} = \Gamma_{DB}\rho_B - (\Gamma_D + \Gamma_{DB})\rho_D,$$

(1)

where $\rho_B$ and $\rho_D$ describe the populations in the bright and dark exciton states, respectively. The spin-flip rates between $|B\rangle$ and $|D\rangle$ are denoted by $\Gamma_{BD}$ and $\Gamma_{DB}$. $\Gamma_B = \Gamma_{B,\text{rad}} + \Gamma_{B,\text{spin}}$ is the total decay rate of the bright state (and similarly for $\Gamma_D$). Equations (1) can be solved exactly, leading to a bi-exponential decay of $\rho_B$ and $\rho_D$. However, before writing the solution, we make the following simplifying assumptions: (1) The exciton spin-flip rates are fast compared to the exciton decay rates such that $\Gamma_{BD}$ and $\Gamma_{DB}$ must drive the populations $\rho_B$ and $\rho_D$ toward thermal equilibrium. The relation $\Gamma_{BD} = \Gamma_{DB} e^{-\Delta/kT}$ will assure this, where $\Delta$ is the energy splitting between the bright and dark states, $k$ is Boltzmann’s constant, and $T$ is the temperature. (3) Immediately after laser excitation and subsequent carrier relaxation (which takes place on a sub-picosecond time scale) the exciton ground states the population of the exciton states is random: $\rho_B(0) = \rho_D(0) = \frac{1}{2}$. We then get:

$$\rho_B(t) = \frac{1}{2}[1 - e^{-\Delta/kT}] e^{-\gamma t} + e^{-\Delta/kT} e^{-\gamma t},$$

$$\rho_D(t) = \frac{1}{2}[1 - e^{-\Delta/kT}] e^{-\gamma t} + e^{-\Delta/kT} e^{-\gamma t},$$

(2)

where the fast decay rate characteristic of the spin thermalization is given by: $\gamma_f = \Gamma_B + \Gamma_D$, and the slow decay rate, $\gamma_s = \Gamma_{B,\text{rad}} e^{-\Delta/kT} + \Gamma_{D,\text{rad}} e^{-\Delta/kT}$, characterizes the total population decay: $\rho_B(t) + \rho_D(t) = e^{-\gamma t}$. Note that for times, $t \gg \gamma_f^{-1}$, the exciton populations have thermalized: $\rho_B(t)/\rho_D(t) = e^{-\Delta/kT}$.

The time-dependent probability of photon emission depends on the radiative decay rates: $p(t) = \Gamma_{B,\text{rad}}\rho_B(t) + \Gamma_{D,\text{rad}}\rho_D(t)$, and is written:

$$p(t) = \frac{1}{2}(\Gamma_{B,\text{rad}} - \Gamma_{D,\text{rad}})(1 - e^{-\Delta/kT}) e^{-\gamma t} + \Gamma_{B,\text{rad}} e^{-\Delta/kT} + \Gamma_{D,\text{rad}} e^{-\Delta/kT} e^{-\gamma t}$$

$$\equiv A_t e^{-\gamma t} + A_s e^{-\gamma t},$$

(4)

where $A_t = \frac{\Gamma_{B,\text{rad}} - \Gamma_{D,\text{rad}}}{2}$, independent on temperature. This reflects the initial random population of the exciton states. At longer times, $t \gg \gamma_f^{-1}$, the second term determines the light emission. Experimentally, the detected fluorescence from a sample containing NCs will depend on NC density, excitation power, detection efficiency of the entire optical setup, etc. Hence an unknown front factor must be multiplied to Eq. (4) and we cannot determine $\Gamma_{B,\text{rad}}$ and $\Gamma_{D,\text{rad}}$ on an absolute scale but only the ratio, $R = \Gamma_{D,\text{rad}}/\Gamma_{B,\text{rad}}$, as was also pointed out previously. However, the ratio, $\frac{A_t}{A_s} = \frac{1}{R} e^{-\Delta/kT}$, is independent on the specific experimental setup. Information about the total decay rates, $\Gamma_B$ and $\Gamma_D$, and the spin-flip rates, $\Gamma_{BD}$, $\Gamma_{DB}$, can be extracted from $\gamma_s$ and $\gamma_f$, respectively. In practice, the decay curves will not be single-exponential due to inhomogeneous broadening of the decay rates. However, it can easily be shown that the predictions for $A_t$ and $A_s$ are valid provided that $\Gamma_{B,\text{rad}}$ and $\Gamma_{D,\text{rad}}$ represent the mean values of the radiative decay rates.

Time-resolved decay curves were obtained for nine different temperatures between 16 K and 294 K at detection wavelengths following the center of the late-time emission spectra (Fig. 2). Four representative curves are shown in Fig. 2(a,b). In Fig. 2(a) it can be seen that the zero-time fluorescence is essentially independent on temperature while it is very different after one microsecond.
This is consistent with our assumption of initial random population in |B⟩ and |D⟩ followed by thermalization. In Fig. 2(b) the decay curves are shown for the entire laser repetition period of 1 ms. The characteristic decay time decreases with decreasing temperature since the population freezes out in the dark state, |D⟩. Fig. 2(a,b) clearly demonstrate that the spin thermalization is much faster than the exciton population decay as was assumed in the model. At the lowest temperatures, the population decay time is comparable to the laser repetition period, which must be taken into account when extracting the slow amplitude, $A_s$, from these curves. The fast amplitude, $A_f$, is extracted by comparing the initial part of the decay curves in Fig. 2(a) with a local single-exponential fit in the time range 2-5 μs (marked by straight lines for two of the curves in Fig. 2(a)).

The extracted values of $A_s$ and $A_f/A_s$ are plotted in Fig. 3(a) and compared to the model of Eq. (1) (red curve). We find a reasonable agreement when $R = 0.013 \pm 0.003$ and $\Delta = 15.0 \pm 1.5$ meV. The data in Fig. 3(a) is a consequence of thermal equilibrium and essentially confirms previously reported results. The observation that the data in Fig. 3(b) follows our model is strongly supporting the assumption that the initial decay (Fig. 2(a)) is caused by spin thermalization between the bright and dark exciton states.

Since the decay curves shown in Fig. 2(a,b) are in general not single exponential, we make a multi-exponential fit, $f(t) = \sum p_a \exp(-\gamma_at)$, to the curves and define the characteristic decay rate, $\gamma^* = \sum p_a/\sum p_a$]. This decay rate corresponds to a single-exponential decay preserving the initial amplitude and the area under the decay curve. The data in Fig. 2(b) has been fitted using three terms, and the resulting characteristic decay time, $1/\gamma^*$, is plotted in Fig. 3(c). The data ranges from 45 μs at 294 K to 1.1 ms at 16 K. The fact that the relative change in $\gamma^*$, which depends on $\Gamma_B$ and $\Gamma_D$, is comparable to the relative change in $A_s$, which depends on $\Gamma_{B,\text{rad}}$ and $\Gamma_{D,\text{rad}}$, indicates that the quantum efficiency of the exciton light emission is relatively high.

The initial thermalization part of Fig. 2(a) is fitted using one or two exponential terms, two examples are shown in Fig. 2(c,d) for 16 K and 294 K, respectively. As exemplified, the lowest temperatures require two terms in the fit, while one term is sufficient for the highest temperatures. The characteristic thermalization time, $1/\gamma^*$, is plotted in Fig. 3(d), and we see that for low temperatures the thermalization time is approximately 100 ns. For higher temperatures, the initial random population is much closer to thermal equilibrium, which seems to slow down the thermalization rate. This slowing down is also indicated by the requirement of a bi-exponential fit in Fig. 2(c), although we cannot exclude inhomogeneous broadening effects on the spin-flip time. In the literature, a commonly applied model for the spin-flip rate is: $\Gamma_{BD} = \Gamma_0(N + 1)$, $\Gamma_{DB} = \Gamma_0 N$, where $\Gamma_0$ is a characteristic zero-temperature rate and $N = (e^{\Delta/kT} - 1)^{-1}$ is the number of phonons available at the transition energy, $\Delta$. This model is certainly invalid in our case. Although the two-state model in Fig. 1(b) assumes the (unknown) splitting between heavy and light holes to be larger than $kT$, the analysis shows that the model captures the main characteristics of the spin-flip dynamics.

The results can be compared to bright/dark-state spin-flip times in other NC systems at low temperatures. For InAs$^{12}$ and InGaAs$^{10,13}$ NCs similar time scales of the order of 100 ns have been reported. However, this is not unique for all NCs. In CdSe$^{11}$ NCs the spin-flip time is of the order of 10 ns, whereas a much faster upper bound of 200 ps was reported$^{14}$ for InP NCs (in this case a constant low-temperature spin-flip time was also reported).

In conclusion, we have measured the spin-flip thermalization time between bright and dark exciton states in silicon nanocrystals and found a constant thermalization time of 100 ns below 100 K and counter-intuitively increasing with temperature above 100 K. This work was supported by The Danish Council for Independent Research | Natural Sciences (FNU) and Technology and Production Sciences (FTP, SERBINA project). We are grateful to Brian Bech Nielsen for supplying the cryo cooler and for useful discussions.
1. L. T. Canham, Appl. Phys. Lett. 57, 1046 (1990).
2. M. Bayer, G. Ortner, O. Stern, A. Kuther, A. A. Gorbanov, A. Forchel, P. Hawrylak, S. Fafard, K. Hinzer, T. L. Reinecke, S. N. Walck, J. P. Reithmaier, F. Klopf, and F. Schäfer, Phys. Rev. B 65, 195315 (2002).
3. P. D. J. Calcott, K. J. Nash, L. T. Canham, M. J. Kane, and D. Brunhead, J. Phys.: Condens. Matter 5, L91 (1993).
4. S. Lüttjohann, C. Meier, M. Offer, A. Lorke, and H. Wiggers, Europhys. Lett. 79, 37002 (2007).
5. M. L. Brongersma, P. G. Kik, A. Polman, K. S. Min, and H. A. Atwater, Appl. Phys. Lett. 76, 351 (2000).
6. V. Vinciguerra, G. Franzo, F. Priolo, F. Iacona, and C. Spinella, J. Appl. Phys. 87, 8165 (2000).
7. F. Iacona, G. Franzo, and C. Spinella, J. Appl. Phys. 87, 1295 (2000).
8. G. Franco, M. Miritello, S. Boninelli, R. Lo Savio, M. G. Grimaldi, F. Priolo, F. Iacona, G. Nicotra, C. Spinella, and S. Coffa, J. Appl. Phys. 104, 094306 (2008).
9. L. Tsybeskov, J. V. Vandyshhev, and P. M. Fauchet, Phys. Rev. B 49, 7821 (1994).
10. I. Favero, G. Cassabois, C. Voisin, C. Delalande, P. Roussignol, R. Ferreira, C. Couteau, J. P. Poizat, and J. M. Gérard, Phys. Rev. B 71, 233304 (2005).
11. B. Patton, W. Langbein, and U. Woggon, Phys. Rev. B 68, 125316 (2003).
12. J. Johansen, B. Julsgaard, S. Stobbe, J. M. Hvam, and P. Lodahl, Exciton spin-flip rate in quantum dots determined by a modified local density of optical states, preprint at http://arxiv.org/abs/0905.4493.
13. J. M. Smith, P. A. Dalgarno, R. J. Warburton, A. O. Govorov, K. Karrai, B. D. Gerardot, and P. M. Petroff, Phys. Rev. Lett. 94, 197402 (2005).
14. D. W. Snoke, J. Hübner, W. W. Rühle, and M. Zundel, Phys. Rev. B 70, 115329 (2004).
15. O. Labeau, P. Tamarat, and B. Lounis, Phys. Rev. Lett. 90, 257404 (2003).
16. Strictly speaking, $\Gamma_{DB} \gg \Gamma_B$ does not hold at low temperatures but the impact on the data analysis is negligible.
17. F. Trojanek, K. Neueldert, P. Malý, K. Dohnalova, and I. Pelant, J. Appl. Phys. 99, 116108 (2006).
18. Al. L. Efros, M. Rosen, M. Kuno, M. Nirmal, D. J. Norris, and M. Bawendi, Phys. Rev. B 54, 4843 (1996).