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Optical absorption cross section and quantum efficiency of a single silicon quantum dot

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ABSTRACT

Direct measurements of the optical absorption cross section (σ) and exciton lifetime are performed on a single silicon quantum dot fabricated by electron beam lithography (EBL), reactive ion etching (RIE) and oxidation. For this aim, single photon counting using, an avalanche photodiode detector (APD) is applied to record photoluminescence (PL) intensity traces under pulsed excitation. The PL decay is found to be of a mono-exponential character with a lifetime of 6.5 μ s. By recording the photoluminescence rise time at different photon fluxes the absorption cross could be extracted yielding a value of $1.46 \times 10^{-14} \text{ cm}^2$ under 405 nm excitation wavelength. The PL quantum efficiency is found to be about 9% for the specified single silicon quantum dot.

Keywords: Single silicon quantum dot, absorption cross section, quantum efficiency (QE), photoluminescence (PL) decay, luminescence rise time, silicon nanocrystals

1. INTRODUCTION

Quantum efficiency estimation of individual silicon quantum dots is of considerable importance, since it is one of the essential parameters influencing their applicability in optoelectronic and photonic devices. In order to determine the efficiency of an optical process in a nanocrystal, the physics of the photon absorption process as well as the emission mechanism must be well understood.

For years bulk silicon was considered as an inefficient light emitter due to its indirect band gap nature. After the discovery of strong photoluminescence (PL) emission of porous silicon at room temperature^{1,2}, silicon nanocrystals became the center of interest for many researchers^{3,4}. The quantum confinement model is believed to be relevant for silicon nanocrystals^{5,6}, coupling the observed increase of the band gap energy with the decrease of nanocrystal size. The development of the single-dot spectroscopy technique⁷ led to a deeper insight of the photophysics of nanocrystals, however, many aspects of the light emission mechanisms are still not well understood. In particular, studies of photoluminescence absorption and decay have been mainly focusing on ensembles of silicon nanocrystals so far^{8,9,10}, in which the effects of size and Si-SiO₂ interface nature of individual dots are averaged.

In the current work the results of PL lifetime and absorption cross section measurements of a single silicon quantum dot are presented. The samples were fabricated by electron beam lithography (EBL) and reactive ion etching (RIE), followed by self-limiting oxidation¹¹. The well-defined positions of individual silicon quantum dots formed by this method enable repeatable single-dot spectroscopy. The measurements were carried out under different excitation laser power densities, using an avalanche photodiode detector (APD) for recording luminescence traces. Blinking and spectroscopy experiments were also performed on the same dot as complementary measurements. An estimate of the quantum efficiency of this nanocrystal, taking into account the detectivity of the PL setup, is presented.

2. EXPERIMENTAL

The experimental PL setup consists of a conventional wide field optical microscope system connected to a spectrograph (Andor, Shamrock 500i) and an EMCCD camera (Andor, iXon3) at one port and to an avalanche photodiode (Becker & Hickl, DPC-230) at another port. A flipping mirror inside the microscope enables switching between these two ports.

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Figure 1 shows a simple schematic of the PL setup. The sample is excited using a UV laser (405 nm). Depending on the type of the PL measurements, the laser is operated in continuous or pulsed mode. For PL decay and absorption cross section measurements, pulsed excitation with a repetition rate of 20 kHz and on-time duration of 10 μ s is used. This is done at different excitation laser power densities (8- 80 Wcm^{-2}). On the other hand, for blinking measurements the PL intensity traces are recorded by the APD under continuous excitation (8 Wcm^{-2}). The laser beam has an angle of $\sim 30^\circ$ with respect to the sample surface and the emission is collected through a high numerical aperture lens (NA= 0.7) with 100x magnification. Appropriate optical components such as high quality filters and mirrors are used to block background luminescence.

Figure 1. A Schematic of the experimental PL setup. The excitation laser beam (405 nm) impinges on the sample surface at an angle of $\sim 30^\circ$. The emitted light is guided through an optical microscope and collected by an APD or spectrometer connected to an EMCCD camera for photon counting or spectral measurements, respectively.

The samples are fabricated in three steps. Electron beam lithography is used to define a pattern of undulating nano-walls on an n-type silicon wafer. Walls with three different thicknesses (40, 65 and 90 nm) are then formed by reactive ion etching (RIE). A simple schematic of one undulating nano-wall is shown in figure 2a. Finally, self-limiting oxidation inhomogeneously reduces the silicon structures, yielding individual silicon nanocrystals within the oxidized walls¹¹. Due to large pre-selected separation between the dots ($\sim 2 \mu\text{m}$), it is possible to perform several repeatable photoluminescence measurements on exactly the same dot. Applying short or long oxidation duration, single or double quantum dots can be formed in the thinnest and medium parts of the walls respectively¹¹. Figure 2c shows a typical PL image of the sample after short oxidation and under cw UV excitation. Figure 2b is an enlarged scanning electron microscope (SEM) image of the area specified by the gray rectangle in figure 2c. All the measurements are focused on one single silicon quantum dot indicated by the red arrow in figure 2c.

3. RESULTS

Figure 2d shows the room temperature PL spectrum of the single silicon quantum dot, specified by the red arrow in figure 2c, under 8 Wcm^{-2} cw excitation power density. The emission energy peaks at 1.695 eV with a line width of 100 meV. This is typical for single silicon nanocrystals at room temperature⁶. The low-energy satellite peak at a distance of 60 meV to the main peak is ascribed to TO phonon interactions. Previously it was shown that at lower temperatures the line-width of the main peak is narrower (~ 0.4 meV at 10K) and the TO-phonon replica can be better resolved^{12,13}. Blinking studies are also conducted on the same quantum dot based on single photon counting. For this purpose the PL intensity traces are recorded using an APD detector under continuous excitation of 8 Wcm^{-2} . For the particular dot studied, the emission intensity is relatively constant and blinking is only observed once at the end of the recorded trace, see Figure 3a.

Figure 2. (a) Schematic of an undulating silicon nano-wall with three different thicknesses. (b) SEM image of such nano-walls after RIE and before oxidation. (c) Photoluminescence image of single silicon quantum dots formed inside the thinnest part of the walls after short oxidation¹¹. The SEM image in (b) shows the details of the similar area determined by the grey rectangle. The single quantum dot under investigation is specified by a red arrow. (d) PL emission spectrum at room temperature and Gaussian fits to main (red) and satellite (blue) peak. Emission peaks at 1.695 eV with full width half maximum (FWHM) of 100 meV at an excitation power density of 8 Wcm^{-2} , the TO-phonon sideband is shifted 60 meV to lower energy with respect to the main peak.

From this, two distinct intensity levels, denoted as ON and OFF, can clearly be defined from its histogram (Figure 3b). The dashed line in between ON and OFF indicates the threshold that is used for the distinction between the two states. Blinking statistics of similar single silicon quantum dots have been studied in detail in earlier work¹⁴. Blinking and spectral measurements confirm that the luminescent object under investigation is indeed a “single” silicon quantum dot.

Figure 3. (a) PL Intensity traces of the studied single silicon quantum dot recorded at room temperature. (b) Corresponding histogram of the blinking traces, demonstrating the two distinct states (ON and OFF). A threshold line is considered in between the two levels.

Figure 4. Photoluminescence decay and rise of the single silicon dot specified by the red arrow in figure 2c, under two excitation power densities of 8 and 64 Wcm⁻². The solid lines are mono-exponential fits. (a) The photoluminescence decay exhibits a lifetime of 6.5 μs for both laser power densities, whereas the rise time strongly depends on excitation.

The photoluminescence transient decay and rise is studied under pulsed laser excitation at a frequency of 20 kHz using an on-time duration of 10 μs. The emitted photons are collected by the APD detector based on the single photon counting technique. The results are shown in figure 4 for two excitation power densities (8 and 64 Wcm⁻²).

A clear mono-exponential character with a lifetime of ~ 6.5 μs can be observed for the PL decay under different excitation laser power densities. This is consistent with the results obtained from an earlier study on several single quantum dots performing time-resolved measurements¹⁵.

The kinetics of the luminescence rise, as the laser is switched on, follows a mono-exponential function, as well. In this case, the obtained rise time (τ_{rise}) values under 8 and 64 Wcm⁻² excitation power densities are 3.76 μs and 0.49 μs, respectively.

Figure 5 shows the dependence of the luminescence rise rate on the excitation power density. A linear increase of the luminescence rise rate with excitation power can clearly be seen. This is expected from the equation of the temporal shape of the luminescence rise time¹⁶:

$$I(t) = I_0 \left\{ 1 - \exp \left[- \left(\sigma \phi + \frac{1}{\tau} \right) t \right] \right\} \quad (1)$$

Where ϕ is the excitation flux and τ is the photoluminescence decay time.

Thus, the slope of the linear function in figure 5 yields the absorption cross section to a value of $\sigma = 1.46 \times 10^{-14} \text{ cm}^2$ for the specified single silicon quantum dot under 405 nm excitation. This is within an order of magnitude in agreement with the values reported by other groups^{9,10} from measurements on ensemble of silicon nanocrystals.

The luminescence quantum efficiency (QE) is calculated using the formula for the excitation regime below saturation:

$$I = P \times \sigma \times D \times QE \quad (2)$$

Where P is the excitation flux, σ the absorption cross section and D the system detectivity¹⁷.

The system detectivity is measured for different optical components in the PL setup as the percentage of efficient light transmission/reflection through each of them. Approximately 10 % of the light is considered to be emitted efficiently

into the upper hemisphere of the single quantum dot from the surface¹⁸. Finally the obtained quantum efficiency is $\sim 9\%$, which is close to a previously reported value ($\sim 15\%$)¹⁹.

Figure 5. Reciprocal of the luminescence rise time versus photon flux under the saturation level. The luminescence rise rate is a linear function of the excitation flux.

4. CONCLUSION

Measurements of luminescence decay and rise time under different laser excitation power densities on an individual silicon quantum dot, using the photon counting technique, were performed. Two distinct emission intensity states, as well as spectral measurements, confirm the observation of a single silicon quantum dot. The decay time is of mono-exponential character with $6.5 \mu\text{s}$ decay time, which is in agreement with results obtained from time-resolved PL decay measurements on similar single silicon quantum dots¹⁵. The slope of the linear increase of the luminescence rise rate yields an absorption cross section value of $1.46 \times 10^{-14} \text{cm}^2$. The measured value of the absorption cross-section allowed us to estimate the quantum efficiency of this particular dot to be $\sim 9\%$.

It could be shown that luminescence transients can be successfully measured for a single silicon nanocrystal. This enables studies on many individual objects and subsequent comparison of their properties amongst each other, as well as to ensembles. Individual variations between single emitters can be resolved and possibly correlated to their structural differences in future work. In addition, the density of states of a nanocrystal can possibly be probed using this technique by applying different excitation wavelengths.

REFERENCES

- [1] Canham, L. T., "Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers," *Appl. Phys. Lett.* 57, 1046-1048 (1990).
- [2] Lehmann, V. and Gösele, U., "Porous silicon formation: A quantum wire effect," *Appl. Phys. Lett.* 57, 856-858 (1991).
- [3] Kovalev, D., Heckler, H., Polisski, G., Diener, J. and Kock, F., "Optical properties of silicon nanocrystals," *Optical Materials* 17, 35-40 (2001).
- [4] Meier, C., Gondorf, A., Lüttjohann, S., Lorke, A. and Wiggers, H., "Silicon nanoparticles: Absorption, emission, and the nature of the electronic bandgap," *J. Appl. Phys.* 101, 103112 (2007).
- [5] Wilson, W. L., Szajowski, P. F. and Brus, L. E., "Quantum Confinement in Size-Selected, Surface-Oxidized Silicon Nanocrystals," *Science* 19, 1242-1244 (1993).
- [6] Valenta, J., Juhasz, R. and Linnros, J., "Photoluminescence spectroscopy of single silicon quantum dots," *Appl. Phys. Lett.* 80, 1070-1072 (2002).
- [7] Moerner, W. E. and Fromm, D. P., "Methods of single-molecule fluorescence spectroscopy and microscopy," *Rev. Sci. Instrum.* 74, 3597-6319 (2003).
- [8] Linnros, J., Lalic, N., Galeckas, A. and Grivickas, V., "Analysis of the stretched exponential photoluminescence decay from nanometer-sized silicon crystals in SiO₂," *J. Appl. Phys.* 86, 6128-6134 (1999).
- [9] Kovalev, D., Diener, J., Heckler, H., Polisski, G., Kunzner, N. and Kock, F., "Optical absorption cross sections of silicon nanocrystals," *Phys. Rev. B* 61, 4485-4487 (2000).
- [10] Garcia, C., Garrido, B., Pellegrino, P., Ferre, R., Moreno, J. A., Morante, J. R., Pavesi, L. and Cazzanelli, M., "Size dependence of lifetime and absorption cross section of Si nanocrystals embedded in SiO₂," *Appl. Phys. Lett.* 82, 1595-1597 (2003).
- [11] Bruhn, B., Sangghaleh, F. and Linnros, J., "Fabricating single silicon quantum rods for repeatable single dot photoluminescence measurements," *Phys. Status Solidi A* 208, 631-634 (2011).
- [12] Sychugov, I., Valenta, J., Mitsuishi, K., Fujii, M. and Linnros, J., "Photoluminescence measurements of zero-phonon optical transitions in silicon nanocrystals," *Phys. Rev. B* 84, 125326 (2011).
- [13] Kovalev, D., Heckler, H., Ben-Chorin, M., Polisski, G., Schwartzkopff, M. and Koch, F., "Breakdown of the k-conservation rule in Si nanocrystals," *Phys. Rev. Lett.* 81, 2803-2806 (1998).
- [14] Bruhn, B., Valenta, J., Sangghaleh, F. and Linnros, J., "Blinking statistics of silicon quantum dots," *Nano Lett.* 11, 5574-5580 (2011).
- [15] Sangghaleh, F., Bruhn, B., Schmidt, T. and Linnros, J., "Exciton lifetime measurements of single silicon nanocrystals," *Nanotechnology*, in press (2013).
- [16] Priolo, F., Franzo, G., Pacifici, D., Vinciguerra, V., Iacona, F. and Irrera, A., "Role of the energy transfer in the optical properties of undoped and Er-doped interacting Si nanocrystals," *J. Appl. Phys.* 89, 264-272 (2001).
- [17] Valenta, J., Juhasz, R. and Linnros, J., "Photoluminescence from single silicon quantum dots at room temperature," *Journal of Luminescence* 98, 15-22 (2002).
- [18] Sychugov, I., Omi, H. and Kobayashi, Y., "On the role of the substrate in light-harvesting experiments," *Optics Lett.* 33, 1807-1809 (2008).
- [19] Sychugov, I., Galeckas, A., Elfström, N., Wilkinson, A. R., Elliman, R.G. and Linnros, J., "Effect of substrate proximity on luminescence yield from Si nanocrystals," *Appl. Phys. Lett.* 89, 111124 (2006).
- [20] Garrido Fernandez, B., López, M., García, C., Pérez-Rodríguez, A., Morante, J. R., Bonafos, C., Carrada, M. and Claverie, A., "Influence of average size and interface passivation on the spectral emission of Si nanocrystals embedded in SiO₂," *J. Appl. Phys.* 91, 798-807 (2002).