Synthesis and properties of single luminescent silicon quantum dots

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Abstract

Silicon is an ubiquitous electronic material and the discovery of strong room temperature luminescence from porous Si in 1990 raised hopes it may find a new lease of life in the emerging field of optoelectronics. First, the luminescence was shown to be emitted from nanostructures in a porous Si network. Later the same emission was seen from Si nanocrystals and the concept of a Si quantum dot emerged. A number of different models have been proposed for the origin of the light emission. Some involve interface states between a Si nanocrystal and a surrounding shell, while others consider the effect of quantum confinement in an indirect bandgap semiconductor.

In this work single Si nanocrystals were addressed to shed light on the mechanism of luminescence. Nanocrystals were prepared using e-beam lithography with subsequent etching and oxidation of silicon nanopillars. In particular, the non-uniform oxidation known as self-limiting oxidation was successfully used to form a single nanocrystal with characteristic size of several nanometers inside a nanopillar. This preparation method allowed optical probing of a single nanocrystal with far-field optics.

Results revealed sharp luminescence spectra at low temperatures with a linewidth of ~ 2 meV, which is less than the corresponding thermal broadening. This property is a signature of energy level discreteness, which is, in turn, a straightforward consequence of the quantum confinement model. Another effect observed was a random on-off blinking, which is also regarded as a hallmark of single fluorescent objects. This effect appeared to be dependent on the excitation power density suggesting the involvement of Auger-assisted ionization in the dynamics of nanocrystal luminescence. In addition, it was shown how a change in the surrounding optical mode density affects the main parameters of luminescence from Si nanocrystals, such as the radiative lifetime, the quantum efficiency and the total yield.

Finally, in order to clarify the influence of morphological properties, such as size or shape, of a Si quantum dot on its luminescence, combined low-temperature photoluminescence and transmission electron microscopy investigations were initiated. A method was developed using focused ion beam preparation for such a joint characterization.

To conclude, the work presented in this thesis gives support to the quantum confinement effect in explaining the light emission mechanism from nano-sized Si, as well as highlighting the importance of both nanocrystal morphological structure and surrounding matrix optical properties in the luminescence process.
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List of symbols and acronyms

CCD – Charge-coupled device
CdSe – cadmium selenide
DOS – Density of states
E-beam – Electron beam (lithography)
EL – Electroluminescence
FIB – Focused ion beam
FWHM – Full-width at half-maximum
GaAs – gallium arsenide
HF – Hydrofluoric acid
HMDS – hexamethyldisilazane
HeCd – helium cadmium laser
LA – Longitudinal acoustic (phonon)
LDOS – Local density of optical (states) modes
LO – Longitudinal optical (phonon)
PL – Photoluminescence
RIE – Reactive ion etching
SEM – Scanning electron microscopy
Si – silicon
STM – Scanning tunneling microscopy
TA – Transverse acoustic (phonon)
TEM – Transmission electron microscopy
TO – Transverse optical (phonon)
VLSI – Very large scale integration
XPS – X-ray photoelectron spectroscopy
Z – Nucleus charge
a_B – Exciton Bohr radius
E_g – Bandgap energy
k_B – Boltzmann constant (1.38·10^{23} J/K)
μ-PL – microphotoluminescence
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Chapter 1. Introduction

Silicon has emerged as a dominant material from the dawn of microelectronics back in 1950s. Today it still plays a fundamental role in the semiconductor industry. According to a recent article (M. Ieong et al., Science 306, 2057; 2004) by 2016 inventive new device architectures may well take silicon electronics comfortably into the regime where components are smaller than 10 nm. On top of the related problems with existing crystal-growth methods, current insulating materials and defect control, new physical effects are coming onto the scene. At this range of sizes purely quantum effects, such as quantum confinement, become significant. The quantum mechanical effects may impose insurmountable problems for future devices but may, just as well, provide new pathways.

The quantum confinement effect, being a direct confirmation of elementary quantum mechanics and the Schrödinger equation, has been widely investigated in direct bandgap nanocrystals due to their straightforward optical applications. This research field goes back to the beginning of the 1980-s, when the theoretical background was put forward. Nowadays, some quantum dot related devices, such as lasers, can compete on equal terms with other designs for occupying a niche in the market.

These two major semiconductor topics, silicon and nanocrystals, started merging together with the prospect of application in optoelectronics in the beginning of the 1990-s, fostering a strong interest in the research community. First in the form of nanoporous silicon, then as nanocrystals (or, for amorphous phase, nanoclusters) embedded in a silicon dioxide matrix. Although the on-chip laser appeared to be more difficult to reach than first anticipated, other unforeseen applications, including ones in biology, gradually emerged.

The fabrication of silicon nanocrystals and the investigation of their optical properties on a single-dot level in order to reveal the basic mechanism of luminescence was the main goal of the present work. It is extremely difficult to control several nanometer size objects with ordinary macroscopic techniques. Common methods produce compounds with a surface density of nanocrystals of more than $10^{10}$ cm$^{-2}$. This mass production is certainly desirable for a number of applications. However, when basic physical properties are of interest, the contribution from many nanoparticles to the signal and possible cross-talk between them become an unwanted side-effect. Thus, a special preparation method must be used in order to gain access to silicon nanocrystals on a single dot level. On the other hand, for optical characterization, the main disadvantage of such nanocrystals is their low emission rate. In practice this led to half an hour or even one hour long exposure times in order to get one
photoluminescence spectrum! In addition, the requirements on the mechanical and thermal stability during the data acquisition were quite strict. However, when the experiments eventually succeeded, the results appeared to be novel and of some interest to the community.

The thesis is organized as follows. First, the main concepts and basic properties of quantum dots are introduced together with main areas for application and current trends (Chapter 2). Second, the properties of silicon from the viewpoint of light extraction are discussed (Chapter 3). Methods and techniques used in this work are described in Chapter 4. An extended summary of included papers is presented in Chapter 5 as well as the main results. A short overview of the thesis and a brief summary constitute Chapter 6.
2.1 Basic optical properties

2.1.1 Background

Bulk semiconductor materials have electrons with energy distributed in continuous bands, separated by the energetically forbidden zone known as the bandgap. In the case of high-purity semiconductors at low temperature, the lower-lying valence band is filled and the other, the conduction band, is empty. One can populate the conduction band with carriers by doping, elevating temperature or providing the necessary energy, for example, by impinging light. Reverse spontaneous transitions, from the conduction to valence bands, are accompanied by energy emission as a propagating electromagnetic wave in order to obey the energy conservation law. The light emission is quantized as photons and their energy directly related to the bandgap energy.

In general, the existence of continuous bands can be considered as a result of an elementary splitting of the degenerate levels of a single atom in the perturbing field of the other atoms constituting a crystalline lattice. By reducing the number of perturbing atoms one can achieve a structure where the continuous band of the bulk material transforms into a set of discrete energy levels, similar to that of a single atom. This is schematically shown in Fig. 2.1, where a

![Diagram showing density of states for various geometries of semiconductor materials: (a) 3-D bulk, (b) quantum well, a 2-D structure, (c) quantum wire, a 1-D structure, and (d) quantum dot, a 0-D entity. The dotted line in (a) is the thermal distribution of carriers [1].]
continuous parabolic dependence of the density of states on energy in the bulk material reduces into a number of discrete levels for a quantum box.

The characteristic size of a structure, when such a transition occurs, is defined by the exciton Bohr radius. That is the typical size of a bound electron-hole pair in a semiconductor, introduced in analogy with an electron Bohr radius of a hydrogen atom. This value is several nanometers for most semiconductors. Thus these nanostructures possess unique optical and electrical properties for solid state objects.

In addition to the discretization of energy levels when approaching nanometer range of sizes, the value of the bandgap also changes. This effect can also be considered as a reduction in the energy level splitting, bringing the valence and conduction bands further away from each other. A well-known effect, similar to this one, is bandgap narrowing in bulk semiconductors, where at lowering temperature the bandgap increases. The value of the bandgap increase can be estimated for weak \((a>a_B)\) and strong \((a<a_B)\) confinement regimes from a quantum mechanical “particle-in-a-box” problem [2]. The energy of an exciton in the weak confinement regime is

\[
E_{nm} = E_g - \frac{R_y^*}{n^2} + \frac{\hbar^2 \chi_{ml}^2}{2MR^2},
\]

where \(R\) is the QD radius, \(\chi_{ml}\) are roots of the spherical Bessel functions \((m – \) number of the root, \(l – \) order of the function), \(R_y^*\) is the exciton Rydberg energy given by \(R_y^* = \frac{e^2}{2\varepsilon a_B}\), and \(M = m_e^* + m_h^*\). For the strong confinement regime:

\[
E_{nl} = E_g + \frac{\hbar^2 \chi_{nl}^2}{2\mu R^2}.
\]

The graphical representation of these solutions is given in Fig. 2.2a, while in Fig. 2.2b the numerical values of the bandgap are presented for a number of common semiconductors [2].

Fig. 2.2 (a) Quantum confinement effect in dimensionless units calculated using strong \((a>a_B\), dashed line) and weak \((a<a_B\), dotted line) regimes approximations, (b) Corresponding bandgap energies for various semiconductors as a function of quantum dot radius [2].
Chapter 2 Quantum dots

2.1.2 Homogeneous linewidth of a quantum dot

The quantized levels of a quantum dot have been generally believed to be as sharp as a $\delta$-function, reflecting its atomic character and size (Fig. 2.3). However, as a result of unique dephasing mechanisms in quantum dots, the homogeneous width of a quantum dot is not always as sharp as a $\delta$-function, but is found to be of a finite width and is sometimes broader than that of bulk crystals [1]. In this chapter the parameters that affect the homogeneous linewidth of a quantum dot are discussed in more detail.

For simplicity, let us consider the case of a constant dephasing rate for a given excited state (so-called Markovian relaxation). Here, the electron-phonon scattering is considered to be an instantaneous process. Then, the corresponding line-shape is Lorentzian [2]:

$$I(\omega) = A \frac{\Gamma^2}{(\omega - \omega_0)^2 + \Gamma^2},$$  \hspace{1cm} (2.3)

where $A$ – frequency independent coefficient, $\Gamma$ – phase relaxation rate (FWHM/2), $\omega_0$ - resonant frequency.

The phase relaxation rate (dephasing rate) consists of a number of independent processes characterized by the corresponding time constants:

$$\Gamma = \frac{\hbar}{2T_{\text{pop}}} + \sum_i \frac{\hbar}{T_i},$$ \hspace{1cm} (2.4)

Fig. 2.3 Ultra-narrow zero-phonon lines, observed at low-T from different single CdSe QDs [3].
where $T_{\text{pop}}$ – the pure population lifetime, $T_i$ – the lifetime of the pure (adiabatic) dephasing processes. The first term comes from real transitions of the relevant exciton state to the other states (inelastic). The last term arises from the virtual processes that start from the relevant state and, through some excursion in the intermediate states, return to the same initial state (elastic). These pathways are schematically shown in Fig. 2.4.

Within the framework of the perturbation approach, for a two-level model consisting of the ground $|0\rangle$ and the lowest excited state $|1\rangle$ of an exciton, the first, population term in (2.4):

$$
\Gamma_{\text{pop}} = \Gamma_0 + \gamma_{01} \cdot n(E_{01}, T),
$$

where $\Gamma_0$ – radiative annihilation rate: $\Gamma_0 = \frac{\hbar}{\tau_{\text{rad}}}$, $\gamma_{01}$ – the rate of phonon-assisted transition $|0\rangle \rightarrow |1\rangle$, $n(E_{01}, T)$ - Bose-Einstein distribution function, describing the number of available phonons of suitable energy:

$$
n(E_{01}, T) = \frac{1}{\exp(\hbar \omega/kT) - 1}.
$$

The second term in (2.5), contributing to the population broadening, depends on the availability of the phonons with corresponding energy. Since LO-phonons energies can only deviate weakly from the $E_{\text{LO}}$ value, the transition via LO-phonon(s) requires a strict matching condition for a nanocrystal with a characteristic size “a”:

$$
E_{01}(a) = m \cdot E_{\text{LO}}, \ m = 1, 2, \ldots
$$

Precise quantum-mechanical calculations give a somewhat less strict condition (for the case $m=1$):

$$
E_{01}(a) = E_{\text{LO}} \pm \delta E, \ \text{where} \ \delta E \approx 0.1 \cdot E_{\text{LO}}.
$$

On the other hand, in nanocrystals even the acoustic phonon modes become discrete, which reduces the probability of a multiparticle acoustic phonon assisted transition $|0\rangle \rightarrow |1\rangle$,
providing that the value of $E_{\text{ac}} > \hbar \omega_{\text{ac}}$, $\hbar \omega_{\text{ac}}$ - acoustic phonon energy. It is important to note that a trapped state, associated with the nanocrystal surface or defect with certain energy, may act as the $|1\rangle$ state in the considerations above. Thus, the width of the transition can in principle be dependent on the local environment.

Now, consider the second term in (2.4). The main mechanisms of dephasing are exciton-phonon interaction, exciton-exciton interaction, scattering by defects or impurities, or scattering by surfaces or interfaces [2]. Carrier-carrier interactions are absent under conditions of low excitation when no more than one electron-hole pair within a crystallite is created. The influence of defects can be neglected in perfect nanocrystals. Although at small sizes of nanocrystals surface states may play a significant role, in most cases the second term can be reduced to the exciton-phonon interaction only, which governs basic limits and temperature dependence of the homogeneous linewidth.

According to [4], high-frequency optical modes interacting with the exciton manifests itself in emission/absorption sidebands (phonon replicas), while low-energy acoustic modes cause an energy fluctuation of the exciton level. Moreover, the most efficient coupling to the exciton takes place for acoustic phonons of a certain wave vector and, correspondingly, of a certain energy. According to [5], the homogeneous linewidth due to this fluctuation is proportional to:

$$\Gamma_{\text{ac}} \propto D^2 = \chi^2 + 2 \chi^2 \cdot n(\hbar \omega_{\text{ac}}, T),$$

(2.9)

where $\chi$ is the coupling constant (the matrix element of the electron-phonon interaction), and $n(\hbar \omega_{\text{ac}}, T)$ is Bose-Einstein statistics for the acoustic phonons with the most appropriate energy. It was shown [4], that the low-energy phonons mostly contribute into this interaction. Then for $kT > \hbar \omega_{\text{ac}}$ the previous equation may be written as:

$$\Gamma_{\text{ac}} \propto D^2 \approx \chi^2 + 2 \chi^2 \cdot \left( \frac{kT}{\hbar \omega_{\text{ac}}} - \frac{1}{2} \right) = 2 \chi^2 \cdot \frac{kT}{\hbar \omega_{\text{ac}}}$$

(2.10).

To summarize, two different physical processes contribute to the homogeneous linewidth broadening of a quantum dot. The dependence on temperature for both of them is determined by the phonons which actually participate in the process. The pure dephasing process exhibits a linear temperature dependence in the $kT > \hbar \omega_{\text{ac}}$ regime, since mostly low-energy acoustical phonons are involved. On the other hand, the population decay process takes place only when the energy level structure of a nanocrystal allows phonon-assisted transitions for a given exciton. In this case, the temperature dependence of the linewidth reflects Bose-Einstein population statistics for the phonons with relevant energy.

As an example let us consider CdSe nanocrystals. The energy level splitting has been calculated in detail, including the electron-hole exchange interaction and intrinsic hexagonal lattice symmetry [5]. The calculations revealed the existence of so-called “dark” states, which are optically passive. The splitting between the ground and the first optically active excited state for the exciton was predicted to be in the range of 10-40 meV for a dot down to 2 nm in size. The actual value of the splitting is largely dependent on the shape of the dot. With further decreasing dot size the splitting grows significantly. Acoustic phonon spectra for a 2 nm CdSe quantum dot calculated in [4] shows a set of discrete values from 1 to 12 meV. At the same time the LO phonon energy 28 meV is nearly independent on the wavevector and nanocrystal
size. According to the calculations presented above, optical phonons can contribute to the population decay rate only for a particular kind of CdSe nanocrystal, the so-called “phonon bottleneck”.

For CdSe quantum dots the pure dephasing rate constants were calculated as a function of dot size in [4]. The coefficient at the T-linear term of $\Gamma_{ac}$ from (2.10) for a 2 nm dot was estimated to be $\sim 50 \mu eV$. The acoustic phonon energy corresponding to the maximum coupling with excitons was found to be $\sim 1$ meV. Thus, a linear behavior of the linewidth temperature dependence would be manifested at $T > 30$ K (for $kT \approx 3 \hbar \omega_{ac}$ the error for the Taylor expansion of the Bose-Einstein statistics into linear terms is $\sim 1\%$). Indeed, it was explicitly shown [4] that the pure dephasing process can be used to interpret this commonly observed linear dependence. The characteristic value for the emission linewidth of CdSe nanocrystals of $\sim 20$ meV at 80 K was detected experimentally and predicted theoretically on the basis of the pure dephasing process [4, 7]. However, sometimes the best fit to experimental data can be obtained by using simultaneously both processes responsible for the broadening [8].

When the temperature approaches the energy spacing between the ground and the first excited state of a nanocrystal, a multiphonon assisted activation to the excited state becomes probable. For example, for a 2 nm spherical CdSe dot the splitting value $\sim 20$ meV [5] corresponds roughly to a temperature of $T \approx 200$ K. Above this temperature the deviation from the linear behavior was observed [4]. In the other extreme, for temperatures close to absolute zero, the linewidth becomes ultranarrow, as would be expected for an atomic-like system when phonon involvement becomes negligible. Values of 0.16-0.25 meV for CdSe dots at $\sim 0$ K were deduced by the accumulated photon echo technique [9]. By single-dot spectroscopy, similar widths were observed even at 10 K for some CdSe dots (Fig. 2.3, [3]). Four-wave mixing experiments revealed even smaller values for InGaAs quantum dots (Fig. 2.5, [10]).

The observed difference in absolute values of the homogeneous linewidth at low temperatures for nanocrystals prepared from various materials is a strong indication of the vital role played by the surrounding matrix and the interface, which is unique for each case, in the light emission mechanism of a quantum dot.
2.1.3 Blinking phenomenon

The luminescence response of a quantum dot is not always constant in time. In addition to possible irreversible photodegradation, there are reversible “dark” periods in otherwise stable luminescence. Such sudden intermittence of light emission from quantum dots is normally ascribed to random charging of the nanostructures, making non-radiative processes within them dominant. It is believed that this charging effect results from interaction of the nanocrystal with its close surrounding, namely due to a transfer of carriers to and from quantum dots.

The most straightforward way of blinking analysis is based on a pre-estimated threshold value, separating on and off states. By making a frequency count (statistical analysis) of the recorded intensity values, one can distinguish between these two states in the occurrence distribution and extract the value of the threshold. An example of the sporadic luminescence behavior of a quantum dot is presented in Fig. 2.6, where an intensity trace is shown versus time at different scales. Here the threshold can be intuitively placed at the level of 70-80 counts/10ms.

After the threshold value is established, the traces can be treated statistically, where the number of “on” or “off” intervals of a certain length is plotted versus the length of the interval (Fig. 2.7). Two principal kinds of distributions can be discerned: a single-exponential distribution [11], and a power-law distribution [12]. The exponential distribution manifests a purely random process with fixed transition rates:

\[
p_{\text{on}}(t) = A_{\text{on}} \cdot \exp\left( -\frac{t}{\tau_{\text{on}}} \right), \quad p_{\text{off}}(t) = A_{\text{off}} \cdot \exp\left( -\frac{t}{\tau_{\text{off}}} \right)
\]  

(2.11),

where \(A_{\text{on,off}}\) – amplitudes, \(\tau_{\text{on}}\) and \(\tau_{\text{off}}\) – average times in on and off states.

The power-law dependence, on the other hand, represents a more deterministic one, featuring certain physical restrictions (for example, dynamic transition rates):

![Fig. 2.6 Luminescence intensity trace of a CdSe quantum dot featuring intermittence behavior [13].](image-url)
At the same time, these two can be present in one system, for example, one type of distribution takes place for on-off transition statistics, while the other describes backward, off-on transitions, and vice versa.

Another way to treat the recorded traces is using a normalized autocorrelation function of the second order $g^{(2)}$ for the recorded intensity trace $I(t)$:

$$g^{(2)}(\tau) = \frac{\langle I(t) \cdot I(t+\tau) \rangle}{\langle I(t) \rangle^2}$$

and fitting the curves corresponding to ideal single-exponential or power-law distributions to the obtained function, thus extracting main parameters of the blinking [12]. In this case there is no need to set a threshold level, which can be quite ambiguous in certain cases.

The blinking effect and possible ways to suppress it have attracted strong interest in the research community. Indeed, the blinking lowers the effective quantum efficiency for a QD and thereby degrades the performance of any device built on ensembles of QDs. Recently, for example, it was shown how this effect can be strongly suppressed by choosing an appropriate buffer solution for CdSe nanocrystals [14]. In general, the blinking phenomenon highlights the importance of the surrounding matrix and the interface role on the luminescence properties of a quantum dot. Notably, many systems such as the self-organized InAs quantum dots show no or negligible blinking. This may be ascribed to the smooth interphasing to surrounding materials in the epitaxial growth process.
2.2 Areas of application

2.2.1 Quantum dot based lasers

One of the main envisioned applications of quantum dots is involved with active optical devices, such as lasers. In comparison to conventional atomic or solid state structures they have a number of advantages, combining useful properties of these two (Fig. 2.8). An example of laser design is shown in Fig. 2.9, where stacks of InGaAs quantum dots are embedded into a multilayer structure. A laser based on quantum dots features tunability of emission wavelength by the control of QDs size and composition.

In Fig. 2.10 the breakdown of the development of the threshold current density of semiconductor lasers over last half century is shown. It is seen that devices built on quantum dot ensembles exhibit a higher level of performance compared to their predecessors.

Fig. 2.9 Cross section of a quantum dots based laser with electrical injection of carriers [16].

Fig. 2.8 Schematic representation of the advantages in using QDs compared to other media for lasing applications (DOS – density of states, Filling Factor – number of states per volume unit)[15].
Another, more general, figure of merit is the beam quality factor $M^2$. It is defined as a standard in ISO 11140 as

$$\frac{1}{M^2} = \frac{4\lambda}{\pi} \cdot \frac{1}{d_{\sigma 0} \cdot \Theta_{\sigma}} \quad (2.14),$$

where $d_{\sigma 0}$ – size of beam-waist, $\Theta_{\sigma}$ – divergence angle, $\lambda$ – lasing wavelength. Lower values of this parameter correspond to better beam geometry. It is shown in Fig. 2.11 how this parameter behaves under similar conditions in quantum well and quantum dot structures. Again, the QDs configuration seems more preferable.

Fig. 2.10 Summary of the evolution of one of the key laser parameters: threshold current density at room temperature. Quantum Dot based lasers represent a new generation of devices, following Double HeteroStructure (DHS) and Quantum Well (QW) structures [17].

Fig. 2.11 Beam quality as a function of the output power for quantum well and quantum dot configurations. Better values are achievable using quantum dots throughout a broader operational range [18].
2.2.2 Quantum dots as units for quantum computing, biological tags, etc

A two-state system with ground and excited states of a quantum dot can serve as a basis for logical operations (Fig. 2.12). Here an excitation of an electron to the conduction band, leaving behind a hole, could denote a \(|1\rangle\)-state. However, quantum mechanics allows the system to be in a linear combination of the two states: \(|\Psi\rangle = C_0|0\rangle + C_1|1\rangle\). This can be called a qubit (quantum bit). If the qubit state matches a measurement basis then a deterministic result can be expected. However, dephasing (a random disturbing of the system by external forces) imposes main limitations on the practical use of such systems. Long dephasing times are of largest importance to enable at least one or a number of operations with these logical units. That is why current prototypes work only at extremely low temperatures, where the dephasing rate is suppressed due to low population of phonon modes. Scattering with phonons is the main source of coherence loss and, hence, the capability of definite operations. On the other hand, the advantage of using quantum dots is that they can be reliably loaded with individual electrons and readily integrated into electronic devices.

The tunability of the emission wavelength of QDs together with their resistance to photobleaching are widely used these days in biological applications. In Fig. 2.13 an example of marking a biological object (a frog cell) with quantum dots is shown. QDs are used also as tags, when attached to various molecules, thus tracking possible changes in complex systems.

Other applications of QDs include photodetectors, amplifiers, memories, single-photon light sources and a number of others.

Fig. 2.12 Two-state configuration of an exciton in a quantum dot, which can be used for logical operations: exciton qubit [19].

Fig. 2.13 Quantum dots injected into a frog cell are used as markers for monitoring cell development [20]. (a) The QDs were injected in one cell at a stage where only 8 cells had been formed (upper left); (b)-(e) shows further temporal evolution of the embryo with QDs marking the development of the cell.
References

3.1 Bulk material vs. nano-sized Si as light emitters

In general, there are three major recombination paths for excited carriers to recombine in bulk Si: direct band-to-band transition, a transition with involvement of a phonon, and, finally, via a defect state (which is normally a non-radiative process). The first process is usually classified depending on the excess energy dissipation: a radiative recombination, where the energy is transferred to the propagating wave, and Auger recombination, where the energy is absorbed by another pre-excited free carrier. Due to the indirect band structure of Si (in Fig. 3.1(a) it is seen that minima of the conduction band and maxima of the valence band are displaced in $k$-space) the direct band-to-band transition is of extremely low probability and regarded as “forbidden”. On the other hand, when a phonon with a suitable momentum $k$ is involved, the $k$-conservation rule stands. Such phonon-assisted transitions actually dominate in a measured PL spectrum of bulk Si (in Fig. 3.1b the peaks, corresponding to TO and TA-
phonon assisted processes, are prominent). It should be noted, though, that a three-particle process of the electron-hole recombination with emission of a phonon has still relatively low probability due to its many-body nature. Hence, the recombination becomes totally dominated by non-radiative defect transitions. This prevails even in the high purity material as carrier diffusion to defects or surface is quite efficient. Thus, bulk Si material is by no means a good light emitting medium, with the fixed characteristic photon energy $\sim 1.1$ eV.

These properties change when silicon is nanostructured. The shielding of carriers from escaping to defect centers enhances the probability of radiative recombination for the same given concentration of defects (Fig. 3.2). Consider, for instance, Si nanoparticles of a few nanometers size embedded in a SiO$_2$ matrix. When optically pumped carriers are generated inside these particles. In this case electron and hole wave functions are confined in all three dimensions, which, in turn, makes possible otherwise forbidden in the bulk “no-phonon” transitions. Although this kind of electron-hole recombination is sometimes referred to as “quasidirect”, one should keep in mind that the concept of bands and, consequently, the division of transitions into direct and indirect, is only valid under the assumption of an infinite periodic lattice potential. Apparently, this assumption is too crude in such a case where the exciton Bohr radius in a Si nanoparticle ($a_B = 4.3$ nm) is comparable to the size of the particle itself. As a result of the aforementioned effect of carrier confinement, light emission from Si nanoparticles can be relatively strong. Using the coefficient for radiative recombination in bulk Si at room temperature $B \approx 10^{-14}$ cm$^3$s$^{-1}$ [3] one can roughly estimate the radiative rate in such nanostructures. If one assumes that a defect mediated recombination channel is suppressed due to the spatial localization of carriers and Auger assisted non-radiative transition is hindered for the same reason at low pumping regime of one exciton per nanocrystal, then the bulk carrier density corresponding to one exciton in a $\sim 3$ nm quantum dot is $N \approx 7 \times 10^{19}$ cm$^{-3}$. Finally, the radiative lifetime can be assessed as $\tau_{\text{RAD}} \approx 1/(B \cdot N) \approx 1$ µs. This value is very close to the experimentally observed excitation lifetime values in Si nanocrystals of the order of microseconds. In addition, due to the quantum confinement
effect, the wavelength of light that is emitted from these nanoparticles can be tuned continuously through the infrared and visible range with varying particle size.

In Fig. 3.3 the effect of size change on the electronic structure of a Si entity is shown as an evolution of the discrete levels of an atom towards the continuous bands of the bulk material. In this way, first, four-electron hybridized $sp^3$ atoms create a set of bonding orbitals $\sigma$ and a set of antibonding orbitals $\sigma^*$. 

Fig. 3.3 The evolution of energy levels of a Si atom into continuous bands of bulk Si via hybridized molecular orbitals of a Si cluster and discrete energy levels of a Si nanocrystal (compiled from different sources, the basic concept is adopted from [4]). Upper row (from left to right): the energy levels of a neutral Si atom calculated using Hartree-Fock-Slater method [5]; four-electron $sp^3$-hybridized atoms forming molecular bond orbitals between neighbors – a set of bonding orbitals $\sigma$ and a set of antibonding orbitals $\sigma^*$ [4]; the Si/SiO$_2$ interface energy diagram derived from XPS measurements [6] (inset: hole and electron energy levels for Si nanocrystals with 5 and 8 nm in diameter, as calculated in [7]); DOS for bulk Si as calculated in [8] with the vacuum level definition from [9]. Lower row (from left to right): an artistic impression of a Si atom; one of a few possible Si cluster configurations, as proposed in [10]; a TEM image of a Si nanocrystal in a SiO$_2$ shell [11]; an STM image of cleaved $<111>$ 7X7 surface of bulk Si [12].
Then, when the size of a Si structure increases, splitting of degenerate levels within a set of orbitals leads to the formation of a number of discrete states, eventually becoming the well-known conduction and valence bands of bulk Si with a bandgap energy $E_g = 1.12 \text{ eV}$ at room temperature. It is interesting to note that in atomic and molecular physics, quantum chemistry, nanophysics and physics of semiconductors are all involved in such a representation, highlighting the multidisciplinary nature of the current studies.

In a closer look to Si nanocrystal electronic structure (inset in the upper panel in Fig. 3.3) one can see that calculated energy levels of a nanocrystal are discrete and standing apart from one another by a distance more than the thermal energy ($k_B T = 25 \text{ meV at RT}$) for small nanocrystals. These calculations, performed using the [k·p] method, disregarded spin-orbit interaction in Si [8]. However, since the first discovery of light emission from Si nanostructures in 1990 (porous Si, [13]), no characteristic sharp lines in the PL spectra were observed even at cryogenic temperatures, which was ascribed to inhomogeneous broadening. At the same time, this fact boosted the appearance of other explanations of the light emission mechanism from nano-sized Si, such as recombination via a stable oxygen-related defect center created by annealing [14], involvement of surface states into the recombination process [15], hot carrier ballistic transport towards the Si/SiO$_2$ interface, enhancing the excitation of oxide defect-related photoluminescence [16] and a number of others.

One of the main objectives of the current research project was, by probing properties of Si nanostructures (nanocrystals, porous Si particles…) on a single-particle level, to clarify the mechanism of their light emission. Such a single-dot PL spectroscopy method would be extremely useful as it was the case in the studies of direct-bandgap nanocrystals [19]. The much slower recombination rate in Si nanocrystals (excitation lifetime is 4-5 orders of magnitude larger than in some direct bandgap QDs), however, was the main obstacle in the way of such an experiment.

Fig. 3.4 Low temperature luminescence spectra of porous Si [17] and Si nanocrystals [18]. The broad lines can be attributed to the inhomogeneous broadening.
3.2 Silicon nanocrystals

3.2.1 Porous Silicon

Historically, the first observations of strong room-temperature PL from silicon were performed on porous silicon samples [13]. This sponge-like structure is usually obtained from silicon by exposing it to HF solution under an anodic biasing condition. Depending on the etching parameters, such as bias, HF concentration, hole density in silicon and temperature, one can achieve a regime for pore formation (Fig. 3.5). The other regime is electropolishing, when the whole surface of silicon recess uniformly.

It can be seen from Fig. 3.5 (right) that the characteristic size of silicon entities formed by such a treatment may vary significantly. However, under certain circumstances, the size of nanostructures can be tuned to yield structures in the several nanometers regime, where luminescence in the visible range from silicon nanocrystals can be expected.

There were several attempts to utilize the luminescent properties of porous silicon in light emitting diodes. In order to achieve efficient carrier injection into the porous silicon network metal contacts can be placed in proximity to the porous silicon layer [22]. Another approach is forming a vertical pn diode [23]. High quantum efficiencies were reported (external ~ 0.2 %), but degradation issues appeared to be an overwhelming obstacle to the practical realization of such structures.

Recently a new application of these nanostructures was proposed. Due to the extremely large surface area of porous Si the reaction of oxidation becomes energetically highly dense per unit volume [24]. This leads to an explosive type of reaction under appropriate conditions. This effect can be used in a controllable way. For example, porous Si can be filled with an oxygen-rich substance and, when some threshold energy is transferred to this mixture, an explosion may occur [25].

![Fig. 3.5 Formation of porous silicon. (Left) SEM image illustrating the three typical etching regimes in silicon: porous formation, transition regime with pillar-like structures, and electropolishing [20]. (Right) TEM micrograph of porous Si grains with characteristic size of several nanometers [21].](image-url)
3.2.2 Si nanocrystals in SiO₂ produced by implantation of Si atoms

An alternative method of nanocrystal manufacturing represents a bottom-up approach, where atoms are precipitating from a supersaturated solution to form nanostructures of a desired size. This is in contrast to the so called top-down concept, discussed previously on the example of etching of bulk Si and porous silicon formation.

By creating an excess of Si atoms in an otherwise stoichiometric SiO₂ matrix with subsequent annealing one can trigger a precipitation process, where excess atoms diffuse to some agglomerating centers [26]. One of the most straightforward ways to introduce such an excess is by implantation of Si ions into silicon dioxide (Fig. 3.6). This method became widespread due to its VLSI compatibility and good control of main parameters, such as the amount of excess atoms (controlled by the implantation dose) and nanocrystal depth profile (by tuning the implantation energy). This method was used in the present work also.

The energy of an ion beam can be changed from several keV, which corresponds to 10-20 nm implantation depth, to several hundred keV, bringing the profile several hundred nanometers below the surface. The effect of various implantation doses on obtained nanocrystal size and, hence, on the luminescence spectra are shown in Fig. 3.6 (Right).

Recently, this technique was extended to implantation through a mask in order to form pre-defined luminescence patterns in silica [27] with a resolution of several hundred nanometers.

![Diagram](image_url)

Fig. 3.6 (Left) Formation of silicon nanocrystals in a SiO₂ shell by implantation of Si ions of 270 keV energy into silicon dioxide with subsequent annealing. (Right) Depending on the implantation fluence [Si/cm²] the mean size of nanocrystals may vary: with increasing fluence larger nanoparticles are created, shifting the luminescence peak closer to the value of bulk Si ~ 1.1 µm.
3.2.3 Other preparation methods

There are other ways to create non-stoichiometric films with Si, annealing of which can yield nanocrystals. One of them is co-deposition of materials in, for example, an rf magnetron discharge (Fig. 3.7, left). Here the sputtering targets can be chosen arbitrary so that the chemical composition of the film may vary. Usually, the plasma is struck in an inert gas like Ar and by means of physical sputtering elements from the targets can reach the substrate and form composite films. By changing the volume ratio of targets it is possible to control the relative chemical composition of the obtained sample. The advantage of this method is the large choice of initial materials, which can be used for manufacturing of nanocrystals in various matrices. For instance, Ge quantum dots embedded into silicon dioxide can be formed by this technique [29].

Silane gas (SiH₄) decomposition in various plasma reactors, like PECVD [30] or others [31] with subsequent accumulation of the products on a substrate is another widely used method for nanocrystal formation. Here, initial mixture of gases can be modulated during the process in order to control the excess of Si atoms in the film [30]. In Fig. 3.7, right, the scheme of a reactor [31], where a non-thermal plasma is created with hot electrons (2-5 eV) and cold, RT atoms and ions is shown. This configuration enables formation of large quantities of nanocrystals on the substrate on a very short time scale with suppression of excessive agglomeration due to negative charging of the particles.

Fig. 3.7 (Left) Magnetron rf sputtering device, similar to the one used in the pioneering work [28]. (Right) Silane decomposition unit, where a gas discharge is used to form silicon nanocrystals [30].
3.3 Scope for development

Recent trends in the research of optical properties of silicon nanocrystals include attempts aimed at improving the luminescent parameters, such as lifetime, using, for example, surface plasmons [32] or photonic crystals [33]. Small metallic structures can serve as nano-antennas for enhancing the spontaneous radiative recombination rate in silicon nanocrystals. The oscillations of free electrons (plasmons), which can easily react on the incoming excitation, perturb local near-fields, thus affecting luminescence parameters of nanocrystals brought in proximity to these metallic objects (Fig. 3.8). The other approach deals with changing of the optical mode density around nanocrystals by placing them in a photonic crystal. The physical foundation of this method is the fact that spontaneous recombination rate $W(r)$ depends on the number of available final states, according to Fermi’s Golden Rule:

$$W(r) \sim |M|^2 \cdot \left( \frac{\rho(\omega, r)}{\epsilon(r)} \right) = |M|^2 \cdot \text{LDOS}(r)$$  (3.1),

where $|M|$ – matrix element of the interaction and LDOS $(r)$ – local density of optical modes. Photonic crystals are periodic structures with lattice spacing in the order of the designed wavelength, which can be treated in a similar way as solid-state crystals. An analogy is that electron behavior in the energy bands of bulk materials is similar here to the photon propagation in such a structure. Thus, the pattern of light propagation can be changed as well as the local light velocity enabling such features as negative index of refraction or the slowing of light. Hence, luminescence can be collected more efficiently at some points or in some directions. However, these structures are capable of not only acting passively, similar to diffraction gratings, but can also affect the excitation lifetime. It was shown that a photonic crystal with a bandgap (span of wavelengths forbidden for propagation, as an energy bandgap for electrons in a semiconductor) inhibits radiation for in-plane waves, increasing the excitation lifetime [34]. In a continuation to this approach one can benefit from the possible coupling of a quantum dot to cavity modes in the photonic crystal [35].

![Fig. 3.8 Enhancement of luminescence from silicon nanocrystals caused by the proximity of metallic islands acting as nano-antennas: for the following parameters $p=400$ nm, $\Delta = 13$nm, and $d=165$, 185, 190, 230, 260 and 320 nm (right, from top to bottom), the resonant wavelength of the PL enhancement shifts accordingly [32].](image)
On the other hand, long excitation lifetimes in silicon nanocrystals can be advantageous for some applications. In this respect one of the most promising is sensitization. In general, nanocrystals can be excited more efficiently than atoms, which typically require strict resonant excitation conditions. Then, via a near-field energy transfer mechanism, such as the Förster transfer, excitation can be non-radiatively passed to desired atomic species. Usually, these acceptors are erbium [36] or oxygen atoms [37]. The former is of interest in the field of telecommunication due to the match of certain interlevel transitions in Er$^{3+}$ with the absorption minima in standard silica optical fibers at 1.54 µm (Fig. 3.9). The latter sensitization mechanism can create the chemically active singlet oxygen state, normally achieved only at elevated temperatures, thus promoting controlled “cold” reaction of oxidation. This can be of use even in cancer treatment methods, where nanocrystals are first localized in the tumor area, then irradiated with coherent light [38]. When the energy is transferred to surrounding oxygen, it becomes aggressive towards cells selectively in this part of the body.

Another important aspect is the control and correct assessment of luminescence quantum efficiency (the relative number of radiative transitions). Typically the reported values are in the order of tens of percents, which make silicon nanocrystals comparable to their direct bandgap counterparts from this viewpoint. There are reports on even higher values for a fraction of nanocrystals [39]. Up to date the consensus is that the quantum efficiency of luminescent nanocrystals is high; however the quantum yield (the relative number of optically active nanocrystals) is typically low. That suggests the existence of two kinds of defect states in nanocrystals: one that completely quenches luminescence and the other with characteristic time comparable to the radiative recombination time. This leads to strong absorption and poor overall conversion of energy into useful propagating electromagnetic radiation for these nanostructures.
References

Chapter 3 Silicon as an active optical material

Chapter 4 Experimental methods

Our distinctive approach in fabrication of single Si quantum dots for optical characterization involved manufacturing of silicon nanopillars with subsequent oxidation. The pillars were arranged in a pre-defined array using e-beam lithography. The separation between nanopillars was ~ 1 µm, which was chosen to overcome the diffraction limit of light, thus enabling far-field optical characterization. The subsequent self-limiting oxidation of silicon nanostructures at 900 °C, below the temperature of silicon dioxide flow, led in some cases to the formation of a silicon nanocrystal inside nanopillars. In this temperature range the concave outer shape of a silicon nanostructure undergoes faster oxidation, while the oxidation rate of a convex surface is somewhat lower. This effect was reported in application to silicon nanopillars in the beginning of 1990-s [1]. Below, experimental procedures of nanostructure fabrication used in this work are described.

4.1 Electron beam lithography and post-lithography processing

Electron beam lithography is a tool for nanostructure manufacturing but mainly for research purposes due to its low throughput rate. The electron beam hardens (negative) or softens (positive) a resist layer on a chip where exposed (Fig. 4.1). Subsequent chemical treatment (development) selectively targets non-exposed or exposed areas. Thus, created patterns can be transferred down to the chip by, for example, reactive ion etching in a plasma reactor.

4.1.1 Si nanopillars fabrication using positive resist

The following experimental procedure was used to fabricate silicon nanopillars containing a quantum dot, using positive resist as a mask for etching (Fig. 4.2):

- thermal growth of a ~ 20 nm dioxide layer on top of a (001) n-doped 20-40 Ω·cm Si substrate;
- coating of the substrate with ~ 60 nm of positive resist ZEP 520A diluted in anisole with 1:2 ratio;
- e-beam lithography to open dots in the resist layer with diameter defined by the pre-
  arranged design, typically 100-200 nm;
- deposition of a metal film (~ 15 nm of NiCr) and lift-off in ultrasound to invert the
  pattern;
- wet etching of the dioxide layer in HF using metallic dots as a mask;
- wet removal of the NiCr mask;
- RIE of the silicon substrate using dioxide islands as a mask to form silicon
  nanopillars;
- HF dip in order to etch away silicon dioxide mask leftovers;
- two oxidation steps with HF etching in between in order to form Si nanocrystals inside
  pillars.

4.1.2 Si nanopillars fabrication using negative resist

Next, in order to simplify the process, a negative resist was used, which hardens under the
exposure to the electron beam, in contrast to the described above positive type (Fig. 4.3):

- surface coating of the (001) Si chip with a negative resist (ma-N 2405);
- e-beam lithography to create dots with diameters 100-150 nm, resist developing;
- RIE in oxygen plasma to remove undeveloped resist around the structures and to clean area
  around structures from remnants of the resist;
- dry etching of silicon in a RIE reactor using defined structures of negative resist as a mask.
- hydrogen peroxide etching to remove mask leftovers from the etched silicon structures.
- two oxidation steps with HF etching in between in order to form nanocrystals inside pillars;

![Fig. 4.1 Electron beam lithography typically allows writing on the field size of 100x100 µm without
stage movements [2].](image-url)
Fig. 4.2 SEM images of nanopillar manufacturing process in positive resist, taken at different stages: (a) holes with diameter ~ 150-200 nm are defined in a positive type of resist deposited on the surface of a Si wafer (cleaved); (b) a zoomed image shows an “undercut” formed by scattered from the resist-silicon interface electrons; (c) metallic (Cr) dots are formed on the sample surface after metal deposition and a consecutive resist lift-off (top view); (d) a zoomed image reveals that it is possible to create almost perfectly round metallic dots by such a technique; (e) pillars of Si ~ 200 nm tall are made using reactive ion etching with previously formed structures as a mask (tilt 45° view); (f) a zoomed image reveals that etching goes also in a lateral way, making the top of a pillar less in size than its base; (g) schematic representation of the pillar manufacturing process using positive resist.
4.1.3 Preparation of a Si nanopillar for TEM imaging

In order to correlate measured optical properties of a Si nanocrystal with its structural features, such as size, shape, degree of stress a combined PL study with TEM characterization should be applied. Here, we used the FIB method for TEM preparation. This technique allows targeting specific area on the chip by milling a foil thin enough for subsequent TEM characterization. However, very rigid site-selectivity requirements, i.e. we aim at a particular pillar containing the luminescent nanocrystal, together with a small pillar diameter of ~ 30-40 nm made standard FIB milling method inapplicable.

A special method was developed to image single Si nanocrystals embedded into SiO₂ pillars with TEM. The main difficulty with conventional technique was the screening of the structures by a high-Z protection material, normally deposited on a sample to suppress charging during FIB processing. Thus a two stage protection scheme for FIB was developed in order to replace high-Z materials on the edges of the pillar of interest with a low-Z substance, namely a carbon-based polymer (positive resist ZEP520) (Fig. 4.4).

An additional problem was the fact that once being covered with resist, the structures become inaccessible by SEM built-in to the FIB machine. Since electron beam is absorbed in the deposited resist layer on top of structures it becomes impossible to target a specific area on the chip with FIB. Thus, first, the area around the pillar of interest was to be precisely cleaned from the resist. For this purpose e-beam lithography with a two-stage alignment routine was used. The overall processing sequence is described below:

- creating a hand-made mark on a chip with nanopillars of interest;
- measuring coordinates of the nanostructures and hand-made marks on a chip with SEM;
- spinning ~ 500 nm thick positive resist to cover the structures with a low-Z material;

Fig. 4.3  SEM images of nanopillars manufacturing process in negative resist: (a) a set of resist dots on silicon surface after exposure and development, (inset) zoomed in dot with characteristic diameter of about 100 nm, (b) etched Si pillar with resist mask leftover on top.
- manually cleaning area on the edge of the sample where the hand-made mark is located;
- recalculating positions of the structures, using now-visible in SEM hand-made mark;
- sending the beam to the newly calculated positions of the small alignment marks;
- exposing 20×20 µm areas on them (typical positioning error due to uncertainty of the stage movement ~ 10 µm);
- developing resist thus cleaning small alignment marks from the resist;
- locating now-visible small marks in SEM and performing fine alignment within one writing field (typical positioning error < 100 nm);
- exposing final patterns around the row with the pillar of interest;
- developing resist to finalize resist openings around the row with the pillar of interest;
- depositing second protective layer, Pt, over the whole chip in FIB machine;
- digging out a section containing the pillar of interest with FIB (Fig. 4.4, right);
- picking up the cut-out foil with a glass needle outside FIB machine;
- placing it onto a standard grid for subsequent TEM observation or placing it onto a SiO₂ grid and subsequent oxygen plasma etching of the protective resist layer before TEM observation.
There are two main approaches in manufacturing of nanocrystals: top-down and bottom-up. The first method, when a large structure is reduced to a nanometer-range object, is described in previous sections. In this work another technique, when nanocrystals are formed by precipitation of atoms, was also tested. Here, nanocrystals were formed by creating excess of Si atoms by implantation in thermally grown silica and subsequent annealing. Atoms precipitate around segregation centers and, when parameters of the annealing are chosen properly, luminescent nanocrystals can be fabricated. The goal of this experiment was to etch very small mesas in a thin layer of silica, doped with nanocrystals, in order to get access to a single nanocrystal. This goal was never realized, however, possibly due to the still large concentration of nanocrystals in thus-prepared mesas. The general process sequence was:

- thermal growth of ~ 20 nm of SiO₂ on top of a (001) Si wafer;
- deposition of a sacrificial ~ 160 nm thick p-Si layer by the rf magnetron discharge;
- introducing excess Si atoms (5-10 at. %) in SiO₂ by implantation;
- annealing at 1100 °C for 1 hour to form nanocrystals in the ~20 nm thin SiO₂ layer;
- wet etching of p-Si layer remnants;
- spinning negative resist ~ 200 nm thick on top of a sample with an HMDS layer;
- defining dots by e-beam lithography with diameter 100-200 nm;
- RIE in oxygen plasma to reduce the size of the resist dots (down to ~ 30 nm);
- transferring of the pattern to the SiO₂ layer by RIE of the dioxide;
- formation of Si pillars by RIE etching of Si (~ 250 nm) in order to distance light emitters from the substrate;

Fig. 4.5 (Left) Negative resist dots formed by e-beam lithography with subsequent size-reduction by reactive ion etching in oxygen plasma. The diameter is about 30 nm and the resist thickness ~ 200 nm. (Right) Silicon pillars with silica nanomesas doped with nanocrystals on top. Thus a point-like light source is removed from the high refractive index substrate. The RIE etch did, however, not work successfully in formation of vertical pillars and the diameter of Si pillar became larger then the diameter of SiO₂ nanomesas.

4.1.4 Formation of nano-mesas in SiO₂ doped with Si nanocrystals

There are two main approaches in manufacturing of nanocrystals: top-down and bottom-up. The first method, when a large structure is reduced to a nanometer-range object, is described in previous sections. In this work another technique, when nanocrystals are formed by precipitation of atoms, was also tested. Here, nanocrystals were formed by creating excess of Si atoms by implantation in thermally grown silica and subsequent annealing. Atoms precipitate around segregation centers and, when parameters of the annealing are chosen properly, luminescent nanocrystals can be fabricated. The goal of this experiment was to etch very small mesas in a thin layer of silica, doped with nanocrystals, in order to get access to a single nanocrystal. This goal was never realized, however, possibly due to the still large concentration of nanocrystals in thus-prepared mesas. The general process sequence was:
4.1.5 Formation of SiO₂ nanopillars doped with Si nanocrystals

When tall pillars in silicon dioxide (~ 1 µm high) are to be fabricated, the negative resist itself does not provide sufficient selectivity to SiO₂ in RIE machine. At the same time its thickness cannot be increased more than ~ 500 nm because resist pillars would not stand upright due to the high aspect ratio. To circumvent this problem a double-mask approach was used, when negative resist worked as mask for ~ 500 nm thick poly-Si layer, which, in turn, acted as a mask for subsequent silicon dioxide etching. Here we targeted at the formation of a photonic crystal structure composed of silicon dioxide pillars doped with silicon nanocrystals. It was designed so that the bandgap matches the peak of the of luminescence spectra in order to observe redistribution of light emission from silicon nanocrystals. This is an ongoing project and the results are not published yet. The manufacturing procedure was as follows:

- implantation of Si atoms into SiO₂ substrate, thus introducing excess Si atoms in SiO₂;
- annealing at 1100 °C for 1 hour to form QDs in the top layer of ~ 1 µm thickness;
- deposition of a ~ 500 nm poly-Si layer;
- patterning the structure in the negative resist using e-beam;
- transferring the pattern down to poly-Si by RIE (Figs 4.6 a, c);
- transferring the pattern down to nc’s rich fused silica substrate by RIE (Figs 4.6 b, d).

Fig. 4.6 Preparation of tall pillars in silica doped with silicon nanocrystals: (a), (c) poly-Si pillars acting as a mask for dioxide etching; (b), (d) final structures in silicon dioxide forming a photonic crystal.
Photoluminescence measurements

Luminescence from a semiconductor excited with photons (photoluminescence) or by electric current (electroluminescence) is a powerful tool in studies of its properties. This method can provide information on the optical bandgap, carrier relaxation, possible defect configurations and a number of other characteristics (Fig. 4.7). A modified version of this technique – micro-PL – was used in the current work. The main advantage of it is the fact that not only spectral characteristics of luminescence can be detected, but also the spatial configuration of it can be mapped with resolution ~ 1 µm. The latter was used when the signal from a Si quantum dot embedded in a silica nanopillar was to be addressed. When nanopillars are distanced more than 1 µm from each other they can be separately probed by this method.

For PL characterization samples were mounted on a finger of the Oxford Instruments Microstat cryostat. One can achieve temperatures of 5-10 K at the sample area with this cryostat using liquid helium. However, a larger flux of the coolant usually brings significant mechanical instability to the system, which is detrimental to long-term exposures. Photoluminescence was excited by the 325 nm UV line of a He-Cd continuous wave laser IK 5351R-D by Kimmon Electric. The choice of excitation wavelength is based on the high absorption cross-section of Si nanocrystals in this optical range. Another reason is the strong absorption of UV light by the fused silica components of the microscope. This, in turn, suppresses possible stray light influence on the signal. The emitted light is guided through the microscope Nikon Optishot-150 (with objective lenses Nikon X100 for RT and window-correction Olympus X60 for low-T measurements) and through the imaging spectrometer Jobin Yvon Triax 190 (Fig. 4.8). The latter has a turret with a mounted mirror and gratings of different resolution. Depending on the task it is possible to monitor a white light reflection image of the sample or, instead, acquire luminescent spectra from the area of interest. Finally, the signal is collected by a Hamamatsu C4880 Dual-mode liquid nitrogen cooled CCD camera. The sensitivity of about 3.8 photons per count appeared to be sufficient for single Si

Fig. 4.7 Schematic representation of the phenomenon of photoluminescence in bulk material; (a) an electron-hole pair is created by an incident photon with energy exceeding the bandgap – non-resonant excitation; (b) by scattering with phonons carriers are thermalized to the edge of the corresponding band; (c-e) various ways of carrier recombination with emission of a characteristic photon: (c) band-to-band, (d) via a donor state, (e) via an acceptor state. A surface/interface state can act as a donor or acceptor state in such a representation.
Fig. 4.8 The scheme of the experimental setup for PL studies. A sample is mounted on a finger of a liquid helium cooled cryostat. Luminescence is excited by the UV-line (325 nm) of a cw He-Cd laser. The emitted light is collected via an optical microscope through an imaging spectrometer onto a Si chip-based CCD camera: (a) overall view of the setup [3]; (b) enlarged drawing of the sample area.
nanocrystal spectroscopy. Time-resolved PL measurements of ensembles of nanocrystals were performed using a pulsed YAG laser at 355 nm with 3 ns pulse and 90 Hz repetition rate and the photoluminescence emission was detected during a 10 µs-wide gate.

When a sample is cooled a condensate is formed on its surface. This frozen water and organic compounds from the vacuum give significant bluish emission under UV excitation. The spectral tail of it can interfere with the weak signal from nanocrystals, which is normally in the red part of the visible spectrum. In order to avoid this effect a rapid heating of the cryostat finger tip, where a sample is mounted, was carried out. The condensed vapors become volatile around 273 K and get trapped on still cold parts of the cryostat, away from the tip. At this moment heating is stopped and the sample is cooled again to desired cryogenic temperatures yet without a luminescent film on the surface.

References

Chapter 5. Main results

5.1 Optical properties of a single silicon nanocrystal

5.1.1 Photoluminescence spectroscopy

Silicon nanocrystals for single dot spectroscopy were formed inside silicon pillars by oxidation, as shown by TEM micrographs in Figs. 5.1 (a)-(c). It is seen that the oxidation can lead to the formation of a quantum dot near the top of the pillar (a) or a nanorod in the middle of the pillar (b). Quite often, however, the pillar is fully oxidized and no silicon core is left (c). This process is somewhat random and depends largely on the initial pillar size. Indeed, the reduction from initially defined pillars of ~ 100 nm diameter down to ~ 5 nm is huge and limits the precision of the remaining core. The effect of “self-limiting oxidation” is crucial in formation of the quantum dot (see chapter 4). Note that images in Fig. 5.1 (a-c) reflect ongoing work and these pillars do not contain a luminescent silicon nanocrystal.

Fig. 5.1 (a)-(c) TEM micrographs of silicon pillars, which were oxidized at 900°C. The dark core is remaining crystalline silicon, while bright shell around is amorphous SiO₂. At certain oxidation stages (a) or (b) a luminescent silicon nanocrystal with size <5 nm can be formed; (d) Array of pillars seen in optical microscope and its corresponding photoluminescence image. Each bright spot can be traced back to a certain pillar, which is indexed in the array.
A large separation between neighboring pillars, as defined by e-beam lithography, made possible far-field optics to be applied for characterization of these nanostructures. In Fig. 5.1 (d) a white light reflection image of the pillar array is shown together with a corresponding PL image. Each light source can be traced back to a certain pillar indexed in the array.

In Fig. 5.2 (a) the spectra of a Si nanocrystal measured at room temperature and at 80 K are shown. It is seen that a broad, featureless room-temperature spectrum decomposes into two distinct contributions at lower temperature: the main line and the Si TO-phonon (~60 meV) replica. The main line presumably originates from a quasidirect transition in silicon.

Fig. 5.2 (a) Typical PL spectra from a Si nanocrystal at room temperature and at 80K. The featureless spectrum at room temperature decomposes into the main line and the TO-phonon assisted one at 80 K (b) The ratio of quasidirect transition to the conventional silicon TO-phonon assisted one as a function of emission photon energy: open circles for spherical quantum dots (ensemble measurements from [2]), dark squares for samples from this work. Confinement energy is an addition to the Si bandgap of ~ 1.1 eV, originating from the quantum confinement effect.

A large separation between neighboring pillars, as defined by e-beam lithography, made possible far-field optics to be applied for characterization of these nanostructures. In Fig. 5.1 (d) a white light reflection image of the pillar array is shown together with a corresponding PL image. Each light source can be traced back to a certain pillar indexed in the array.

In Fig. 5.2 (a) the spectra of a Si nanocrystal measured at room temperature and at 80 K are shown. It is seen that a broad, featureless room-temperature spectrum decomposes into two distinct contributions at lower temperature: the main line and the Si TO-phonon (~60 meV) replica. The main line presumably originates from a quasidirect transition in silicon.

Fig. 5.3 (a) Two spectra from different nanocrystals measured at 35 K. It is seen that the main line from the previous figure is composed of a true main line and a ~6 meV sideband, tentatively attributed to torsion or spherical acoustic phonon modes. (b) Statistical breakdown of the number of nanocrystals with various emission photon energies. Altogether they fit into a typical ensemble spectra, measured elsewhere (see, for example, [7]).
nanocrystals, since if it were a conventional TO-phonon recombination the second peak would correspond to the 2TO-phonon transition, which is highly unlikely from the momentum conservation rule under non-resonant excitation conditions. Such quasidirect transitions in silicon quantum dots were predicted [1] and indirectly observed [2] in ensemble studies previously with the rate of the transition being a function of nanocrystal size.

Fig. 5.2 (b) summarizes the influence of emission photon energy (nanocrystal size) on the probability of a quasidirect transition. The open circles are data obtained in [2] for spherical nanocrystals and dark squares are values measured in this work. The clearly seen size-dependence for spherical nanocrystals can be readily explained considering larger degree of electron and hole wavefunction overlap for a smaller nanocrystal [1]. The lack of a clearly observed effect of confinement energy on the peak ratio in this work is ascribed to strong non-uniformity of nanocrystals prepared by the current method. Variations in shape or in the degree of stress can enhance or decrease the probability of quasidirect transition in addition to the frequently referred size effect. It was shown that an elongated nanorod of CdSe nanocrystals [3], for example, has stronger oscillator strength of carrier interaction due to the more pronounced effect of dielectric confinement. As for the effect of strain, theoretical calculations [4] predicted that the existence of strained interface regions in the oxidized Si nanocrystals, which is the case for the present experiment, leads to the localization of carriers and a drastic increase of the no-phonon transition probability. In fact, only 1/3 of all measured dots at 80 K revealed a TO-phonon replica, which suggests the dominating role of stress on recombination in such prepared silicon nanocrystals.

Fig. 5.3 (a) shows how the emission line of a Si nanocrystal reduces further at a lowering of the temperature down to 35 K. The fine structure of the main line is shown in Fig. 5.3 (a) for two different nanocrystals (TO-phonon assisted lines are not shown). It is seen that this line consists of a true main line, corresponding to the interlevel transition in nanocrystals, and a ~6 meV sideband, attributed tentatively to torsion or spherical acoustic phonon modes, predicted [5] and indirectly observed [6] previously. The linewidth of the true main line is less than $k_B T$ at this temperature, proving a discrete nature of energy states in a silicon quantum dot. At even lower temperatures, however, no consistent PL was detected. We ascribe this effect to singlet-triplet splitting of the first excited state in a silicon quantum dot, where a transition from the lower lying triplet state to the ground level is optically forbidden. Thus only the transition involving the singlet state can be detected and spectrally resolved by our system. Hence, the PL intensity becomes too low to be detected by our system at temperatures below ~35 K.

Another important result of the work is presented in Fig. 5.3 (b), where it can be seen that different nanocrystals possess various emission wavelengths presumably due to size dispersion in accordance with the prediction of the quantum confinement theory. It is important to note here that if the luminescence originated from some kind of defect or interface state at this wavelength range, it would be impossible to observe such practically continuous tunability of emission wavelength since each defect state would be a certain configuration of Si/O atoms yielding a fixed energy of the corresponding optical transition.
5.1.2. Blinking phenomenon

The main results of the luminescence behavior investigation for Si nanocrystals in the time domain are shown in Fig. 5.4. An example of the intensity trace is given in Fig. 5.4 (a) with 15 seconds integration time per interval. A reversible switching is seen between two discrete states “on” and “off”.

The influence of the variable excitation power density on the blinking parameters was studied and results are given in Fig. 5.4 (b). The underlying data analysis is outlined in Appendix A.

The switching rate for the on-off transition is clearly dependent on the pumping power, while the reverse off-on process is nearly excitation independent. On the same figure the value of the luminescence intensity in on-state is shown. The deviation from the linear regime and bending of the curve towards the saturation takes place at the same excitation level as the growth of the on-off switching rate. Such saturation-like behavior in the optical response of a nanocrystal is typical when two excitons are formed at a time in a quantum dot. This effect can be explained invoking a non-radiative Auger process, when energy from exciton recombination is transferred to other available free carriers instead of being coupled to the far-field.

It would be reasonable to suggest a similar mechanism for the observed sensitivity of the on-off switching rate to the pumping power. Indeed, the energy obtained by another electron-hole pair can be sufficient to move one of the carriers through or above the potential barrier surrounding the nanocrystal to a localized trap state in silica bandgap. This effect charges the nanocrystal and subsequent luminescence is quenched by three-particle Auger recombination. A consequent restoring of the initial conditions by transfer of the carrier back to the nanocrystal neutralizes an excess carrier and brings luminescence back in the on-state.

Fig. 5.4 (a) Luminescence behavior of a Si quantum dot in time domain. Sudden interruptions of light emission – blinking – are seen. (b) Dependence of the blinking parameters on excitation conditions. While the on-off switching rate grows quadratically with excitation power density, the reverse, off-on switching frequency is basically independent on the pumping power.
5.2 Effect of optical mode density on luminescence parameters

The influence of the high-n substrate proximity on optical properties of a quantum dot was investigated. It is schematically shown in Fig. 5.5 (a) and (b) how the presence of a high refractive index material can introduce anisotropy in the dipole emission. The two cases of close proximity (a) and complete remoteness (b) were experimentally realized by distancing a sub-wavelength light source, an ensemble of Si nanocrystals, away from the substrate using reactive ion etching. Structures shown in Fig. 5.5 (c) and (d) correspond then to cases of dipole emission depicted in Fig. 5.5 (a) and (b).

In Fig. 5.5 (e) the measured dependence of the total luminescence yield on remoteness from the substrate for such a point-like light source is shown. The light was detected in the upper hemisphere since the substrate material is opaque for these wavelengths ($\lambda \approx 800$ nm here). It is seen that at height $\sim 250$ nm a decoupling of the emitter from the substrate occurs and the yield changes. Note that the pillar itself does not contribute much to the experiment, since emission is only sensitive to the local optical environment in the sphere with a radius $\sim \lambda/\pi$. The observed decoupling distance agrees well with that calculated in [8] for the depth of perturbation $\sim \lambda/\pi$, caused by a high-n material on the interface dipole emission rate.

At the same time, along with the spatial redistribution of the light emission, the presence of a high optical mode density substrate shortens the excitation lifetime of silicon nanocrystals. However, real nanocrystals have QE<100%, which leads to the screening of the changes in the radiative rate for an observer measuring the total decay rate by the non-radiative recombination inside the nanocrystals. From this approach one can roughly estimate the value of quantum efficiency for nanocrystals. By measuring the change in the total decay rate with decoupling emitter from the substrate and comparing to expected values for the radiative component we estimate a QE $\approx 10\%$ for thus prepared silicon nanocrystals.

Fig. 5.5 (a) A dipole emission pattern in proximity to a high refractive index substrate. (b) Isotropic emission for a dipole suspended in air/vacuum. (c) Experimental realization of the case a): a point-like light source, an ensemble of nanocrystals, is located directly on a high-n Si substrate. (d) An ensemble of nanocrystal removed from the substrate by etching of Si, bringing the structure closer to the case b) of dipole emission. (e) Dependence of the measured luminescence yield on remoteness of the light source from a high optical mode density substrate (silicon, $n \approx 3.5$).
References

Chapter 6. Summary

6.1 Comments on the appended papers

*Paper I “Narrow luminescence linewidth of a silicon quantum dot”*

The paper extends our previous work (Paper IV), where first results on low temperature photoluminescence spectroscopy of single Si nanocrystals were reported. Here, the series of experiments was performed at lower, cryogenic temperatures in order to get better insight into the elementary processes of light emission from single silicon nanocrystals. This allowed to observe that the structure of the main emission line consists of the sharp peak and a somewhat broader satellite, separated by ~6 meV. We tentatively attributed this peak to a low-frequency phonon assisted transition.

The main result of the paper, namely the broadening of the luminescence lines being less than thermal in a certain temperature range, manifests that Si nanocrystals can be considered in a similar way as their direct bandgap semiconductor counterparts, despite the substantial difference in the zone structure of the corresponding bulk materials.

*Paper II “Luminescence blinking of a Si quantum dot in a SiO₂ shell”*

In this work we turned to one of the most intriguing phenomena observed for quantum dots – sudden luminescence intermittence. This phenomenon, often referred to as “blinking”, is interesting not only from a physical viewpoint, but also has a certain practical value. Indeed, the blinking lowers the effective quantum efficiency for a quantum dot and degrades the performance of any device built on ensembles of quantum dots. Finally, the observation of blinking can provide firm evidence that only a single light emitting center is probed. In order to understand the physics behind the observed emission intermittence, sufficient statistics should be acquired and data must be analyzed. The proper way of treating the recorded intensity traces was not obvious from the very beginning. First, it was found that only traces recorded with certain time resolution could be used in data analysis. It is only them, which reveal blinking between two discrete levels (on/off). Since the switching rate is a function of excitation intensity, the time resolution value is subject to changes under variable experimental conditions. In other words, the proper time resolution must be chosen individually for each set of experimental conditions.

As a result of such an analysis, we have found strong dependence for the on-off switching rate on excitation power density. We ascribe this fact to Auger-assisted ionization, which
promotes charge fluctuation of a quantum dot. Moreover, SiO₂ as a capping layer appeared to be effective in charge capture, which manifests in various characteristic blinking times for different nanocrystals, ascribed to variations in trap geometry around each dot.

**Paper III “Effect of substrate proximity on luminescence yield from Si nanocrystals”**

Here we investigate how the main parameters of nanocrystal luminescence, such as spontaneous emission rate, quantum efficiency and luminescence yield are affected by changes in its optical environment. Using e-beam lithography and reactive ion etching we prepared a set of samples with point-like light sources (ensemble of nanocrystals) remote by various distances from a high refractive index substrate (bulk Si). Small islands of nanocrystals were located on top of pillars of various heights, representing point-like emitters differently distanced from the substrate.

We applied both time-resolved and time-integrated methods to characterize the structures. Time-resolved measurements were quite difficult due to the low emission rate from small ensembles of nanocrystals. The time-resolved measurements yielded a higher decay rate (shorter lifetime) when nanocrystals were in close proximity with the substrate. This would, indeed, be anticipated due to the much higher density of optical modes in the substrate.

The results highlight the anisotropic nature of light emission at the interface. We found that the luminescence yield can be increased by a factor of two by decoupling the light source from the substrate. At the same time, in close proximity the quantum efficiency of silicon nanocrystal doubles due to the leaking of light to the material with high density of optical modes.

**Paper IV “Single dot optical spectroscopy of silicon nanocrystals: low temperature measurements”**

The paper is a part of the Proceedings of the European Materials Research Society 2004, Symposium A1: “Si-based photonics: towards true monolithic integration”. We included our first results on low temperature photoluminescence spectroscopy of single Si nanocrystals.

There were a number of difficulties in the way of the experiment we report. The first and the foremost is a very low emission rate of photons from a single silicon nanocrystal (of the order of 10 detected photons per sec). Secondly, it was quite challenging to produce nanocrystals well separated spatially so that far-field spectroscopy could be applied. Finally, all these adversities were multiplied by the need for low-temperature measurements, where thermal expansion of the cryostat finger must be suppressed to less than ~ 1 µm.

Here, we show that carefully prepared and patiently probed silicon nanocrystals do exhibit relatively narrow luminescence linewidth at 80 K. In addition, the Si TO-phonon (~60 meV) replica is observed for a fraction of investigated dots. Also we show that the temperature bandgap narrowing, common for bulk Si, can be seen in our nanocrystals as well, which supports the origin of light emission being that of band-to-band recombination.

**Paper V “Light emission from silicon nanocrystals: probing a single quantum dot”**

This paper was a contribution to the ACSIN-8 (Atomically Controlled Surfaces and Interfaces) conference, which took place in the summer of 2005 in Stockholm. Here we
analyzed data obtained by low-T spectroscopy of single silicon nanocrystals. The main
emphasis was made on the differences in some optical properties, such as linewidth and
luminescence yield, which we attributed to strong non-uniformity of quantum dots.

From this perspective it is important to combine optical characterization methods with
structural imaging in order to get information on both optical and morphological properties of
a single nanocrystal. This can help in understanding how size, stress or shape affects the
optical response from silicon nanocrystals.

**Paper VI “Structural and optical properties of a single silicon quantum dot: towards
combined PL and TEM characterization”**

In this work, which was a part of EMRS-2006 meeting, we report first results on combined
optical and structural characterization of single Si quantum dots. A special sample protection
scheme was developed in order to use a conventional focused ion beam machine for sample
preparation. The requirement of site-selectivity along with small size of pillars, containing the
quantum dots, made standard sample preparation techniques virtually impossible.

Using the e-beam machine we covered a row of pillars, containing the pillar of interest, with
resist, which is a carbon-based polymer. Afterwards the sample underwent Pt deposition to
suppress charging during the sputtering. Such a “sandwich” protection method allowed to
observe the silicon core in the oxidized pillars and to visualize luminescent silicon
nanostructures. One can see how the oxidation develops with time and at which stage
nanostructures appropriate for luminescence can be formed. To this point, we have not yet,
however, successfully correlated structural and optical properties on a single dot level.

**6.2 Conclusions and outlook**

The optical and electronic properties of semiconductors may change dramatically when scaled
into nanometer dimensions. Among semiconductors, silicon is the most ubiquitous electronic
material today and there is a chance this material may find new lease of life in the field of
optoelectronics in the future. Silicon nanocrystals (structures of less than 5 nm in size) are one
of several possible ways to obtain light emission from silicon. This is due to better
confinement of carriers, preventing them from migration to non-radiative centers, as occurs in
bulk material. Visible photoluminescence from silicon nanostructures (in the form of porous
silicon) was first observed more than a decade ago. However, the mechanism of that process
has remained the subject of debate for a long time. This is due to common observations of
very broad luminescence bands from practically all kinds of silicon nanoparticles.

In our project we designed and produced silicon nanocrystals in a silicon dioxide shell for
optical characterization by the low-temperature single-dot spectroscopy technique. This
method addresses one nanocrystal at a time and, avoiding inhomogeneous effects, represents
an effective tool for the investigation of basic properties of nanocrystals. Despite the obvious
advantages of this method, there were no reports on the application of such a technique to Si
nanocrystals. Although diluted porous Si particles were probed before, they still remain
conglomerates of several chromophores even after many filtering and thinning out steps.

On the experimental stage we indeed encountered many difficulties both in preparation and
characterization steps (Paper IV). One of the major physical obstacles was the long lifetime
(tens of microseconds) of the excitation in silicon nanocrystals, which still preserves the indirect bandgap structure of bulk Si. This fact implies the need of a phonon for the recombination of carriers, making it a low-probability three-particle process. Experimentally, that corresponds to a very low signal-to-noise ratio when such nanostructures are optically probed.

Being eventually successful, the experiments revealed several new physical properties of a silicon quantum dot in a dioxide shell. For the first time narrow luminescence lines were detected at low temperatures, corresponding to discrete energy levels of a Si nanocrystal (Paper I). These lines were shifted in energy for different dots as would be expected from differently sized nanocrystals. This result is a very strong indication towards quantum confinement origin of light emission from silicon nanocrystals.

Luminescence blinking, i.e. arbitrary intermittence of emission was measured and analyzed (Paper II). The bimodal distribution of luminescence intensity supports the origin of luminescence being of a single emitter. In addition we found strong variation in luminescence properties from dot-to-dot, ascribed to structural non-uniformity (Paper V). The latter highlighted the need for both luminescence and structural characterization of such nanostructures (Paper VI).

Our results, however, indicate major problems for the practical application of such nanocrystals. Among them is the weak quasidirect recombination of carriers due to spatial confinement of corresponding wave functions. We found that the no-phonon line can be only several times stronger than the conventional, weak phonon-assisted one. In addition, another disadvantage was confirmed by the blinking measurements. Namely, the high probability of non-radiative Auger processes, which takes place when more than one electron-hole pair is present in a Si quantum dot.

Possible ways to circumvent related difficulties would be using amorphous nanocrystals in order to break crystalline order, or embedding them in, for example, a silicon nitride matrix. In that case one can expect a dominance of quasidirect transitions in small nanocrystals. Another approach is to modify their spontaneous emission rate (Paper III). In this work we considered the effect of optical properties of the surrounding media on nanocrystal luminescence. Quantum efficiency and luminescence yield were altered due to the modification of the density of optical modes around nanocrystals and it was shown that the value of quantum efficiency of these structures remains relatively high (~ 10 %). The spontaneous emission rate could also be enhanced by coupling to surface plasmons on nanostructured metals in proximity, which work as small antennas for coupling light to the far-field.

This work gave rise to some intriguing questions, which appeared only after a single Si nanocrystal had been accessed. Strong non-uniformity in observed nanocrystal optical properties suggests the crucial role of the quantum dot shape, interface conditions and the host matrix configuration on luminescence parameters. This is also true for local environment around the nanocrystal. Indeed, observed variations in blinking suggest various scenario of possible carrier capture in the surrounding shell for different nanocrystals.

To summarize, we investigated basic optical properties of silicon nanocrystals in a SiO$_2$ shell on a single-dot level, and probed into possible ways of modifying them. In our work for the first time successful experimental probing of a single silicon nanocrystal was achieved.
Appendix A Blinking data analysis

Threshold approach in the analysis of the recorded PL traces

The most straightforward way of blinking analysis is based on a pre-estimated threshold value, separating on and off states. Making frequency count (statistical analysis) of the intensity trace, one can distinguish between these two states. Ideally, such statistical breakdown of the intensity trace would yield two δ-functions, corresponding to each state. In practice, the chosen time resolution, the Poisson noise of the detected counts and the CCD read-out noise transform the δ-functions into Gaussian-shaped curves (Figs. A.1 (a) and (b)).

Such statistical analysis can reveal the presence of two discrete states only if the time resolution is chosen correctly. If the chosen time interval value is too long, then many intermediate states would enter and statistical breakdown of the trace would not reveal any on and off states at all. On the other hand, the interval value should not be too small either due to signal/noise considerations. These two limitations define the acceptable range for acquisition time per frame. When the data were acquired with proper time resolution, a threshold value can be established (Figs. A.1 (a) and (b)).

The statistics of the plateau durations for on and off states can be calculated, assuming that all data points below the threshold correspond to the off state, while the rest – to the on state. In Fig. A.2 calculated distributions are shown for two different values of excitation intensities for the same quantum dot at RT. The fitting is based on a random switching model:

Fig. A.1 Statistical breakdown of intensity traces for dot A3IB at RT at two different excitation intensities: a) 0.38 W/cm² and b) 0.8 W/cm². On and off states can be discerned and threshold values can be estimated. Note that time-per-frame value is different in a) and b).
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where \( A_{on,off} \) – amplitudes, \( \tau_{on} \) and \( \tau_{off} \) – average times in the on and in the off state, respectively.

Thus two main parameters characterizing the blinking phenomenon \( \tau_{on} \) and \( \tau_{off} \) can be found.

The main advantage of this method is its simplicity. However, there is some uncertainty in the threshold value estimation due to the imperfectness of statistical distributions. This leads to a slight error in determining \( \tau_{on} \) and \( \tau_{off} \).

**Autocorrelation function**

Along with the threshold approach for analyzing the PL trace of a quantum dot there is another method based on the autocorrelation function. By definition, a second order normalized autocorrelation function for a signal intensity trace \( I(t) \) is given by:

\[
g^{(2)}(\tau) = \frac{\langle I(t) \rangle \cdot \langle I(t + \tau) \rangle}{\langle I(t) \rangle^2} \quad (A.2)
\]

According to [3], for a random telegraph signal, whose on and off periods succeed one another without any memory of former on and off times, the Laplace transform is related to those of on and off time distributions:

\[
\tilde{g}^{(2)}(s) = \frac{1}{s} \left( 1 + \frac{\langle \tau_{off} \rangle}{\langle \tau_{on} \rangle} \right) \cdot \frac{1 - (1 - \tilde{P}) \cdot (1 - \tilde{Q})}{s \cdot \langle \tau_{on} \rangle \cdot (1 - \tilde{P}Q)} \quad (A.3)
\]
Appendix A Blinking data analysis

where $<\tau_{on}>,(<\tau_{off}>)$ - average on time (off time), $\tilde{P}(s)$, $\tilde{Q}(s)$ – the Laplace transforms of the normalized on and off time distributions.

In [3] two particular cases were considered: the first when $P(t)$ and $Q(t)$ are power-law dependencies and the second with $P(t)$ – exponential and $Q(t)$ – power-law. For the case of silicon nanocrystals observed in this work, none of the models used in [3] are applicable. Distributions of both on and off times, obtained from the threshold approach, appear to be single-exponential (Fig. A.2). Therefore, an analytical expression for the autocorrelation function should be calculated.

We use normalized single-exponential distributions: $P(t) = (1/\tau_{on})\exp(-t/\tau_{on})$, $Q(t) = (1/\tau_{off})\exp(-t/\tau_{off})$ and their Laplace transforms:

$$\tilde{P}(s) = \int_0^\infty P(x)\exp(-s \cdot x) \, dx = \frac{1}{1 + s \cdot \tau_{on}} \quad (A.4a),$$

$$\tilde{Q}(s) = \int_0^\infty Q(x)\exp(-s \cdot x) \, dx = \frac{1}{1 + s \cdot \tau_{off}} \quad (A.4b).$$

Then (A.3) becomes

$$\tilde{g}^{(2)}(s) = \frac{(s \cdot \tau_{off} + 1)(\tau_{on} + \tau_{off})}{s \cdot (s \cdot \tau_{on} \cdot \tau_{off} + \tau_{on} + \tau_{off})} \equiv \frac{u(s)}{v(s)} \quad (A.5).$$

Using the Heaviside formula for the inverse Laplace transform for the case of polynomials $u(s)$ and $v(s)$ in the numerator and denominator, respectively:

$$\tilde{g}^{(2)}(\tau) = \sum_k \frac{u(s_k)}{v(s_k)} \cdot \exp(s_k \cdot \tau),$$

![Fig. A.3](image)

Fig. A.3 Calculated autocorrelation functions for PL traces for dot A3IB at RT at two different excitation intensities: a) 0.38 W/cm² and b) 0.8 W/cm². Solid lines are fittings based on a completely random switching model. Extracted values of $\tau_{on}$ and $\tau_{off}$ are in interval units.
where $s_k$ – zeros of $v$ polynomial, we obtain:

$$g^{(2)}(\tau) = 1 + \frac{\tau_{\text{off}}}{\tau_{\text{on}}} \cdot \exp\left(-\left(\frac{1}{\tau_{\text{on}}} + \frac{1}{\tau_{\text{off}}}\right) \cdot \tau\right)$$

(A.6).

By fitting this formula with two parameters $\tau_{\text{on}}$ and $\tau_{\text{off}}$ to the autocorrelation function calculated from the intensity trace (A.2), one can get values of $\tau_{\text{on}}$ and $\tau_{\text{off}}$ (Figs. A.3 (a) and (b)).

The advantage of using this approach is that no pre-defined threshold value is needed. However, it can be seen in Fig. A.3 (b) that the fitting is to be done to one data point only when the switching frequency is relatively high. The corresponding large error imposes limitations on employing the autocorrelation function at this regime of blinking. On the other hand, obtained frequency values for the lower switching regime are in good agreement with those from the threshold approach (cf. Fig. A.2 (a)).

**Switching frequencies for on-off and off-on processes**

In the following chapter the formula for switching frequency of on-off and off-on processes will be obtained from known $\tau_{\text{on}}$ and $\tau_{\text{off}}$ values. Using the single-exponential distribution (A.1a) one can write the total number of on-off switching events as

$$N_{\text{onoff}} = \sum_{n=1}^{\infty} A_{\text{on}} \cdot \exp(-n / \tau_{\text{on}})$$

(A.7).

Total number of intervals spent in on-state:

$$N_{\text{on-state}} = \sum_{n=1}^{\infty} A_{\text{on}} \cdot \exp(-n / \tau_{\text{on}}) \cdot n$$

(A.8).

Then, the switching frequency for on-off process

$$f_{10} \equiv \frac{N_{\text{onoff}}}{N_{\text{on-state}}} \cdot \frac{1}{\Delta t} = \frac{\sum_{n=1}^{\infty} \exp(-n / \tau_{\text{on}})}{\sum_{n=1}^{\infty} \exp(-n / \tau_{\text{on}}) \cdot n} \cdot \frac{1}{\Delta t}$$

(A.9),

or, using series sum formulas:

$$f_{10} = \left[1 - \exp\left(-\frac{1}{\tau_{\text{on}}}\right)\right] \cdot \frac{1}{\Delta t} [\text{Hz}]$$

(A.10a).
In a similar way, for off-on process:

\[
f_{01} = \left[ 1 - \exp\left( -\frac{1}{\tau_{\text{off}}} \right) \right] \cdot \frac{1}{\Delta t} \quad [\text{Hz}] \quad (A.10b),
\]

where \( \tau_{\text{on}} \) and \( \tau_{\text{off}} \) – average times in on and off state, [number of time intervals], \( \Delta t \) – time interval length, [seconds].

For large values of \( \tau_{\text{on}} \) and \( \tau_{\text{off}} \) formulas (A.10a, b) can be simplified:

\[
f_{10} \approx \frac{1}{\tau_{\text{on}}} \cdot \frac{1}{\Delta t}, \quad f_{01} \approx \frac{1}{\tau_{\text{off}}} \cdot \frac{1}{\Delta t} \quad [\text{Hz}].
\]

These expression were used in [4] as “characteristic switching frequencies”.

**Fraction of time spent in on-state**

Another important parameter of the blinking process for a nanocrystal is the fraction of time spent in on-state, \( \alpha_{\text{ON}} \). It can also be deduced from known \( \tau_{\text{on}} \) and \( \tau_{\text{off}} \) values.

Using (A.8) one directly obtains

\[
\alpha_{\text{ON}} = \frac{N_{\text{on-state}}}{N_{\text{on-state}} + N_{\text{off-state}}} = \frac{\sum_{n=1}^{\infty} A_{\text{on}} \cdot \exp\left( -n / \tau_{\text{on}} \right) \cdot n}{\sum_{n=1}^{\infty} A_{\text{on}} \cdot \exp\left( -n / \tau_{\text{on}} \right) \cdot n + \sum_{n=1}^{\infty} A_{\text{off}} \cdot \exp\left( -n / \tau_{\text{off}} \right) \cdot n} 
\]

(A.11).

Taking into account the fact that the number of on-off switching events equals to the number of off intervals (and vice versa):

\[
\sum_{n=1}^{\infty} A_{\text{on}} \cdot \exp\left( -n / \tau_{\text{on}} \right) = \sum_{n=1}^{\infty} A_{\text{off}} \cdot \exp\left( -n / \tau_{\text{off}} \right) 
\]

(A.12),

equation (A.11) then becomes

\[
\alpha_{\text{ON}} = \frac{\sum_{n=1}^{\infty} \exp\left( -n / \tau_{\text{on}} \right) \cdot n}{\sum_{n=1}^{\infty} \exp\left( -n / \tau_{\text{on}} \right) \cdot n + \sum_{n=1}^{\infty} \exp\left( -n / \tau_{\text{off}} \right) \cdot n}
\]

or, using series sum formulas:
\[
\alpha_{ON} = \frac{\exp\left(-1/\tau_{off}\right) - 1}{\exp\left(-1/\tau_{off}\right) - 1 + \exp\left(-1/\tau_{on}\right) - 1} \cdot 100 \equiv \frac{f_{01}}{f_{01} + f_{10}} \cdot 100 \ [%] 
\] (A.13).

Again, in the case of large \(\tau_{on}\) and \(\tau_{off}\) values, expansion in Taylor series yields a more simple expression:

\[
\alpha_{ON} \approx \frac{\tau_{on}}{\tau_{on} + \tau_{off}} \cdot 100 \ [%] 
\] (A.14).

References