Fabrication and characterization of single luminescing quantum dots from 1D silicon nanostructures

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Abstract

Silicon as a mono-crystalline bulk semiconductor is today the predominant material in many integrated electronic and photovoltaic applications. This has not been the case in lighting technology, since due to its indirect bandgap nature bulk silicon is an inherently poor light emitter. With the discovery of efficient light emission from silicon nanostructures, great new interest arose and research in this area increased dramatically. However, despite more than two decades of research on silicon nanocrystals and nanowires, not all aspects of their light emission mechanisms and optical properties are well understood, yet. There is great potential for a range of applications, such as light conversion (phosphor substitute), emission (LEDs) and harvesting (solar cells), but for efficient implementation the underlying mechanisms have to be unveiled and understood. Investigation of single quantum emitters enable proper understanding and modeling of the nature and correlation of different optical, electrical and geometric properties. In large numbers, such sets of experiments ensure statistical significance. These two objectives can best be met when a large number of luminescing nanostructures are placed in a pattern that can easily be navigated with different measurement methods.

This thesis presents a method for the (optional) simultaneous fabrication of luminescent zero- and one-dimensional silicon nanostructures and deals with their structural and optical characterization. Nanometer-sized silicon walls are defined by electron beam lithography and plasma etching. Subsequent oxidation in the self-limiting regime reduces the size of the silicon core unevenly and passivates it with a thermal oxide layer. Depending on the oxidation time, nanowires, quantum dots or a mixture of both types of structures can be created. While electron microscopy yields structural information, different photoluminescence measurements, such as time-integrated and time-resolved imaging, spectral imaging, lifetime measurements and absorption and emission polarization measurements, are used to gain knowledge about optical properties and light emission mechanisms in single silicon nanocrystals.

The fabrication method used in this thesis yields a large number of spatially separated luminescing quantum dots randomly distributed along a line, or a slightly smaller number that can be placed at well-defined coordinates. Single dot measurements can be performed even with an optical microscope and the pattern, in which the nanostructures are arranged, enables the experimenter to easily find the same individual dot in different measurements. Spectral measurements on the single dot level reveal information about processes that are involved in the photoluminescence of silicon nanoparticles and yield proof for the atomic-like quantized nature of energy levels in the conduction and valence band, as evidenced by narrow luminescence lines (~500µeV) at low temperature. Analysis of the blinking sheds light on the charging mechanisms of oxide-capped Si-QDs and, by exposing exponential on- and off-time distributions instead of the frequently observed power law distributions, argues in favor of the absence of statistical aging. Experiments probing the emission intensity as a function of excitation power suggest that saturation is not achieved.

Both absorption and emission of silicon nanocrystals contained in a one-dimensional...
silicon dioxide matrix are polarized to a high degree. Many of the results obtained in this work seem to strengthen the arguments that oxide-capped silicon quantum dots have universal properties, independently of the fabrication method, and that the greatest differences between individual nanocrystals are indeed caused by individual factors like local environment, shape and size (among others).
Appended Publications

(I) B. Bruhn, J. Valenta, J. Linnros, “Controlled fabrication of individual silicon quantum rods yielding high intensity, polarized light emission”, Nanotechnology 20, 505301 (2009)

Contributions: Fabricated the samples, conducted FIB/SEM work, performed part of the PL measurements, lead the discussion and wrote the paper.


Contributions: Fabricated the samples, performed SEM measurements, conducted part of the PL measurements, lead the discussion and wrote the paper.

(III) B. Bruhn, J. Valenta, I. Sychugov, K. Mitsuishi, J. Linnros, “Transition from silicon nanowires to isolated quantum dots: Optical and structural evolution”, manuscript

Contributions: Fabricated the samples, performed SEM measurements, performed part of the PL measurements, conducted the data analysis, lead the discussion and wrote the paper.


Contributions: Fabricated the sample, performed FIB/SEM work, correlated SEM and PL data and took part in the discussion.


Contributions: Fabricated the sample, performed part of the blinking measurements, developed analysis software, conducted the data analysis, lead the discussion and wrote the paper.

Contributions: Fabricated the sample and took part in the discussion.

(VII) F. Sangghaleh, B. Bruhn, T. Schmidt, J. Linnros, “Exciton lifetime measurements on single silicon quantum dots: explanation of stretched exponential decay”, manuscript

Contributions: Fabricated the sample, performed SEM measurements and took part in the discussion.

Other Publications

(VIII) B. Bruhn, P. Palmgren, H. von Schenck, J. Weissenrieder, M. Göthelid, C. Sun “Structure, adsorption energy, charge density and chemical reactions in iodine layers on Pd(111)”, manuscript


International Conferences (Presentations/Posters)

(X) E-MRS Spring meeting 2008, Strasbourg

(XI) Silicon based emission technology (SiBET) 2009, Manchester

(XII) E-MRS Spring meeting 2010, Strasbourg

(XIII) MRS Fall meeting 2010, Boston
To my family

...and to love,
the greatest power
of them all
I want to thank Jan Linnros, my dedicated and demanding supervisor, for giving me the possibility to engage in such an interesting and diverse project. You provided the framework, defining a general direction, but also much freedom, encouraging me to take responsibility and assume the lead in my project. I learned a lot during these years and made a huge step both in my personal and professional development.

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All my other colleagues and fellow researchers shall receive my gratitude for creating and maintaining such a nice, inspiring work environment. Collaboration, teamwork, lively communication and social interaction are essential for promoting creativity and efficiency and I experienced our workplace as a great example for all that.

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Last in the list, but far from least in priority, I want to give special thanks to my family. You have always been there for me, no matter what, and selflessly supported me. I feel truly blessed. Without you, I would not be who and where I am today.

_Benjamin Bruhn_
Stockholm, October 2012.
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<th>Abbreviation</th>
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<tr>
<td>DLP</td>
<td>Degree of linear polarization</td>
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<tr>
<td>EBL</td>
<td>Electron beam lithography</td>
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<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
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<td>HF</td>
<td>Hydrofluoric acid</td>
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<td>MEG</td>
<td>Multi-exciton generation</td>
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<td>NC</td>
<td>Nanocrystal</td>
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<td>NW</td>
<td>Nanowire</td>
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<td>PL</td>
<td>Photoluminescence</td>
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<td>pSi</td>
<td>Porous silicon</td>
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<td>QC</td>
<td>Quantum confinement</td>
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<td>QD</td>
<td>Quantum dot</td>
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<td>QE</td>
<td>Quantum efficiency</td>
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<td>QR</td>
<td>Quantum rod</td>
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<td>QW</td>
<td>Quantum wire</td>
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<tr>
<td>RIE</td>
<td>Reactive ion etching</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
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<tr>
<td>Si</td>
<td>Silicon</td>
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<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
</tbody>
</table>
# Contents

Acknowledgements xi

Abbreviations xiii

Contents xiv

1 Introduction 1
   1.1 Introduction .................................................. 1
   1.2 Aim of the thesis ............................................... 3
   1.3 Recommended reading ........................................... 3

2 Basic concepts 5
   2.1 Semiconductors and their band structure .................... 5
   2.2 Nanocrystals .................................................... 7
   2.3 Excitons ........................................................ 7
   2.4 Phonons ......................................................... 8
   2.5 Quantum confinement .......................................... 9
   2.6 Nanostructures: What makes them special ................... 10

3 Quantum dots 13
   3.1 Optical properties of quantum dots ......................... 13
   3.2 A brief history of silicon nanocrystal research ............. 16

4 Silicon Quantum Dot Fabrication Methods 19
   4.1 Overview ....................................................... 19
   4.2 Laterally spaced Si quantum dots by nano-lithography ....... 20

5 Photoluminescence Measurements 23
   5.1 Principle ....................................................... 23
   5.2 Components of a PL system .................................... 24
   5.3 Single dot spectroscopy ....................................... 24
   5.4 PL imaging ..................................................... 26
   5.5 Spectral measurements ....................................... 27
1.1 Introduction

Silicon is the second most abundant element in Earth’s crust, next to oxygen, and it is non-toxic to life as we know it. In the table of elements, silicon is classified as a group IV semiconductor with a diamond crystal lattice. Its tunable electrical properties make it suitable as transistor material and, indeed, silicon is the dominating platform for microprocessors and integrated circuits. As of today, the solar cell business is largely based on this material, as well. Being an indirect bandgap semiconductor, silicon could not be utilized as active material in lighting and photonics technology, though. Optical transitions, which lead to light emission, are too slow and inefficient and the rather narrow bandgap only supports photon energies in the infrared range.

With the development of quantum physics and the advent of nanotechnology it became clear that materials change their properties when feature sizes become very small (in the range of a few billionth of a meter) and quantum physical effects like quantum confinement begin to play a major role. In nanoscopic dimensions crystals cannot be regarded as an infinite periodic structure anymore, which means that boundary conditions and surface effects become increasingly important the smaller a structure is. Therefore, surface passivation often plays a major role in optical and electrical properties of nanostructures, as well as their actual size and shape.

Silicon nanocrystals can emit light in the visible range, as quantum confinement results in quantized energy levels for electrons and holes, which assume higher energy levels in their respective energy bands the smaller the crystal becomes. When using the term “energy bands”, one has to keep in mind that the band structure is not exactly the same as in bulk silicon, since it derives its properties from the assumption of an infinite periodic lattice. Actually, due to changes in the band structure and strong confinement of charge carriers, which leads to a stronger overlap of their wavefunctions, optical transitions in nanocrystals become more efficient than in bulk material.
The discovery of porous silicon as efficient emitter of red light at room temperature [1] sparked great interest in silicon nanocrystals and the new field began growing exponentially, as the number of new publications per year in Figure 1.1 demonstrates.

Knowledge about the physics involved in mesoscopic and nanoscopic silicon structures has increased significantly within the last two decades and a lot of applications have been developed or are close to implementation. Among others this involves solar cells [3], ink for flexible electronics [4], charge storage in computer memory [5], photosynthesis of oxygen for biomedical applications [6, 7], single electron transistors [8], spin transistors [9], LEDs [10, 11], fluorescence markers [12] and phosphor alternatives in lighting technology. However, not all properties of silicon quantum dots are well understood yet and more research is required to fill the gaps.
1.2 Aim of the thesis

The main goal of this work was to gain more knowledge about the physics of silicon quantum dots and the mechanisms that drive photoluminescence and govern the nanocrystals’ optical properties. A fabrication method for single silicon nanocrystals was developed, which allows for repeatable single dot measurements. This method utilizes electron beam lithography and plasma etching to fabricate nanometer-sized patterns on a mono-crystalline silicon wafer, as well as oxidation below the flow temperature of silicon dioxide for shrinking the active silicon structure and creating luminescent quantum dots and wires. By designing the patterns accordingly, optical measurements on single nanocrystals can be enabled. Furthermore, optical and electron microscopy characterization of the fabricated structures was carried out. The analysis of results from scanning and transmission electron microscopy, photoluminescence imaging, PL spectral and lifetime measurements and blinking measurements yielded new insights regarding the mechanisms that the photophysics of silicon nanocrystals are based on.

1.3 Recommended reading

2.1 Semiconductors and their band structure

Most semiconductors are crystalline materials either from group IV in the table of elements or III-V or II-VI compounds. Their well ordered atomic structure imposes periodic boundary conditions on electrons (or electronic wavefunctions) within the material. Solving the Schrödinger equation for electrons (plane wave function) in a crystal (periodic potential) yields solutions in the form of Bloch waves. For any given wavevector $k$ there are several solutions, yielding different eigenenergies. A plot of those energies as a function of the wavevector is called a band diagram, as shown in figure 2.1. The name results from the fact that bands of allowed energies are separated by so-called bandgaps, in which energy values are not allowed for electronic wavefunctions within a periodic potential.

Figure 2.1: a) Direct semiconductor (GaAs) band structure with direct transition. b) Silicon (indirect semiconductor) bandstructure with indirect transition including a phonon for momentum conservation. Detailed data for the two graphs can be found in references [18] and [19] and references therein.
The electrons in the material occupy all energy levels up to the Fermi level, which usually lies in the band gap between two bands referred to as the valence band (VB) and the conduction band (CB). VB is the highest-lying band completely filled with electrons, whereas CB does not contain any electrons under normal circumstances. In order to conduct a current, a band has to be partially filled with charge carriers. When electrons from the valence band are promoted across the bandgap into the conduction band, a current can flow. Conduction and valence band overlap in metals, which makes them conductive, whereas insulators exhibit a large, almost insurmountable spacing between the two.

When an electron from the valence band transfers to the conduction band, it leaves an empty state behind, which is referred to as a “hole” and behaves as a positively charged quasi-particle. Photons (light particles) of sufficient (at least the bandgap) energy can be absorbed by the semiconductor, creating such electron-hole pairs. The most important type in this context is the exciton, in which the created charge carriers are bound to each other. In figure 2.1a photon absorption would promote an electron from the lower red circle to the higher red circle, leaving a hole behind. When the two charge carriers recombine, their annihilation energy is emitted as a photon with an energy equal to the bandgap energy.

Electrons in the CB strive to fill energy levels at the band edge minimum and holes assume according positions in the VB (at VB maxima). Thus, if carriers are excited with highly energetic photons, they relax via ultrafast processes from their initial high energy levels to the respective unoccupied lowest levels.

Silicon is today the most used semiconductor in the electronics and photovoltaic industries. This fact can be attributed to its excellent surface properties, where thermal oxide can provide a well controlled interface, to its tunable electrical properties, far developed processing technology, non-toxicity, abundance and low cost. Unfortunately, in terms of light generation bulk silicon has severe disadvantages in comparison to many other materials. It belongs to the family of indirect semiconductors and is therefore inherently inefficient as a light emitter. While direct semiconductors allow fast direct transitions of charge carriers between the maximum of the valence band and the minimum of the conduction band (see figure 2.1a, indirect materials require the participation of an additional, momentum-conserving quasi-particle, a phonon, since the valence band maximum and conduction band minimum are not at the same position in k-space (see figure 2.1b. This makes the radiative recombination process rather slow (approximately five orders of magnitude difference can be observed).
2.2 Nanocrystals

Materials with a well ordered, periodic atomic structure are called crystals. Semiconductors have a crystalline composition, which causes the formation of bands and band gaps through periodic variation of the electronic potential that an electron encounters along its path through the material. The prefix “nano” denotes the dimension of the crystal, one nanometer being a billionth of a meter \(10^{-9} \text{ m}\). Correspondingly, the term nanocrystal is used for clusters of a few thousand atoms arranged in a crystalline lattice; that would typically be grains of a few (up to a few dozen) nanometers in diameter. Those dimensions are so small that quantum effects (e.g. quantum confinement, to name the most prominent) often play a major role in such systems. Another strong influence on the nanoparticles’ properties is exerted by their local environment and surface passivation, due to the high surface to volume ratio.

2.3 Excitons

Excitons are electron-hole pairs, where the two charge carriers are bound to each other (resulting in slightly lower energy compared to free electrons and holes). A photon absorption process can lead to the creation of excitons by exciting an electron, which leaves an unoccupied lower energy level, a so-called hole, behind. This process is shown in figure 2.2a,b.

There are two basic types, the Frenkel exciton and the Wannier-Mott exciton. While the first one is observed in molecules and low dielectric materials, the latter one dominates most semiconductors. It has a radius larger than the unit cell and its charge carriers’ effective mass depends on the lattice potential. When a semiconductor structure is smaller than the exciton radius, the exciton is confined, which increases
its energy, but also results in a larger overlap of electron and hole wavefunction, increasing the probability of recombination. When an exciton recombines, i.e. an excited state transfers back to the ground state, it can do so by photon emission (also shown in figure 2.2b) or via non-radiative paths, such as multiple phonon emission. In the case of indirect semiconductors, optical transitions are usually accompanied by phonon interaction in order to conserve momentum (electron and hole are in different positions in k-space, see figure 2.1b). In nanostructures, this k-conversation rule can break down due to the strong overlap of the charge carriers’ wave functions, enabling direct optical transitions without phonon participation.

2.4 Phonons

Phonons are quanta of lattice vibrations and therefore being described as quasi-particles. They can interact with photons and be created or absorbed in radiative recombination processes. Figure 2.3a shows how an oscillating electric field (e.g. that of a photon) causes vibrations of the crystal lattice it passes. A phonon carries momentum, which is its key property for radiative recombinations of electrons in the X-valley and holes in the Γ-valley in silicon, since a photon cannot carry any momentum and the two valleys are separated in k-space. In optical phonons, the two adjacent atoms of the unit cell vibrate in opposite directions, whereas they are in phase in acoustic phonons. Of each type there are two sub-types: Transverse and longitudinal. The oscillation is perpendicular to the propagation direction in the first one and parallel to the propagation direction in the latter, which makes coupling to photons much more efficient for transverse phonons in the largest part of the spectrum, since their electromagnetic field oscillates perpendicular to their propagation direction. For ε = 0, however, there is efficient coupling between photons and longitudinal phonons. Figure 2.3b shows the dispersion relation of different phonons in silicon between the Γ- and the X-point.

In silicon nanocrystals there can be optical transitions without any phonon involvement, which result in a no-phonon peak in the emission spectrum. Transitions
with phonon involvement are observed at lower energy in an emission energy spectrum, with the phonon energy as distance between the phonon replica and the no-phonon peak.

2.5 Quantum confinement

This term denotes a quantum mechanical effect that arises from spatial confinement of a material in one or more direction(s). In a confined direction, boundary conditions apply to wave functions, which reduces the density of states and increases the level of the smallest allowed energy. Energy levels that charge carriers can reside in change from a quasi-continuum to a set of quantized states. Therefore, the lowest state energy in a semiconductor quantum dot lies above the bulk bandgap value, the difference being determined by the size of the nanocrystal. Figure 2.4 demonstrates these principles in a simplified way. The energy levels can be calculated by solving the Schrödinger equation for a system with appropriate boundary conditions.

![Figure 2.4](image_url)

**Figure 2.4:** a) The conduction band of bulk material contains a quasi-continuum of energy levels. b) When a structure becomes small, quantum confinement quantizes the energy levels and pushes the lowest levels away from the bandgap and into the band. c) Even more confined structures exhibit larger energy level spacing and the lowest energy level is further away from the bulk band edge. d) Wave functions of the first three energy levels. The lateral confinement imposes boundary conditions that allow for specific energies only. e) More confinement than in (d) leads to shorter wavelengths of the wavefunctions.

Note that by simply changing the size of nanoparticles, and thereby strengthening quantum confinement, while keeping all other properties (like surface passivation, etc.) unaltered, one can tune the light emission of quantum dots to different colors in the visible spectrum. Figure 2.5 shows an example of this intriguing fact.
2.6 Nanostructures: What makes them special

As can be derived from their name, their size is characteristic and important for nanostructures. It turns out that spatial confinement to dimensions of a few to a few tens of nanometers can change a material’s electrical and optical properties significantly. In general, there are three different types of nanostructures, also shown in figure 2.6: Quantum wells (two-dimensional), wires (one-dimensional) and dots (zero-dimensional). Their size is confined in one, two and three directions, respectively. Stronger confinement imposes more rigid boundary conditions on the charge carriers’ wavefunctions within the material and also increases the surface to volume ratio, granting surface or interface states an important role.

Quantum wells are thin sheets of semiconductor material sandwiched between layers of a different (usually semiconducting) material. Charge carriers can move freely in the sheet plane, whereas boundary conditions apply perpendicular to it,
confining electrons and holes. Carriers cannot diffuse out of the narrow active region (e.g. to unpassivated surface states), while good interface design helps to avoid carrier recombination at interface states. Single or multiple quantum well structures are used in a variety of applications, among which are laser diodes and other LEDs, optical modulators, field effect transistors, quantum well infrared photodetectors and resonant tunneling diodes (see e.g. references [21, 22]).

Quantum wires can be approximated as high aspect ratio cylinders of a semiconducting material, which is capped by another (semiconducting) material. One rather obvious application of nanowires is to transport small electrical currents, which is needed for energy-efficient nanoelectronic devices (see e.g. [23]). Due to a large surface to volume ratio, charge carriers in the wire are easily influenced by changes in the local environment, e.g. molecules that attach to their (functionalized) surface, which makes them suitable as electrical sensors for chemical changes in a medium or biomolecule detection (see reference [24] and references therein). Nanoribbons, a subgroup of nanowires that is only strongly confined in one dimension, can effectively be used for this application as well. [25] Upon sufficient confinement semiconductor quantum wires emit strongly linearly polarized light when electrically or optically excited. Light emission and absorption are generally both strongly linearly polarized along the long axis of the wire, which can be attributed to dielectric contrast and quantum confinement effects (see among many others [26, 27]).

A quantum dot is created either by structural or electronic confinement. While the prior has a core comprised of one semiconducting material and a surrounding shell of another semiconducting material with a wider bandgap, the latter can be achieved by placing ring electrodes as gates on the sides of a quantum well or by placing gate electrodes on a quantum wire. Applying a voltage will then create a field that confines carriers in the enclosed structure. For one of the first gate-defined quantum dots see reference [28] and for a review [29]. Typically, the dimension at which quantum confinement plays a roll in nanocrystals is the exciton Bohr radius of the respective material, which is the size of this neutral quasi-particle. It ranges from 1.8 nm in ZnO [30], via 3.0 nm in GaN [30] and 4.9 nm in silicon [31], up to 12 nm in GaAs [32] and even 60nm in InSb [31], just to name a few examples. Quantum dots are especially interesting from an application point of view, as their optical absorption and emission spectrum can easily be tuned by changing the quantum dot core dimensions. Doing so can even prove useful for applications where the energy levels of several components have to be aligned, e.g. in quantum dot enhanced quantum well infrared photodetectors. Other thinkable applications and products are lasers, fluorescence markers for fluorescence microscopy, phosphor substitutes for light conversion, light emitting diodes (LED) and even computer memory (where charge is stored in a quantum dot layer).
3.1 Optical properties of quantum dots

As already described, the effective band gap of a quantum dot can be tuned by its size. The smaller a quantum dot is, the larger the spacing between energy levels in the valence and conduction band. Figure 3.1 shows schematically how both absorption and emission spectra shift with a change in nanocrystal size (indicated by the colored circles). Absorption starts at the bandgap energy (which means that the material is transparent for light with lower energy than the bandgap) and PL emission consists of a peak at the effective bandgap energy value.

In indirect bandgap materials like silicon, several emission peaks can be found, which are caused by phonon contributions to the radiative recombination process. Interestingly, a no-phonon PL emission peak can be observed in optical spectra of silicon nanocrystals, as opposed to spectra measured on bulk silicon. A direct

![Figure 3.1: Schematic drawing of absorption (top) and PL emission (bottom) spectra of quantum dots with different sizes.](image-url)
transition is not allowed in bulk silicon, since the X-valley (minimum of the conduction band) and the Γ-valley (maximum of the valence band) are located at different positions in k-space. Therefore, unlike in direct semiconductors, which have both extrema at the Γ-point, a momentum-conserving particle is required for optical transitions. In a nanocrystal, the band structure is altered and the electron and hole wavefunctions overlap significantly, allowing recombination without phonon contribution. This phenomenon is known as the breakdown of the k-conservation rule.[33, 34] Schematic example spectra are shown in figure 3.2. Note that the phonon replica can be found at approximately the values that are plotted in figure 2.3.

The width of the emission peaks differs between different materials. CdSe quantum dots, for example, have been reported to have homogeneous emission linewidths of as little as 32 µeV [35], which lies far below the thermal energy $k_B \cdot T$ and is therefore proof of the existence of atomic-like quantized energy levels. Silicon nanocrystals have several distinct peaks at low temperature. The NP peak can also have a FWHM below $k_B \cdot T$ (e.g. FWHM of 2 meV at 35 K in reference [36]), while the phonon-related peaks are usually broader. Due to thermal broadening and higher phonon population at elevated temperature, the different peaks merge and only one broad peak of 100-150 meV FWHM can be observed at room temperature.

Not only the spectra of differently composed quantum dots are different, but also the exciton lifetimes. In direct semiconductor nanocrystals like CdSe and CdTe, excitons decay on timescales of the order of nanoseconds (see e.g. [37, 38, 39]). Radiative recombination processes in silicon nanocrystals are about three orders of magnitude slower; usually values between a few µs and several hundreds of µs are reported.[40, 41, 42] This means, that e.g. CdSe-QDs can be excited with much higher power than Si-QDs, before their PL emission starts to only increase sub-linearly. The change from linear emission increase as a function of excitation power to sub-linear increase is attributed to non-radiative Auger recombination processes when several excitons are created at once in a single nanocrystal.[43, 44] While emission from bi-excitons and even the next higher exciton energy level could be observed in direct semiconductor nanocrystals (see e.g. [45]) a corresponding
3.1. Optical properties of quantum dots

Figure 3.3: Schematic drawing of a blinking trace, where a quantum dot switches between an ON- and an OFF-state. On the right hand side a neutral (ON) and charged (OFF) quantum dot and their corresponding exciton recombination mechanisms are shown.

observation in silicon is missing. It has therefore been postulated that all excess excitons in a Si-QD decay very fast via non-radiative paths and only the last remaining exciton can emit a photon upon recombination.\cite{46} On the other hand, a sub-linear, but steady increase of PL emission upon increased pumping has been reported. It has been shown that in porous silicon, the existence of several excitons in the same quantum dot leads to a lifetime shortening,\cite{43} enabling stronger pumping. Possibly multi-exciton radiative recombination does exist and just has to be observed yet.

A phenomenon that literally covers the whole range of quantum emitters, from organic molecules to inorganic semiconductor quantum dots, is so-called blinking or emission intermittency. Those terms describe the switching between an on- and an off-state, just like when a switch for light bulb is pressed repeatedly. The mechanisms behind blinking are not fully understood yet, but the dominant model regards a charged state of the emitter as cause for the OFF-state, since then a non-radiative pathway for exciton recombination opens up. Upon charge neutralization of the emitter, it returns to the emissive ON-state, where newly created excitons recombine via photon emission.

Blinking is widely believed to be responsible for aging in nanocrystal ensembles under excitation. The term aging denotes a decrease of the PL signal in time. While luminescent biomolecules experience permanent photobleaching due to chemical changes, the emission intensity of nanocrystals recovers in a period of non-excitation. The temporary loss of light output from a QD ensemble could therefore be a statistical artifact that follows from the statistics of the blinking process.\cite{47,48}

The internal quantum efficiency of a quantum dot is defined as the ratio of radiative recombinations to overall recombination of excitons. For each absorbed photon, an exciton is created in the quantum dot, but not all of these recombine upon photon emission, which makes the IQE lower than unity. For silicon quantum dots, published values range from 20% to 80%. External quantum efficiency is the ratio of emitted photons to absorbed photons. This quantity can, under certain circumstances (involving multiple exciton generation), assume values greater than 100% (see e.g.
MEG has been reported in a variety of direct semiconductor material quantum dots, but also in Si-QD [50, 51]. For reviews about MEG, see references [52, 53]. It is promising for the application of quantum dots in photovoltaics, since part of the heat losses due to carrier excitation by high energy photons and subsequent carrier cooling can be avoided.

3.2 A brief history of silicon nanocrystal research

Silicon has been known to be an indirect bandgap semiconductor with poor optical properties for a long time. Even though porous silicon was accidentally discovered by Uhlir [54] already in 1956, it was not until the 1990’s, when Canham [1] demonstrated efficient light emission at room temperature and Lehman et al. [55] invoked quantum confinement to explain features of porous silicon absorption spectra, that interest in silicon nanocrystals arose and this new field of research was created. The number of publications per year regarding the subject increased exponentially and the focus moved from other (thermal and electrical) properties to optical properties.

Three distinct photoluminescence bands could be observed, one in the infrared, one in the red and one in the blue light range. While dangling bonds were quickly identified as the origin of the infrared band, which was therefore dismissed as a subject of minute interest, there was a lively discussion about the mechanisms that caused the other two emission bands. Quantum confinement, as already proposed by Canham upon his discovery [1], is nowadays widely accepted as the explanation for the red emission. However, other mechanisms than QC have been proposed as the origin of light emission in SiQDs, e.g. surface and interface states, and it is likely that a mixture of the two coexists. [56] The red photoluminescence’s lifetime, ranging from a few to a few hundred microseconds, is several orders of magnitude longer than that of emission from direct bandgap semiconductors. As opposed to that, the blue band lifetime of several nanoseconds is comparable to that of direct semiconductor bandgap quantum dots. A commonly accepted model regards oxide-or carbon-related defects as the origin of blue emission from oxide passivated silicon nanocrystals. However, the discussion is still ongoing and recent studies suggest e.g. phonon-free recombination of non-equilibrium electron-hole-pairs as origin of the blue PL band (see e.g. [57]).

During the course of the two decades following the discovery of porous silicon, a range of different fabrication methods for silicon nanocrystals has been developed. A short overview will be given in chapter 4.

One of the major initial questions was, why porous silicon and other silicon nanocrystals could emit light so efficiently, while bulk material was a rather poor photon source. Heisenberg’s uncertainty principle in conjunction with the quantum confinement model provides an explanation for direct band-to-band transitions, which would enable radiative recombination of electrons in the conduction band and holes in the valence band without interaction with a phonon. A spread of the
wavefunction of charge carriers upon strong lateral confinement increases the overlap in k-space significantly, greatly increasing the probability of recombination. Note that the product of uncertainty in position and momentum of a particle cannot be less than half the reduced Planck constant. Indeed, an additional peak, originating from radiative exciton recombinations without phonon involvement, is found in a silicon nanocrystal emission spectrum compared to the spectrum of bulk silicon. This breaking of the k-conservation rule has been calculated by Hybertsen et al. [33] in 1994 and demonstrated experimentally by Kovalev et al. [34] in 1998.

Observations of a limitation of the range of emission energies of oxide-passivated SiQD to red light could be explained by Wolkin et al. [58] in 1999. The pinning of the emission energy could be ascribed to oxide-related defects, which move into the bandgap and act as recombination steps in small nanocrystals. Silicon quantum dots passivated by hydrogen or different organic cappings do not experience the same limitations and therefore have an emission that is tunable throughout the whole visible range.

A phenomenon previously known from organic dye molecules and other quantum dots, has also been reported for silicon nanocrystals [59]: Blinking (or emission intermittency). The term denotes a switching process between an optically active bright state, in which excitons can recombine radiatively, and an optically inactive dark state that favors non-radiative recombination processes. The latter is believed to be caused by charging of the quantum dot (e.g. by electron emission into a trap state, accompanied by a remaining positive charge in the QD core), which would then be governed by Auger processes. Recently, even two different types of blinking were proposed to co-exist in a nanocrystal [60]. However, the blinking mechanism and its origin are not fully understood yet, despite intensive research and ongoing development of non-blinking quantum dots.

Positive optical gain is another point of ongoing discussion and research. Promising results in that direction have been published in 2000 [61], but could since then not be reproduced and confirmed. Basically, there are two major mechanisms hampering positive gain, one of which is free-carrier absorption, and the other being scattering. Inhomogeneous broadening due to a certain size distribution of nanocrystal ensembles poses another problem, since a large fraction of the quantum dots do not contribute to the desired emission energy. Should gain be possible in silicon, the all-silicon laser could become a reality.

A rather obvious, but nonetheless important insight is that measurements on individual quantum dots are required for gaining a deep understanding of the photophysics of quantum dots and the correlations of different (e.g. geometric and optical) properties. In this way, inhomogeneous spectral broadening and other ensemble effects can be overcome and phenomena like spectral diffusion, blinking, the Stark effect and strong linear polarization can be detected. Due to the relatively low light yield from single SiQD and difficult preparation methods, it was not until the late 1990’s that methods originally developed for single molecule studies were applied to single silicon nanocrystal studies and there has constantly only been a small circle of research groups deploying single SiQD spectroscopy. Both in theoretical studies
Quantum dots

[62] and in practice it could be shown that not only the nanocrystal size, but also the geometry, among other factors, plays a major role in determining the quantum dots’ optical properties, making repeatable measurements of different types on the same individual quantum dots all the more important.

Besides the aforementioned phenomenon of blinking, a spectral width of the emission peak of single silicon nanocrystals below the thermal broadening could be demonstrated in 2005 [36], providing clear evidence for the atomic-like energy level quantization in the energy bands of SiQD. In 2007 [50], multi exciton generation (MEG) was reported, lifting the limit for external quantum efficiency above unity. Otherwise a wide range of values (up to 80%) for QE in silicon quantum dots can be found in the literature.

Recently, a large part of the research engaging silicon nanocrystals has moved towards erbium-doped quantum dot systems and different cappings of nanocrystals in solution. However, some work is also done to answer other remaining questions, which mostly deal with blinking, multiple excitons, gain and the direct and quasi-direct radiative recombination processes.
Chapter 4

Silicon Quantum Dot Fabrication Methods

4.1 Overview

Since the discovery of porous silicon and its new optical properties [54, 1, 55], numerous silicon nanocrystal fabrication methods have been developed, incorporating a range of bottom-up and top-down approaches. So-called bottom-up techniques start with small building blocks, e.g. atoms or molecules, and assemble those into the end product, in this case nanocrystals. Top-down methods, on the other hand, rely on size reduction of bulk material until appropriate nanoscopic dimensions are reached.

The probably most frequently used fabrication technique for spherical silicon nanocrystals in a silicon dioxide matrix consists of annealing of a non-stochiometric silicon oxide. Such can be obtained by a variety of methods, among others ion implantation [63], chemical vapor deposition [64] and sputtering [65]. The excess silicon diffuses through the dioxide and nucleates into nanocrystals.

In another bottom-up approach silane gas undergoes decomposition induced by a radio frequency coil [66] or laser pulses [67], leading to silicon cluster formation.

When it comes to top-down fabrication methods, electrochemical etching for porous silicon formation [54] has been the first known method for (generally non-spherical) silicon nanocrystal fabrication and still remains the most widely used technique. A silicon wafer, acting as anode, is placed in a hydrofluoric acid bath with a negative counter-electrode. At the solid-liquid interface the electronic holes then enable a reaction that etches silicon and leaves $\text{SiF}_4$ and $\text{H}$ as byproducts. This process requires p-type material or generation of excess carriers by e.g. light. Under appropriate conditions a fine network of silicon strands is being created, which then partly oxidizes into a silicon dioxide network containing silicon quantum dots.

Laser ablation is another popular method, in which a silicon wafer is being exposed to a highly energetic pulsed laser. Each pulse supplies a high amount of energy to the bulk silicon surface, causing small silicon clusters to leave the bulk material. See e.g. reference [68].

A recent approach consists in grinding silicon bulk material in a mill and then
exposing the resulting dust to a solution that both oxidizes the silicon and etches the oxide. The etching time defines the size reduction of the silicon dust particles. Large particles can be filtered out of the solution. Finally, the method used in this work - electron beam lithography in conjunction with reactive ion etching and oxidation - enables fabrication of structures that contain single silicon nanocrystals in well-defined positions on a silicon sample. The method, schematically shown in Figure 4.1, and its resulting structures shall be described in detail at this point, since they constitute an important part of this project.

4.2 Laterally spaced Si quantum dots by nano-lithography

In early approaches [70, 71], arrays of holes were created in an electron-sensitive positive resist layer on a silicon wafer with a thin top oxide layer by electron beam exposure and chemical development. Metal deposition and lift-off then changed the pattern to arrays of circles and wet etching in hydrofluoric acid (HF) transferred it to the dioxide hard mask on the silicon substrate. Subsequent reactive ion etching was used to fabricate arrays of pillars, which in a final step could be oxidized in order to shrink the silicon core. Under appropriate oxidation conditions, single silicon nanocrystals could be obtained in the top of these pillars. This requires oxidation in the self-limiting regime, which means at a temperature around 900 degrees Celsius, which is below the oxide flow temperature. During the oxidation process, stress builds up along concave and convex surfaces, respectively accelerating or decelerating the oxidation rate. [72, 70, 73] Due to the significant differences in curvature, the pillars oxidize faster in the center than at the top, leaving a teardrop-shaped, nearly spherical quantum dot in the pillar head.[71, 74] Different oxidation stages of silicon pillars are shown in Figure 4.2.

Despite good spatial positioning potential for quantum dots made from pillars, successful fabrication of these structures is strongly dependent on oxidation time.
and, due to random size fluctuations, yields only small amounts of luminescing nanocrystals. In addition, the initial shape of the pillar has a considerable influence on the remaining core shape. Therefore, many samples (containing pillars with the wrong shape) do not yield luminescing nanocrystals at all.

Recent results show that spatially well separated single silicon nanocrystals can also be obtained by oxidation of silicon walls. The fabrication of such follows a similar approach as that of pillars. Instead of a mask inversion process, negative resist (HSQ) is used in the electron beam lithography step to define arrays of lines on a silicon substrate. Reactive ion etching and oxidation at 900 degrees Celsius are used to shape walls and shrink the silicon core until luminescing nanostructures are obtained within the wall. Again, the center part oxidizes faster than the top part and any thickness variations are amplified by the self-limiting oxidation, creating an undulating nanowire in the top of the silicon wall. Undulating means that the diameter of the wire is not constant along the wall. The wire usually also contains protrusions (silicon bulges sticking into the oxide), which can act as quasi-quantum dots, as will be explained in chapter 6. Upon further oxidation, the wire breaks up into separated nanocrystals. Different oxidation stages of a straight silicon wall are shown in Figure 4.3.

The creation of luminescing nanocrystals from silicon walls is much more rigid towards variations in oxidation time than is the case in pillars, since existing nanocrystals might be destroyed, while new ones are created throughout the whole oxidation process. Even though it is difficult to define a success ratio, typically at least one quantum dot per micrometer wall length is created on average under appropriate conditions.

Since reduced lateral positioning capability in the rather random nanocrystal creation in straight walls poses a severe drawback in comparison to the pillar method, another more recently developed method can be deployed, which combines the high yield of the straight wall approach with the precise positioning of the pillar approach. In this method walls with stepwise varying thickness are etched from a silicon substrate, so that upon oxidation the thinnest part of the undulating wall produces luminescent nanostructures first. Figure 4.4 shows such undulating walls in different

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**Figure 4.2:** Silicon pillars in different oxidation stages (oxide removal after each oxidation). The remaining silicon core looks bright, whereas the surrounding oxide is darker and somewhat transparent. Possibly in (c) the head contains a nanocrystal, which is too small to see with a SEM.
oxidation stages. Success rates for obtaining luminescent nanocrystals in an array of undulating walls are rather high under appropriate oxidation conditions. While the oxidation time is somewhat more crucial than in the straight wall method, variations do not play as big a role as in the pillar method.

Fabrication recipes for samples containing pillars, straight and undulating walls can be found in Appendix A. A few noteworthy hints and tricks regarding different processing steps are listed in Appendix B.
5.1 Principle

The term photoluminescence denotes a process in which light of a certain energy or energy range is absorbed and subsequently light of a different (longer) wavelength is emitted. In semiconductor nanocrystals the absorbed photons need to have an energy that is larger than the bandgap, while the emitted photons have an energy that is equivalent to the difference between the highest energy level in the valence band and the lowest level in the conduction band. Upon photon absorption, electron and hole pairs are created. In a radiative recombination process, the two carriers annihilate each other and energy is released in form of a photon. Highly excited carriers usually undergo ultrafast relaxation processes to those lowest energy levels in their respective bands before the comparatively slow recombination. For weak quantum confinement the energy of emitted photons is approximately equal to the width of the bandgap. By measuring the photoluminescence emission of a quantum dot one can obtain knowledge about e.g.

- the quantum confinement strength (by comparing the emission energy to the bulk bandgap)
- the number of excitons recombining radiatively (by measuring spectra and intensity increase at high excitation)
- the exciton lifetime (by measuring the PL decay after an excitation pulse)
- nanocrystal absorption cross section (by measuring the PL rise during an excitation pulse)
- radiative and non-radiative recombination paths
5.2 Components of a PL system

In practice, a setup for conducting different photoluminescence experiments is comprised of many components. The excitation laser light is first filtered to ensure monochromatic excitation and can optionally be attenuated, e.g. by an optical density filter, as well as polarized by a polarization filter. It then excites structures on a sample that can optionally be mounted in a cryostat for temperature control. In one of the setups used in this work, the incident angle was not perpendicular to the sample surface, but at an angle of approximately 50 degrees in order to minimize excitation stray light entering the objective lens. In the other (confocal) system the laser is focused onto the sample surface by the objective lens of the microscope. Light emitted by the structures enters an optical microscope through an objective lens. A special corrected lens is required when a cryostat is used, since a glass window is situated between the sample and the objective lens. An edge filter then removes all excitation light. In the case of a 405 nm laser diode this could be a long wavelength pass filter with a cut-off at 415 nm. Optionally a polarization filter can be used to only transmit one type of polarization, which can be used to characterize the degree of polarization of light emitted by the sample. Finally the image is focused either directly onto a cooled CCD camera or via an image intensifier or a spectrometer for PL lifetime or spectral measurements, respectively. Figure 5.1 schematically shows the optical path in a typical PL setup.

5.3 Single dot spectroscopy

When single quantum emitters shall be measured, the detection efficiency of the system is crucial. First of all, it is essential to diminish any background signal, caused e.g. by scattered light, which can obscure the weak emission of single quantum dots. This requires both filtering of the excitation light, as explained above, and shielding of the light path against external light sources, which in practice usually means to place the PL setup in a dark box. Secondly, it should be taken into account that components in the optical path can reduce the transmission coefficient of a system and thus reduce detection efficiency. Any unnecessary components should therefore be removed. A weak signal usually leads to longer required acquisition times, which in turn both increases the probability of sample drift and therefore causes image smearing and reduces the temporal resolution in blinking or PL lifetime experiments. Thirdly, an objective lens with a high numerical aperture should be used, since the light collection efficiency scales with its square. Finally, the sample geometry itself can influence how much light is emitted within the acceptance angle of the objective lens, as will be discussed further in chapter 6.

In this work two different PL setups were used. One of them (at KTH in Kista, Sweden) was comprised of a continuous wave (cw) 325 nm CdHe laser with an incident angle on the sample of about 50 degrees, a Nikon Optishot-150S optical
Figure 5.1: Schematic of the light path in a typical PL setup.

microscope with a 100x/0.9 objective lens, a Triax 180 imaging spectrometer, a Hamamatsu C7245 image intensifier and a Hamamatsu C4880 liquid nitrogen cooled CCD camera. For certain experiments the CdHe laser was replaced with a 405 nm Omicron Phoxx diode laser and the CCD camera with an Andor iXon X3 888 EMCCD camera. The other setup (at Charles University in Prague, Czech Republic) was built with an Omicron LDM405.120.CWA.L 405 nm cw laser diode, a Janis ST-500 cryostat, an Olympus IX-71 inverted microscope with a 40x/0.6
corrective objective lens, an Acton SpectraPro 2358i imaging spectrometer and a
liquid nitrogen cooled Princeton Spec-10:400B CCD camera.

The following sections explain how and with which modifications of the instru-
mentation different PL measurements are performed.

5.4 PL imaging

Simple photoluminescence imaging requires the least complicated setup, i.e.
only an excitation source, corresponding (cleaning and edge) filters, an optical
microscope and a CCD camera. Luminescent structures are excited by a
light source, usually a laser, with a photon energy higher than the nanostructures’
bandgap. The excitation source is filtered out before detection, so that only the
lower-energetic photoluminescence of the nanostructures can be seen in a PL image.
Figure 5.2 shows an example of optical microscope images of oxidized silicon wall
arrays containing large amounts of quantum dots illuminated by (a) white light and
(b) a UV laser. (a) is called a reflection image, whereas (b) is referred to as a PL
image.

![Figure 5.2](image_url)

**Figure 5.2:** Figure 1 from [75]. (a) shows an optical reflection image of oxidized silicon
wall arrays. (b) is a PL image of the same array. The scale bars indicate a length of 10
µm.

The lateral resolution is defined by the formula \( d = \frac{n \lambda}{NA} \) and thus generally limited
by the detected wavelength. Two spots can be distinguished from another if their
distance to each other measures at least half the wavelength of the light emitted
by them. It is therefore required that in single dot spectroscopy two neighboring
quantum dots have a spacing of at least one micrometer, but preferably more than
two for easier identification and exclusion of signal mixing.
5.5 Spectral measurements

For spectral measurements a spectrometer with an entrance slit has to be placed between the microscope and the CCD camera. In this context the term spectrum means a plot of the intensity of a light signal as a function of wavelength or photon energy.

The microscope image is focused on the entrance slit plane, which allows the signal of one line of the image to enter the spectrometer. A collimating mirror transforms the light into parallel beams and reflects those onto a diffraction grating, where different wavelengths are dispersed (reflected at different angles), and then another mirror focuses the light onto the CCD chip. The image shows one real space coordinate along the slit and the dispersed wavelengths of each spot in the slit on the other axis. Figure 5.3 shows an example of a spectral measurement of one oxidized silicon wall. Since the photons emitted by one spot are spread out over one axis in the image (and also because of some optical loss in the spectrometer), the acquisition time for spectral measurements is considerably longer than for simple PL images.

Figure 5.3: a) PL image of an array of oxidized silicon walls. Both axes contain real space data. b) Spectral measurement of the line indicated by a white rectangle in (a). One axis still contains real space data, on the other axis the wavelengths of the detected light from each spot of the line are dispersed. The spectrum in the upper part is a plot of intensity versus wavelength of the line indicated by a white horizontal rectangle.
5.6 Polarization measurements

Light is generally polarized elliptically, with the two extreme cases being linear and circular polarization. Certain filters can detect specific polarizations by only admitting transmission of corresponding photons, while absorbing or reflecting photons of other polarizations. In the case of a linear polarization filter only linearly polarized light aligned with the filter can pass through, which means that if the light is completely linearly polarized and the filter is in a horizontal position, only horizontally linearly polarized light is transmitted.

In order to measure absorption polarization, a light source is linearly polarized (by filtering out all excitation light that is not aligned with the filter), so that only photons with a certain linear polarization direction are incident on the sample. In this way it can be tested if a sample only absorbs photons of a specific polarization direction. Emission polarization can be measured by filtering the light emitted by a sample before it reaches the detector.

The degree of linear polarization is defined as $\rho = \frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}} + I_{\text{min}}}$, where $I_{\text{max}}$ is the maximum intensity (which would correspond to a certain polarization filter orientation) and $I_{\text{min}}$ the minimum intensity (which would correspond to a 90 degrees rotated polarization filter orientation). Usually many data points are measured for different rotations of the polarization filter and then the plotted data (intensity versus rotation angle) is fitted with a square sine function to obtain $I_{\text{max}}$ and $I_{\text{min}}$.

Spherical emitters are not expected to emit linearly polarized light, whereas one-dimensional emitters should have a rather high DLP value close to unity. Note that dielectric confinement can influence the polarization of emitters significantly, as shall be further discussed in chapter 6.

Figure 5.4 shows an array of horizontally aligned oxidized silicon walls under UV excitation. It is composed of 13 images recorded at different polarization filter orientations indicated by the white arrows on the right hand side. A polarization filter was used to measure the degree of linear polarization. When the filter allows light polarized parallel to a wall to pass, many quantum dots can clearly be seen. After 90 degrees rotation of the filter, the signal is almost completely quenched.
5.7 Blinking measurements

Also referred to as PL intermittency, blinking describes a switching process between emissive ON- and dark OFF-states, which has been observed in a variety of quantum emitters. Silicon quantum dots are no exception, as they switch between a bright and a dark state when excited by a cw laser.

Blinking measurements require acquisition of an image series, if conducted with a CCD camera, or data acquisition with a photodiode. In any case the acquisition time for the sequence frames has to be optimized, so that the two-level blinking can be resolved properly, but the signal is not distorted by too much noise. The system is the same as in PL image acquisition, but a more sensitive camera is needed, the readout frequency of the camera must be higher and the image acquisition time considerably shorter.

The intensity of a specific quantum dot is then extracted from each movie frame, which results in a so-called blinking trace, a plot of an emitters intensity versus time. A histogram can then be used to extract the blinking amplitude (as the distance from ON- to OFF-peak maximum) and distinguish between the ON- and OFF-levels by defining an intensity threshold that separates the two states, resulting in a binary blinking trace. ON- and OFF-time durations, average ON-time and blinking frequency can be extracted from that latter trace, giving insight into the photophysical mechanisms that cause blinking. A discussion of these follows in chapter 6. Figure 5.5 shows a short series of a blinking sequence, an example of a blinking trace and the corresponding histogram.

Note that blinking can only be detected when the signal-to-noise ratio is sufficiently high and when the frame acquisition time is smaller than the ON- and OFF-level durations. In this work, for characterizing SiQD, each frame was acquired in one second, which means that only dots with on- and off-durations of several seconds were able to yield properly resolved two-level intensity traces. In order to increase the signal from a quantum dot and therefore enable shorter acquisition times, the excitation power can be increased. On the other hand, this in turn leads
Figure 5.5: a) Series of frames from a blinking sequence of silicon nanocrystals. The arrow in the bottom right indicates the order of the frames. b,c) Taken from Figure 1b,c in reference [77]. Blinking trace and corresponding histogram of a single nanocrystal. The threshold is indicated by horizontal lines.

to a higher blinking frequency and therefore not improving temporal resolution for the ON- and OFF-time distribution statistics, see chapter 6 for more details.

5.8 PL lifetime measurements

In lifetime measurements the excitation laser source has to be pulsed and a gated image intensifier has to be mounted between the microscope and the CCD camera. Each laser pulse creates excitons in the absorbing nanostructures, which subsequently recombine. After the pulse the image intensifier measures and amplifies emission from the sample in a time window, which is significantly narrower than the off-duration of the laser, and sends the signal to the CCD camera. This procedure has to be repeated for a large number of pulses in order to acquire sufficient data for a proper statistical analysis. For a quantum dot excited with a single exciton, a single photon will be emitted. Since emission is more or less isotropic, only a small fraction enters the optical detection path. Therefore, as little as one out of 100 pulses triggers a count in the detector. A plot of the emission intensity of a nanostructure versus the delay time between pulse and acquisition window is called a PL decay curve. If a single recombination mechanism is responsible for the exciton decay, then a single exponential decay with a characteristic decay time, the exciton
5.8. PL lifetime measurements

The characteristic time constant $\tau$ in $I = I_0 \cdot \exp\left(-\frac{t}{\tau}\right)$ is called lifetime. Note that only a small fraction (≈1%) of the emitted photons trigger counts in the CCD camera, which is due to emission in other directions than into the optical path, losses in the optical path and quantum efficiencies smaller than unity in electrical components. Long measurements have to be performed in order to obtain sufficient statistics.

**Figure 5.6:** a) Ten experiments where an exciton is created and decays radiatively after a random time. b) Average decay curve from a large number of experiments in (a). A constant exciton decay probability per time unit leads to a mono-exponential emission intensity distribution. The characteristic time constant $\tau$ in $I = I_0 \cdot \exp\left(-\frac{t}{\tau}\right)$ is called lifetime. Each excitation corresponds to one laser pulse. The PL decay curve, from which the lifetime can be extracted, is a histogram of the delay times between excitation and radiative decay.

Lifetime measurements may also be accomplished for a single emitter, using a photomultiplier tube (PMT) or an avalanche photo diode (APD).
First of all, an important underlying question for this thesis shall be addressed: Why does one want to perform measurements on single nanocrystals? Any quantum dot fabrication process yields an ensemble of nanocrystals with a certain size distribution, usually characterized by a log-normal function, and even geometric variations (e.g. shapes that are not perfectly spherical) cannot be excluded. It was shown rather early [78] that a single quantum dot with a sharp, quantized energy level, that depends on its size, has a narrower spectrum than an ensemble with a natural size distribution. In fact, the homogeneous linewidth of a quantum dot’s emission can be smaller than the thermal broadening, proving the atom-like energy level quantization that is caused by quantum confinement, whereas an ensemble spectrum is usually much broader than the thermal energy. When blinking was discovered in quantum dots [79] it became clear immediately that the intensity trace of a single nanocrystal looks very different from that of an ensemble, as well. Blinking statistics of single dots could even be invoked to explain the reversible intensity decrease of an ensemble under continuous excitation (see e.g. [59]). The blinking frequency in different nanocrystals on the same sample can differ by orders of magnitude, as well as the blinking amplitude. And there are more examples of properties that are different in ensemble measurements and in single nanocrystals, but at this point the argument should be clear enough: Single dot measurements are required in order to determine the specific set of properties of a single dot in order to understand the mechanisms of light absorption and emission. Especially if the correlation of two properties is supposed to be examined, an ensemble measurement does not yield appropriate data, as all properties are averaged and all detailed information is lost. One should note, though, that with regard to the vast amount of variation in an ensemble, a large number of single nanocrystal measurements has to be performed in order to obtain reasonable results that are statistically significant. It must therefore be a goal to investigate optical and other properties at a single nanocrystal level, gain deep understanding of the underlying mechanisms and be able to predict ensemble behavior as the limit of an appropriate model. This thesis is aiming at exactly that goal and in this chapter
the main results of the fabrication process and single dot measurements on many nanocrystals will be presented and discussed.

6.1 Evolution of silicon nanostructures in oxidized silicon walls

In chapter 4 the fabrication and oxidation of silicon walls was described. Generally, the luminescent nanostructure evolution in those can be split into four stages. In the first oxidation stage, quasi-quantum wires are created in the top by bandgap widening in the thin center part. However, the silicon core still reaches from the wall top to the bottom, as can be seen in figure 6.1a (on the right hand side of rectangle A) and the corresponding part in figure 6.1b.

Most center parts are fully oxidized in the second oxidation stage. Undulating wires with protrusions can be found in the wall top and the bulk part spikes into the oxide, also containing some bulges, see Figure 6.1a (rectangle B), c and d. Both delocalized nanowire and localized quantum dot photoluminescence can be observed.

The third oxidation stage is characterized by fracturing of the top wire and creation of separated nanocrystals, as shown on the TEM image in Figure 6.1e. Delocalized 1D-emission cannot clearly be seen anymore and the average FWHM of the localized spectra becomes narrower.

After even longer oxidation, the wire structure completely disappears (and with it all delocalized silicon-related PL), which only leaves some spatially well separated, SiO$_2$-encapsulated silicon quantum dots with narrow PL emission spectra at low temperature within the wall.

Throughout the whole oxidation process luminescent nanostructures are con-
6.1. Evolution of silicon nanostructures in oxidized silicon walls

Figure 6.2: Parts taken from [76].

a) SEM tilted and top view of an undulating wall. White arrows indicate the borders between compartments of different thicknesses.

b) PL image of an array of undulating walls after short oxidation. The thinnest compartments luminesce. The inset shows a zoomed version of the dotted white rectangle. The white rectangle within the inset contains the nanostructure seen in (a).

c) Same as (b), but after an additional oxidation step.

sumed by the oxide and new ones are created.[80] This makes the oxidized silicon wall as quantum dot host a system that is not crucially dependent on oxidation time.

If precise positioning of emitting nanocrystals is desired, walls containing compartments of different thicknesses can be used instead of straight walls, as explained in chapter 4. Upon oxidation, the thinnest compartment reaches the luminescent stage long before the others. By the time the next thicker compartment contains luminescing nanostructures, the thinnest one is already completely oxidized and lacks any PL emission. Figure 6.2 shows SEM images of an undulating wall and PL images of a sample in different oxidation stages, containing alternating compartments of three different thicknesses. After short oxidation, the thinnest compartment is luminescing. Another oxidation step destroys the luminescence in the thinnest part, while at the same time creating luminescing nanostructures in the medium thickness compartments.

As explained earlier, the fabrication principle and nanocrystal creation mechanism are similar in pillars and walls. Both rely on EBL, RIE and oxidation in the self-limiting regime that non-uniformly reduces the silicon core, giving rise to luminescing nanostructures. However, in pillars quantum dots can only be created in one specific position within the structure. A suitable size and good passivation are required to obtain quantum dots emitting visible light. Since there are already initial size variations in the pillars and each processing step adds to the size dispersion of the remaining silicon cores, overall yield is rather poor. More details about oxidized nanopillars can be found e.g. in references [70, 71, 36].

A third fabrication method relies on the (self-limiting) oxidation of the slightly uneven top layer of a silicon-on-insulator (SOI) wafer, producing randomly situated nanocrystals in a quantum well (QW)/quantum dot (QD) hybrid system.[82] On the one hand the yield is significantly better than in pillars, on the other hand repeatable single dot measurements are difficult to perform, since the dot density
can be rather high and any pattern is missing.

Porous silicon samples contain similar quantum dots as all three of the above methods and allow fabrication of much larger amounts of nanocrystals at lower cost and in less time, but they are not very suitable for repeatable measurements on single quantum dots. For experiments where capping with different materials than silicon oxide plays a role, though, they are the preferential choice.

When it comes to repeatable measurements on oxide-passivated single silicon quantum dots and NW/QD hybrid systems, oxidized silicon walls seem to offer the best advantage to disadvantage ratio of all presented methods. They are not critically dependent on oxidation time, yield a reasonable amount of spatially well separated quantum emitters and are arranged in a pattern that can easily be navigated with different measurement methods.

6.2 Single Si-QD PL measurements

6.2.1 Photoluminescence spectra

Photoluminescence spectra at room temperature do not exhibit any fine structure that could be analyzed in detail, but many of them have a FWHM of 100-150 meV and are slightly asymmetric, which are the typical characteristics found in the literature. At cryogenic temperatures, a much more distinct spectral composition is revealed. There are four components that can be resolved in high resolution PL measurements: A zero-phonon or no-phonon peak (NP), a stretching mode (SM) that appears as a low energy shoulder of the NP peak, a transverse acoustic (TA) phonon peak and a transverse optical (TO) phonon peak. Figure 6.3 shows a typical single dot spectrum containing all four features. The typical approximate distances of SM, TA and TO from NP are 5, 16 and 62 meV, respectively. 

It is remarkable that the TO replicas do not scatter around 56 meV, which is the TO energy at the X-point in bulk silicon, but lie between this value and the one at the Γ-point (64 meV). Cf. figure 2.3. All peaks shift along the silicon bulk bandgap when the temperature is changed (with their respective offset caused by quantum confinement). When the temperature is increased, all peaks are subject to thermal broadening and at room temperature all of them are merged, which makes them appear as a single broad peak.

After short oxidation, many relatively broad spectra can be observed along an oxidized wall, as well as a weaker, broad, delocalized spectrum whose signature suggests one-dimensional nanostructures (nanowires) as the origin.

Arrhenius type PL quenching was observed for increasing temperature for both localized and delocalized spectra.[81] It should be noted that the corresponding activation energy varied significantly for different localized spectra; some disappeared above 50 K, some were still visible at room temperature. Upon further oxidation, the nanowire emission disappears and the average FWHM of the localized spectra becomes significantly narrower. This suggests that the wires are consumed by oxide and the quantum dots’ isolation from their environment becomes stronger. Many
6.2. Single Si-QD PL measurements

![Figure 6.3: Figure 3b from [80]. Single nanocrystals spectrum at cryogenic temperature, comprised of four distinguishable components. The no-phonon (NP) peak is narrower than the thermal broadening ($k_B \cdot T = 1.1$ meV). Stretching mode (SM), transverse acoustic (TA) and transverse optical (TO) phonon peaks have a distance of 5, 16 and 61 meV from NP.](image)

of the NP peaks’ FWHM values even lie below the thermal broadening at the corresponding temperature, which is a clear indicator for the quantum confined nature of the photoluminescence.

For all oxidation stages localized spectra can be found throughout the whole investigated energy range between 1.5 and 1.9 eV. A few narrow spectra without clear phonon replicas could be observed above 1.9 eV, but these could be caused by non-bridging oxygen defects, which are known to assume positions in the same spectral range. [83] In general, the background luminescence increases exponentially towards higher energy in that region, most likely due to different defect centers in the oxide.

Even at cryogenic temperatures some rather broad spectra were visible. However, a discussion about their origin might not be very useful, since there are many possible reasons for their existence, among others a cluster of fluorophores within the same optically resolvable spot, a luminescing nanostructure that is not a quantum dot, a quantum dot that is strongly interacting with its environment or a spectrum that is subject to strong spectral diffusion (probably caused by interaction with the local environment).

It is, however, noteworthy, that the quantum dots fabricated and characterized in this work are visible even at very low temperature (which was also observed by e.g. [84]), while others (see e.g. [36, 85]) observe PL quenching at low temperature. Those results were explained by significantly increased lifetime and singlet-triplet splitting with lower-lying triplet state, i.e. freezing in a state that is forbidden for optical transitions. An upcoming study of the exciton lifetime in the structures fabricated in this work may provide an explanation for this discrepancy.
6.2.2 Linear polarization of absorption and emission

For both short and long oxidations the degree of linear polarization of single spectra was measured at room temperature. In both cases, absorption and emission were linearly polarized to a very high degree of typically between 90% and 100%, see reference [75] and Figure 6.4. Note that others (e.g. [86]) called theoretically calculated DLP values of 30% huge. When the polarization filter only lets light polarized perpendicular to the oxidized silicon wall pass, the signal is completely quenched. Ensemble measurements as in [75] can yield lower DLP values, since the oxide (background) PL does not seem to be polarized and background subtraction is difficult and prone to error in PL imaging.

One reason for the strong linear polarization, as mentioned in [75], can be elongation and therefore one-dimensional emission character of the nanostructures. There are, however, other possible explanations, one of which is the one-dimensional dielectric confinement that the nanocrystals experience in the oxidized wall.[87] The dielectric confinement interpretation is strengthened by the fact that both emission (at around 750 nm wavelength) and absorption (405 nm wavelength) exhibit the same behavior.

6.2.3 Blinking statistics

Using home-built Java add-ons for the ImageJ framework, a number of single silicon quantum dots have been analyzed in terms of their blinking behavior under continuous excitation at different excitation power densities. [77] By extracting the intensity with an automated software, rather than manually, a large number of dots in a movie of arbitrary length can be analyzed simultaneously in a short time. In addition, human errors (like the accidental selection of a wrong area for data extraction) can be avoided. In case of a lateral sample drift, the frames
6.2. Single Si-QD PL measurements

Figure 6.5: Figure 3a from [77]. Typical mono-exponential ON- and OFF-time distributions of a single quantum dot.

of the movie can be shifted so that each quantum dot stays in its assigned data extraction area throughout the whole movie, while defocusing causes loss of intensity and therefore requires a repetition of the experiment. The size of the data extraction area is chosen to accommodate the complete dot signal at all times.

A typical blinking trace and its corresponding histogram are shown in chapter 5. As already mentioned, several entities, of which neither is correlated to another, can be extracted from such a trace: Blinking amplitude and frequency, ON- and OFF-time distributions and average ON-time. If a trace has more than two distinct levels, several fluorophores might reside in the same optically resolvable spot, all contributing to the PL signal. The definition of the threshold should be based on both the trace and its corresponding histogram, since short blinking events, even though they might be clearly visible and well defined in the trace, do not always result in clear detectable peaks in the histogram. Signals with more than two distinct intensity levels or one broad peak must be discarded in a single quantum dot analysis. ON- and OFF-time distributions of single nanocrystals were found to follow mono-exponential functions, as can be seen in Figure 6.5.

The lower temporal resolution limit was set by the minimum required acquisition time (1 s) for an acceptable signal-to-noise ratio, the upper limit by the total duration of the experiment (almost 6000 s). Experiments performed by others [59] were conducted at much higher excitation and with an avalanche photo detector, which is the reason for the difference in time scales. In conjunction with this, it is important to note that the blinking frequency increases with excitation power. As opposed to other findings (e.g. [88, 89]), which mostly measure a quadratic increase associated with Auger processes [62], a linear dependency was observed in this work, as shown in Figure 6.6. This hints at a direct, one-photon absorption process, as opposed to a two-exciton Auger process, which is rather unlikely to occur at low excitation. At this point it is unclear whether the differences lie in the type of
sample, the excitation strength or some other factor.

**Figure 6.6:** Figures 4 and 3b from [77]. a) Blinking frequency of single dots (circles) and the average (diamonds) as a function of excitation power density. The straight line indicates a linear increase. In the inset a histogram of the exponents from power law fits to the single dot data is shown with a Gaussian fit that peaks at unity. b) Similar plot for the switching frequency and the inverse average ON- and OFF-times of a single dot. Again, straight lines indicate a linear increase.

Another important observation is that the blinking frequency of different dots at the same excitation conditions can vary by at least two orders of magnitude and the blinking amplitude by more than one order, exemplifying the individuality of silicon nanocrystals. Whether differing amplitudes, and therefore emission intensities, are related to the quantum dots’ individual exciton lifetime is not clear at this point. Most likely not only size differences cause varying optical properties, but also geometry, local environment and other factors seem to play a major role.

Note that some of the nanocrystals are virtually always found in an emissive state (average ON-time of close to 100%), which is extremely interesting for potential applications. Further research is required to clarify the mechanisms that suppress blinking of these dots.

### 6.2.4 Bleaching and aging

Throughout several weeks and months of experimentation no degradation of the nanocrystal PL was observed, even when samples were frequently irradiated with a UV laser. This hints at high resistance towards photobleaching, which is known to destroy the luminescence of marker molecules used in fluorescence microscopy. Others have demonstrated a temporary decrease of the PL emission in samples containing silicon nanocrystals in a dioxide matrix [59], which was ascribed to statistical aging caused by blinking. In this work, an exponential decrease in the background signal, most likely originating from the oxide surrounding the nanocrystals, was found as well. The nanocrystals themselves, however, did not show any signs of statistical aging. To the contrary, their mono-exponential on- and off-time distributions promote varying intensity around a stable average value.
6.2. Single Si-QD PL measurements

Figure 6.7: Inset of figure 2b in [77]. Intensity trace of a silicon nanocrystal ensemble (black), a reference sample containing only oxide (grey) and the purified quantum dot signal (red), represented by a subtraction of the second from the first.

Figure 6.7 shows an example of an intensity trace of a silicon quantum dot ensemble, an oxide reference and the purified quantum dot signal. Even though intensity fluctuations can clearly be seen, there does not seem to be any aging or bleaching effect affecting the nanocrystal signal.

6.2.5 Photoluminescence intensity versus excitation power

The existence of two distinct levels in blinking measurements, referred to as ON and OFF, has a unique advantage in pumping experiments, where nanocrystals are exposed to increasingly powerful excitation and their PL is measured as dependent variable. Background subtraction in other measurements, especially PL imaging, can be rather difficult. Silicon oxide surrounding the nanocrystals emits light as well when irradiated by a UV laser, and this emission is difficult to distinguish from the quantum dot PL. In blinking measurements, on the other hand, the non-zero OFF level defines the background itself, while the difference between ON and OFF is the pure nanocrystal emission. Thus, blinking provides two useful properties for quantum dot studies: On the one hand it is proof that a single quantum dot is observed, on the other hand it enables a separation of the true intensity from the background.

A set of single silicon nanocrystals was excited by a UV laser with different excitation powers and their PL emission intensity was plotted as a function of excitation power density. At low excitation, a linear increase was observed. Then, a threshold that corresponds to an average occupation of one exciton per nanocrystal occurs, where the emission intensity increase switches to a square root function. Figure 6.8 presents these results. It also becomes clear that, even though the average dot follows this rule, different dots behave differently.

In order to determine whether the square root increase continues even at much higher excitation, or whether the nanocrystals’ emission saturates or even switches off, more experiments should be conducted. Challenges that need to be addressed in that case are the strong background luminescence (which increases linearly with
excitation power) and local heating caused by absorption of light in the surrounding material.

6.2.6 Photoluminescence lifetime

The PL lifetime of a number of single silicon quantum dots was measured [90] and compared to results on ensembles [41] and theoretical calculations [33]. After a fast initial transient, which was not investigated in detail, but shall instead be addressed in future work, the PL decay curves are of mono-exponential character, as demonstrated in Figure 6.9. This is to be expected when a single mechanism dominates exciton recombination or when several independent random mechanisms are present, in which case the combined lifetime becomes $\tau = (\frac{1}{\tau_1} + \frac{1}{\tau_2} + ...)^{-1}$. There is a rather broad distribution of lifetimes (5-45 µs) among different nanocrystals, which does not seem to be correlated to the peak energy position of the corresponding quantum dots’ spectrum and therefore suggests a strong influence of other factors than nanocrystal size. However, the values for the lifetimes are in the same range as measurements on other samples and theoretical calculations.

When several mono-exponential decay curves with different characteristic falloff-times are summed, the result is a stretched exponential with parameter values that are typically found for silicon nanocrystal ensembles. Figure 6.10 shows an example where the mono-exponential data of single silicon nanocrystals (distribution shown as inset) adds up to a stretched exponential. An altered distribution might result in a different stretching factor.
6.2. Single Si-QD PL measurements

Figure 6.9: Taken from Figures 3a and 4 of [90].

a) Single exponential decay curves of two different emitters. b) PL lifetime of different quantum dots and their spectral position. Lines are data from other publications for comparison.

Figure 6.10: Figure 3b from [90]. Stretched exponential resulting from a summation of experimental mono-exponential decay curves of single silicon quantum dots. The inset shows a distribution of single quantum dot PL lifetimes.
Silicon nanowalls were fabricated by electron beam lithography and reactive ion etching. Subsequent oxidation in the self-limiting regime yielded luminescent mono-crystalline silicon nanostructures enclosed by a one-dimensional silicon dioxide shell. Following conclusions can be drawn with respect to the sample fabrication:

- A silicon nano-wall produces luminescing 1D and 0D nanostructures upon oxidation in the self-limiting regime.
- After longer oxidation, more well-isolated quantum dots appear.
- Undulating silicon walls enable controlled placement of single quantum emitters.

Investigations of the optical properties of the quantum dots hosted by an oxidized silicon nano-wall allow following conclusions:

- The spectral fine structure of non-resonantly excited silicon quantum dots is comprised of several different components: A no-phonon (NP) peak, stretching mode (SM), transverse acoustic (TA) and transverse optical (TO) replicas.
- The no-phonon transition can be atomically sharp (below $k_B \cdot T$), just as in direct bandgap semiconductor materials. Thermal broadening causes the different PL peaks to merge, which is the reason for broad single peak observations at room temperature.
- Blinking with a large range of frequencies, intensities and on/off-time ratios can be observed. The on/off times seem to be distributed according to monoeXponential functions, which is in contrast to many results found in the literature. Statistical aging does therefore not occur.
• The process that causes switching between on- and off-states seems to be of direct (one-photon absorption) nature, since the average blinking frequency increases linearly with excitation power. This contradicts the common understanding that blinking is caused solely by Auger processes when a nanocrystal is populated by two excitons simultaneously.

• PL emission does not seem to saturate upon increase of the (continuous wave) excitation power, as would be expected in the case of dominating Auger recombinations. Instead, over a certain threshold, which approximately coincides with an average exciton-occupancy of unity, the intensity increase changes from a linear to a square-root dependence. This might be due to a combination of a somewhat suppressed, relatively slow Auger process and a decrease in radiative exciton lifetime at high excitation.

• The PL lifetime ranges from a few to a few tens of microseconds at room temperature. Even for nanocrystals with the same emission energy there can be significant differences in the lifetime.

• A stretched exponential lifetime distribution in an ensemble of nanocrystals can easily be explained by a distribution in single emitter lifetimes, caused by variations in size, shape and local environment.

• Absorption and PL emission of silicon quantum dots in an oxide wall are linearly polarized to a very high degree (more than 90%). This effect can partly be caused by non-spherical nanocrystal shapes, but also by the one-dimensional dielectric confinement by the surrounding oxide wall.

Following general conclusions can be drawn from a comparison of the obtained results with the scientific literature:

• Oxide-passivated silicon nanocrystals, no matter which fabrication method is used, seem to exhibit the same properties.

• Quantum dots are very individual and each one has a unique set of properties. It is therefore important to characterize them on a single-dot level (detailed understanding), while at the same time analyzing a large number of them (good statistics).
Appendix A

Sample Fabrication Recipes

A.1 Preparation

A silicon wafer is oxidized in an oxidation furnace (900 °C, 30 min), so that an approximately 30 nm thick oxide layer covers the silicon surface. Then any ordinary optical resist layer is spun on the wafer and hardbaked. It serves as protection from dust and other contaminants. The wafer is then diced into pieces of appropriate size (e.g. 10 mm × 10 mm). One day before or on the same day as the actual e-beam lithography procedure, the resist layer is removed in an ultrasonic acetone bath (5 min). In recipe 1 (using positive resist) the oxide layer stays on the silicon surface, as it is needed as a hardmask later. Recipe 2 requires the removal of the silicon dioxide layer by means of wet etching (a short dip in 50% hydrofluoric acid). Since a pure silicon surface is hydrophobic (as opposed to the hydrophilic silicon dioxide), the complete removal of the dioxide layer can easily be confirmed by checking the wetting properties of the sample surface (when all SiO₂ is etched away, the HF pearls off when the sample is retracted from the liquid). The last procedure before the recipe-specific steps is an oxygen plasma cleaning step in a reactive ion etching machine at low power (RIE, 20 sscm O₂, 100 mTorr, 10 W, 2 min) in order to complete remove all organic contaminants and activate the surface for better wetting in the subsequent resist spinning step. After this step is completed, the recipe steps should follow immediately.

A.2 Patterns

A pattern file can be created with the same software that is used to run the EBL system (Raith in this case). Dots, lines, circles and filled areas are the basic geometric elements that can be used to compose patterns. The software then recalculates pixels on the sample where the electron beam has to reside and, depending on the selected dose, how long it resides there. Areas contain many closely spaced pixels and therefore take much exposure time. Each time after a geometric object is finished, the beam relocates and is blanked for a short time in
Figure A.1: Typical pattern for exposure in EBL. Each of the four write fields measures 100 µm * 100 µm and is surrounded by rather large rectangular structures to make the area easier to find in an optical microscope. Structures for pillars, straight and undulating walls and several test structures are present in the different fields.

In order to stabilize, which makes the exposure of a field containing many dots (each of which is one geometric object) time-consuming, as well.

A neat trick to circumvent these problems is to use lines instead. Figure A.1 shows a typical EBL pattern with many different structures. Among those there are line serpentines, which substitute rectangular areas. They are just as easily visible in an optical microscope, but require much less exposure time. In field F4 (bottom right) there is a pattern made of numerous crossing lines. Each single line has a dose that is too little for completely exposing the resist, however, at the crossing points the dose adds up and creates sufficiently exposed points. The total deadtime (compared to a point array) is then reduced from the number of intersects to the number of lines.

By carefully tuning the dose of a geometric object, its width can be varied to a certain degree. When the dose gets too high, though, the resulting structure edges become fuzzy. Therefore, undulating lines, as can be seen in F3 (bottom left), are made of one long thin line which is flanked by another pair of lines in regions of medium thickness and yet another pair of lines in the thickest parts. The distance between neighboring lines should in this case less than half the linewidth.

Note that there are many different landmarks everywhere (e.g. line numbers and small squares around different pillar fields) in order to enable fast and easy orientation. Test structures like hexagons and stars do not only look nice, they can also be used for monitoring the accuracy of the aperture and stigmation settings.
of the exposing EBL system. For example, if the arms of a star have different thicknesses, the parameters were not optimal. Differences in etching and oxidation rates along different crystal planes are other examples of processes that can be tested with such structures.

### A.3 Mask creation recipe 1: Positive resist and lift-off

A positive resist (ZEP-520: anisol 1:2) is spun on the sample (2400 rpm, 60 s) and baked (180 °C, 10 min). After exposure by the electron beam the resist is developed in a liquid bath (p-xylol, 1 min) and then properly rinsed with de-ionized water and dried with a clean compressed air gun. A subsequent oxygen plasma cleaning step (RIE, 20 sccm O₂, 100 mTorr, 10 W, 2 min) can help to remove resist residue from the exposed regions.

After deposition of a thin (20 nm) metal (chromium or NiCr) layer, a lift-off step is performed in an ultrasonic acetone bath (10 min), leaving only a metal mask in places where the resist had been exposed. The following wet-etching step in buffered 5% hydrofluoric acid (BHF:NHF₂ 1:1) transfers the metal pattern into the silicon dioxide layer. When the sample surface becomes hydrophobic and the liquid easily pearls off, the acid has reached the silicon surface and the sample has to be rinsed properly in de-ionized water. The metal is removed using an ammonium cerium (IV) nitrate based solution (e.g. ceric ammonium nitrate : perchloric acid : water 11% : 4% : 85%).

### A.4 Mask creation recipe 2: Negative resist (no lift-off)

Negative resist (HSQ) is spun on the sample (6000 rpm, 40s) and baked (150 °C, 10 min). After exposure the resist is developed in a liquid bath (MF-CD26, 1 min), rinsed with de-ionized water and dried with compressed air. After development the resist is silicon dioxide-like.

### A.5 Pattern transfer

Deep reactive ion etching based on HBr chemistry is used to transfer the pattern from the SiO₂ hardmask to the silicon (10 sccm Cl₂, 30 sccm HBr, 10 sccm He-O₂, 200 W RF power, 125 mTorr). Since the sample is rather small, it has to be mounted on a wafer before it can be inserted into the etching machine. Silicon paste is one possibility for doing this. The carrier wafer surface has an influence on the etching rate: If silicon is used, the etching gas can attack the large open surface and etches the sample itself less than in the case where the carrier wafer surface consists of silicon dioxide. With the given parameters, one minute of etching time is a good value to start experimenting with. When the etching step is too long, underetching occurs and thin structures might be destroyed, as demonstrated in Figure A.2.
A.6 Oxidation

Finally, the sample has to be oxidized below the flow temperature of silicon dioxide. At 900 °C stress builds up in the vicinity of curved surfaces during oxidation, leading to increased (concave) or decreased (convex) oxidation rates. [72, 70, 73] Depending on the thickness and height of the structures, between 30 and 120 minutes of dry oxidation at 900 °C are usually sufficient to yield luminescing nanostructures. Wet oxidation is usually not a good choice, as it results in lower quality Si/SiO₂ interfaces and has a higher, more difficult to control oxidation rate.
Appendix B

Good to Know

This chapter is mainly meant for Ph.D. students who will use similar fabrication methods as presented in this work. Things that can go wrong almost never find their place into any publications, dooming new researchers to repeat the same mistakes their predecessors made. May the description of a few of these help save time, effort and money.

B.1 E-beam dose and proximity effect

In addition to the requirement that the sample surface should be clean from dust and contaminations before any processing step (resist spinning, etching, oxidation), there are a few things to keep in mind. Regarding e-beam lithography, it is important to note that the exposure dose influences the lateral feature size, i.e. a higher dose results in broader lines and larger spots. This is due to the proximity effect, which means that even an area around the exposed spot receives some non-zero dose during exposure. When the dose in an area reaches a certain threshold, it is sufficiently exposed in order to be developed. This effect can, on the other hand, be turned into an advantage in certain cases. When exposing a pattern of points, the beam jumps from one spot to the next and needs to stabilize before exposure continues. Therefore, the deadtime is significant in a large array of small spots. Instead, intersecting lines with doses too small to reach the sufficient exposure threshold can be used. At the intersects, the small doses add up and the threshold is reached. Where the dose is insufficient, the surface will be blank after resist development. An example of pillars fabricated by the intersecting line method is shown in figure B.1.

Another example of the proximity effect is shown in figure B.2, where in an array of spots the ones at the outer perimeter received less dose than the ones in the center, leading to different feature size. It can also clearly be seen that overexposure leads to smeared out structures with fuzzy borders.
Figure B.1: Silicon pillars etched from a mask fabricated by writing underexposed lines into resist. At the intersections of lines the dose was high enough to produce a masking spot. The more lines intersect in a point, the thicker the resulting pillar.

Figure B.2: Array of nanopillars. Each dot is supposed to receive the same dose, according to the file for e-beam exposure, but since the electron beam creates a dose gradient even around the actual main position, spots in the center of the array receive a higher dose than their counterparts at the edge, leading to larger pillar diameters.

B.2 Dirty surfaces

When a surface is contaminated before a processing step, this usually leads to unwanted results. Contaminations can alter the wetting properties of a surface, which is a severe disadvantage when spinning resist. They can block or scatter the electron beam during EBL and therefore destroy or alter the resulting pattern. During etching, they can act as an etching mask, resulting in undesired features that disturb the pattern, as shown in figure B.3. And finally, during oxidation they can cause burn marks on the surface.
B.3 Overetching

Reactive ion etching requires a certain linewidth or dot diameter in order to transfer the mask into silicon. Due to underetching, it is not possible to achieve any desired aspect ratio. When etching pores and holes, the bottom usually becomes arrowhead-shaped, while the upper part often ends up larger than intended. This is due to much higher exposure to the etching agent close to the surface. For large holes and pores the problem is negligible, since exposure is sufficiently efficient all over the structure. Similar challenges can be observed when etching walls and pillars: Thin structures are easily overetched in the top part, as shown in figure B.4, where a thin wall was etched slightly too long in order to achieve a high aspect ratio, resulting in structure resembling a telegraph line, a freestanding wire held by thin masts.
B.4 Defect creation and contamination by SEM

When examining a surface with a scanning electron microscope, defects are created in the silicon and a contamination layer, largely consisting of carbon, is deposited. Strong photoluminescence can be observed in an area that has been exposed to an electron beam and the deposited carbon layer can act as an etching mask. Figure B.5 shows an example where a sample has been examined with a SEM between mask fabrication and reactive ion etching. In a spot where the SEM had resided for a while, the rectangular field of view can be seen after etching. The edges are fuzzy due to adjustment of the magnification. Both induced defects and deposited layer can be removed by an oxidation step (15 minutes at 900 °C suffice).
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