Semiconductor Quantum Dots Studied by Time-Resolved Photoluminescence Techniques

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Abstract

In this thesis time-resolved photoluminescence spectroscopy is presented as a powerful tool to study the carrier dynamics in various self-assembled quantum dot (QD) structures, which are potentially attractive for device applications.

The experiments reveal the impact of proton irradiation on InGaAs QDs and comparable quantum wells. Nonradiative recombination at defects – an important material parameter and “measure” of the structure optical quality – is found to play a much less important role for the QD samples. The superior radiation hardness can be explained as a result of the three-dimensional carrier confinement in QDs.

Comparisons between the structures show a decrease of photoluminescence intensity for quantum wells but a slight increase for QDs irradiated at low to intermediate doses. This somewhat unexpected characteristic is described by an enhanced carrier transfer into the dots via the defects introduced in the material by the protons.

In a different structure carrier dynamics in spatially aligned of InAs QDs are investigated. Alignment along lines is achieved by misfit dislocations deliberately introduced in the substrate. Photoluminescence spectra of the dots exhibit much smaller inhomogeneous broadening than for the reference sample as a result of an improved QD uniformity.

Samples with varying buffer layer thicknesses were grown to study the influence of dislocation related traps on the observed fast photoluminescence decay. It is found that the fast carrier trapping is predominantly caused by point defects close to the QDs or at the QD/barrier interfaces.

Additional numerical simulations confirm the roles of the two independently acting traps in nonradiative recombination.
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Appended papers

**Paper I**


*My contribution:* Parts of the measurements.

**Paper II**


*My contribution:* Time-resolved photoluminescence measurements and analysis.

**Paper III**


*My contribution:* Time-resolved photoluminescence measurements, analysis, parts of the writing, parts of the numerical simulations.

**Paper IV**


*My contribution:* Time-resolved photoluminescence measurements, analysis, parts of the writing, parts of the numerical simulations.
Works not included in the thesis


Conference presentations


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1 Introduction

1.1 Background

The invention of the transistor and subsequent use of this device in technology marked the beginning of a new era in which semiconductors became increasingly important. In fact, it is difficult to imagine life without since they are the building blocks of integrated circuits that drive so many devices.

In 1965 Gordon Moore observed a trend in the development of integrated circuits, which was to become famous as Moore’s Law [1]. In its essence this law claims that the number of transistors per integrated circuits doubles every 18 months (the original statement predicted twice as many transistors per 12 months but this value was adjusted later). Obviously this means that the transistors need to be decreased in size over the years.

The physical properties of materials, however, are undergoing dramatic changes if the sizes become sufficiently small. When electrons or holes are limited to regions smaller than a few tens of nanometers, quantum effects become apparent. Then the material properties no longer depend on the material composition alone but also on the size of the structure. A nanostructure that confines an electron or a hole in all three dimensions and which is sufficiently small to cause quantization of the carrier energy is called a quantum dot (QD). The variety of materials that can be used is as vast as the number of potential applications: laser diodes, photodetectors, labels for biological imaging, different types of memories, single photon sources etc.

In all these fields quantum dot based devices promise improved or even completely novel features. Laser diodes utilizing quantum dots as the active gain medium, for example, have lower power consumption and are less sensitive to temperature changes. Quantum dots as labels can be used to monitor, for example, cancer cells, which evade conventional tests.

A fundamental understanding of the carrier dynamics in quantum dots needs to be developed to allow optimization of the desired properties. This in turn requires well-established and controlled growth techniques as well as characterization methods. By modeling the physics in the structures it becomes possible to understand of how different parameters such as composition, size, density, etc. affect the confinement of the carriers in the structures and thus their energies. Typical investigations of quantum dot structures include various high-resolution microscopy setups like scanning tunneling microscopy, atomic force microscopy or transmission electron microscopy. The electronic and optical properties of the quantum dots are most commonly studied by capacitance-voltage and photoluminescence techniques.

Time-resolved photoluminescence (TRPL) is a powerful tool for the investigation of carrier dynamics in semiconductors. Electrons and holes created in the material by ultrashort laser pulses recombine and emit light, which is subsequently detected. The temporal development of the photoluminescence signal allows one to draw conclusions about the dynamical processes in the sample by comparison with
appropriate models. Since the carrier dynamics can be rather complex, numerical simulations often need to be employed.

In the frame of this work various quantum dot structures were studied using different TRPL techniques.

First the impact of proton irradiation on the recombination processes in quantum dots was investigated. It was found that the radiation hardness of these structures was exceeded that of quantum wells, which are commonly used in today’s optoelectronic devices.

In a second project carrier dynamics in aligned quantum dot structures were examined. In “normal” structures, self-assembled quantum dots are randomly distributed over the sample surface and the interaction with neighboring dots is therefore locally different. Certain applications (such as highly parallel computing architectures), however, require ordered structures. In this work dislocations were deliberately introduced into the substrate before the quantum dot growth resulting in an ordering of the dots along lines. On the other hand, it was not clear if the dislocations would influence the optical properties of the QDs. A simulation was developed for the different samples and it was shown that the observed short decay in the structures is not related to the dislocations in the substrate.

1.2 Outline

In order to allow the reader to appreciate the results in the included papers, the thesis presents an overview over the basic theoretical and experimental concepts of time-resolved photoluminescence spectroscopy on semiconductor quantum dots. The thesis is thus organized as follows: First a brief introduction into fundamental aspects of quantum dots is given in chapter 2. The differences between macroscopic (bulk) and structures with dimensions of only a few nanometers, in which carrier movement is restricted in three dimensions, will be discussed. A few theoretical treatments of obtaining the energy levels in QDs are mentioned as well as some of the problems in their implementation.

In chapter 3 I will elaborate on the fabrication of semiconductor QDs before listing a number of possible applications. For some of these QDs promise to show better device performances whereas other applications cannot even be realized with conventional bulk material.

Chapter 4: Bulk and QDs are compared in terms of the most important carrier dynamics. Understanding carrier transport and relaxation mechanisms is of utmost importance as ultimately the expected device characteristics depend on it. In chapter 5 I therefore present a few methods of determining the carrier dynamics experimentally.

To compare experimental results with theory it is necessary to develop a model that accurately describes the structure under investigation. Chapter 6 discusses in detail how we used a system of coupled rate equations to study the role of dislocation related carrier traps in nonradiative carrier recombination, an information that is otherwise not accessible directly.
2 Fundamental aspects of quantum dots

Describing the fundamental aspects and properties of quantized semiconductor structures requires knowledge of a few basic solid-state physics ideas. In the following chapters these basic concepts are quickly reviewed.

2.1 Energy bands, important particles and quasi-particles

In solids, where atoms are brought close together, the formerly discrete electronic energy levels split into sublevels. Due to the interaction of an enormous amount of atoms, the sublevels are so closely spaced that (quasi) continuous bands of possible energies are formed. In semiconductors, however, these bands are separated by “forbidden gaps”, meaning that certain energies are not allowed for carriers.

In perfect semiconductor crystals at 0 K all electrons possess energies in the so-called valence band. If, for example by absorption of light or heat, an electron picks up enough energy it is excited over the band gap into the conduction band, leaving an empty place, a so-called “hole” behind. In many ways holes can be treated as positively charged particles.

An exciton is formed if an electron and a hole are bound together other via Coulomb interaction. The possible energies of an exciton below the conduction band edge can be described similar to the hydrogen atom as

$$E_n = -\frac{\mu e^4}{2\hbar^2} \cdot \frac{1}{n^2} \cdot \frac{1}{\varepsilon_r} = -\frac{R^*}{n^2}$$

(2.1)

Both \(\mu\) (the reduced mass) and \(\varepsilon_r\) (the relative dielectric constant of the material under consideration) take into account the changes arising from considering carriers in a semiconductor instead of free carriers in vacuum. The reduced mass depends on the effective masses of electrons \(m_e^*\) and holes \(m_h^*\) as

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h}$$

(2.2)

The corresponding effective Bohr radius of the exciton is then given by

$$a_B^* = a_0 \cdot \varepsilon_r \frac{m_e}{\mu}$$

(2.3)

For GaAs and InAs the exciton Bohr radius is of the order of a few tens of nanometers.

Phonons are quasi-particles that represent - in analogy to photons for electromagnetic waves – energy quanta of lattice vibration modes. The concept of
quasi-particles is especially useful for treating the interaction of carriers or photons with the crystal lattice. Quantum mechanical calculations show that these interactions can then be described as elastic collisions (following the laws of conservation of energy and momentum) with phonons, which can be created or destroyed in the collision.

Depending on the energy and energy dispersion characteristics with wave vector \( k \) in the crystal one distinguishes longitudinal optical (LO), transversal optical (TO), longitudinal acoustic (LA) and transversal acoustic (TA) phonons. Typical phonons energies are of the order of a few tens of meV.

### 2.2 Quantization

According to de Broglie, a particle can also be treated as a wave with a wavelength inversely proportional to the absolute value of the particle’s linear momentum \( p = |\vec{p}| \)

\[
\lambda = \frac{h}{p}.
\]  

(2.4)

The absolute value of the momentum is given by the product of particle mass and its velocity. Using the definition of the mean thermal velocity of free carriers one arrives at the following equation

\[
p = m \cdot \langle v \rangle = m \cdot \sqrt{\frac{3kT}{m}} = \sqrt{3kTm}.
\]  

(2.5)

In a semiconductor crystal, however, the mass of the free carrier needs to be replaced by the effective mass \( m^* \) of that carrier in the material. The de Broglie wavelength is thus

\[
\lambda = \frac{h}{\sqrt{3kTm^*}}.
\]  

(2.6)

For electrons in InAs the effective mass is \( m_e^* = 0.026m_0 \)[2], where \( m_0 \) is the free electron mass. The de Broglie wavelength of electrons in InAs at room temperature is therefore \( \lambda \approx 39 \) nm.

It can therefore be expected that quantization effects become apparent for structures of the size of a few tens of nanometers. The carrier wavefunctions (as solutions to the Schrödinger equation in the periodic potential of the lattice) are then localized in space and the corresponding energy eigenvalues are no longer quasi continuous but discrete.

### 2.3 Density of states

As in any physical system, electrons and holes try to occupy low energy positions in conduction and valence band. Quantum mechanical considerations show that only a certain amount of carriers is allowed for any given energy. This is called the
density of states (DOS) defined as the available number of states $N$ per energy per unit volume

$$\rho(E) = \frac{2}{V} \frac{dN}{dE}. \quad (2.7)$$

The factor 2 takes into account the fact that two electrons of opposite spin can occupy each state. Using the effective mass approximation, where the effect of the periodic potential of the crystal lattice on the electrons is treated by introducing an effective electron mass $m^*$ rather than the bare mass $m_e$, the density of states for bulk material is [3]:

$$\rho^{3D}(E) = \frac{1}{2\pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{3/2} E^{1/2}. \quad (2.8)$$

The superscript 3D emphasizes the fact that in bulk materials the carriers can move freely in all directions of space.

While the DOS in the 3D case is growing with the square root of the energy, it shows different behavior for structures where free carrier movement is only possible in two (2D, quantum well, QW), one (1D, quantum wire, QWR) or no (0D, quantum dot, QD) direction.

For the case of QDs it is given by a series of delta-functions (see Figure 2-1) and depends just on the number of confined levels. QDs are therefore sometimes also referred to as “artificial atoms” since the atomic levels are also discrete. In real structures, however, homogeneous and inhomogeneous broadening result in a (narrow) distribution of energies at a certain level.

The homogeneous level broadening is a result of the finite carrier lifetime, carrier-phonon [4] and carrier-carrier interaction [5]. Inhomogeneous broadening, on the other hand, arises from the superposition of many transitions in a quantum dot ensemble. Differences in environment (strain), size and composition lead to slightly different energy levels for the individual QDs [6, 7].

![Figure 2-1: Density of states for three and zero dimensional structures (quantum dots). The dashed line shows the density of states for real quantum dot structures due to inhomogeneous broadening.](image-url)
2.4 Shape and electronic structure

The choice of materials and the methods and parameters used during growth not only affects the island density and size but also the shape of the QDs. For the InAs/GaAs (InAs quantum dots grown on a GaAs substrate) system alone the structures were found to be either lens shaped [8], disk shaped [8], conical dot shaped [9], shaped like pyramids with rectangular [10] or octagonal base [11] or even more complicated forms of lower symmetry [12]. The most commonly used experimental techniques for finding the QD size and shape are atomic force microscopy (AFM), scanning tunneling microscopy (STM) and transmission electron microscopy (TEM).

It is obvious that only a precise knowledge of size and shape (and therefore confining potential) will allow the calculation of the electronic structure in the semiconductor islands.

Additional influences of composition gradient in the dots and strain due to the mismatch of the lattice constants of island and host material make the estimations even more difficult.

The starting point for all calculations is the time-independent Schrödinger equation

\[ H_0 \psi(\vec{r}) = E \psi(\vec{r}) \]  \hspace{1cm} (2.9)

with the Hamiltonian \( H_0 \) being the sum of kinetic and potential energies:

\[ H_0 = -\frac{\hbar^2}{2m_0} \Delta + V(\vec{r}) \] \hspace{1cm} (2.10)

In the equations above \( \psi \) is the electronic wave function, \( E \) the total energy, \( \vec{r} \) the position vector and \( m_0 \) the free electron mass.

The Schrödinger equation can only be solved analytically for simple geometrical shapes (for example spheres or semi spheres) and additional simplifying assumptions like infinite confining potential. Obtaining solutions - at least numerically - becomes exceedingly difficult the more parameters are considered.

Effective-mass approximations not including [13] or including [10] the dependence of the effective mass on position and multiband \( k \cdot p \) methods [14] are examples of macroscopic models. Microscopic models, which provide an atomistic treatment, include tight-binding calculations [6] and pseudopotential techniques [7]. They are better suited for a more realistic description of smaller heterostructures yet the computational demands are very high due to the highly complex nature of the problem.

The more sophisticated models include effects like band-bending (the change of curvature of the energy bands as a function of \( k \) in the crystal lattice), energy splitting of heavy-hole and light-hole band, spin-orbit coupling or the actual shape of the confining potential. Due to strain the latter is no longer simply given by the differences of conduction and valence band edges in dot and barrier material but rather a piecewise continuous function of position [15].
Other parameters influencing the electronic structure are the piezoelectric potential [10] and a non-uniform composition profile in the quantum dot [7]. Finally, the Coulomb interaction between carriers must be taken into account if it is appreciably large compared to the quantization energy, i.e. the level separation in conduction/valence band. This is true in the so-called weak confinement regime where the exciton radius is smaller than the dot radius. In the opposite case of strong confinement (when the quantum dots are smaller than the bulk exciton radius) the electron and hole wavefunctions are largely uncorrelated.
3 Growth and applications of quantum dots

3.1 Growth

Since the dimensions of quantum dots are extremely small, a precise control over the manufacturing process is essential. In early experiments QDs were produced by lithographical methods as for example described by Reed et al [16]. Since the demands on resolution are very high, an electron beam was used instead of UV light in order to define an etch mask on a quantum well structure. After etching the pattern of the mask is transferred to the underlying layers. The structures created in such a fashion had the shapes of pillars with a typical side length of approximately 250 nm. Carriers were confined to the quantum well layers inside the pillars. Their movement was therefore restricted in all three directions and a quantum dot was obtained.

Another possible method that was carried out already very early is the growth of semiconductor nanocrystallites in solution [17] or in a dielectric matrix [18].

In the first case colloidal quantum dots are formed in a controlled chemical reaction in a liquid. The typical size of the crystallites is somewhere in the range from 1 to 100 nm.

In the second case, semiconductor doped glasses containing CdE (where E = S, Se, Te,...) are heated to several hundred degrees Celsius for a few hours resulting in formation of spherical nanocrystals. By choosing appropriate heating temperature and time it is possible to obtain nanocrystallites of desired size ranging from a few to a few tens of nanometers.

One of the most appealing approaches, however, is the use of special combinations of substrate and growth material to realize semiconductor quantum dots on a semiconductor surface without the need of lithography [19].

Depending on the experimental conditions (like substrate temperature, rate of deposition) and material parameters (lattice mismatch between substrate and deposited material, surface energies, ...) the epitaxial crystal growth proceeds via one of the three modes illustrated in Figure 3-1.
Frank-van der Merwe (FvdM) growth occurs when the surface energy of the substrate exceeds epilayer surface energy plus interface energy. Material is added to the crystal layer by layer. In the opposite case, when the substrate surface energy is lower than the sum of epilayer surface energy and interface energy, the growth follows the Vollmer-Weber (VW) pattern and islands rather than continuous layers appear.

The situation is quite different in the presence of strain caused by a mismatch of the lattice constants of substrate and epilayer. The commonly used InAs/GaAs features, for example, a 7% lattice mismatch. When the material is deposited slowly, one or two monolayers (the so-called wetting layer) are formed. Once a critical thickness is reached it becomes energetically more favorable to form separated islands. This process is sometimes referred to as 2D to 3D transition and is the so-called Stranski-Krastanow (SK) mode of growth. The transition, occurring at typical thicknesses between 1.4 and 1.7 monolayers (MLs) of deposited material [20], is rather sharp as observed in situ by reflection high-energy electron diffraction (RHEED). The exact structural changes in surface morphology when approaching the critical thickness, however, are rather complicated and still not well understood.

Obviously these sharp transitions require a precise control over the amount of material deposition. Therefore quantum dot growth is achieved via molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD).

Initially it was believed that the strain relaxation at the transition from the 2D to the 3D mode of growth would introduce misfit dislocations inside the islands or at their interfaces. It was shown, however, that QDs formed during early stages of growth are coherently strained and dislocation free [21]. The QDs obtained in such a way are commonly called self-assembled QDs, SAQDs or SKQDs.

Surprisingly enough the distribution of island sizes can be made quite narrow by optimizing the growth parameters. Additional material deposition after the onset of QD nucleation at the critical thickness leads to an increased dot density while the average dot size and variation of size follows a two-stage process [22]. Initially there
is a rather small distribution of sizes. When the dot density is still low, islands grow
more or less independently and therefore a rather large variation in the lateral
dimensions is found. Indeed, the distribution of island sizes can often be described by
bimodal or even multimodal distribution. The second stage occurs when the islands
are close to each other. Island induced strain fields in the substrate destabilize the
largest dots and the size distribution is decreased.

Since the island distribution on the substrate is completely random, the local
environments for the quantum dots are also different. Dots that are close to each
other will be subject to electronic coupling, arising either from an overlap of
wavefunctions or Coulomb interaction [23]. Naturally, this will lead to completely
different effects from those present on isolated dots, which makes an exact
interpretation of experimentally obtained data difficult. Furthermore it is for some
applications desirable or even essential that all participating QDs behave in the same
way. It is therefore of great interest to produce structures where the QDs are well
aligned.

One possible way of achieving ordering in the lateral plane is lithography. Mui et
al demonstrated the growth of self-aligned InAs islands on etched GaAs ridges [24].
This, however, requires an additional step of defining the nucleation sites for the
semiconductor islands. From a technological point of view alternative methods that
result in self-assembled, ordered structures would be more interesting.

It has been found that quantum dots align along the edges of multiatomic steps
that form on vicinal surfaces, i.e. surfaces misoriented by only a few degrees towards
one of the major crystal directions [25]. In addition to other growth parameters, the
miscut angle determines island density, diameters and uniformity.

In the frame of this work yet another approach was undertaken. An InGaAs
composition graded layer was introduced in the substrate (Figure 3-2). The difference
in lattice constant throughout that part of the structure results in a strain, which is
relaxed upon thermal annealing by formation of misfit dislocations. A more detailed
description of the structure and growth parameters can be found in Paper II.
As a consequence of the strain relaxation in the composition graded layer, the substrate is no longer flat but features undulations along perpendicular directions on the surface. The QDs formed upon deposition of InAs, preferentially nucleate along these undulations as is shown in Figure 3-3. To evaluate the possible influences of the dislocations on carrier recombination inside the QDs, different cap (or barrier) layer thicknesses were used. The exact surface morphology varies between these samples. For 5 nm barrier thickness dots align along long lines and areas largely denuded of QDs form. As the barrier layer width increases the lines get wider and form broader bands of high dot density separated by bands with very few dots.

A clear trend for alignment along the \(\langle 011\rangle\) directions is nonetheless observable for all of them.
Figure 3-3: AFM image of the samples with 5 nm barrier showing how the quantum dots align along the \( \langle 011 \rangle \) directions.

For the sake of completeness some aspects vertical ordering, which is much easier to achieve in practice than lateral ordering, should be mentioned at this point.

When QDs are covered and additional dots are grown on the capping layer, vertical correlation can be observed [26]. For capping layer thicknesses of a few tens of monolayers (MLs), the dots in the new layer form exactly above the ones in the first one. This can be explained by a locally non-uniform strain field induced in the cap by the first dots, providing the driving force for 3D island formation. Upon further increase of the capping layer thickness the vertical correlation between quantum dots in different layers is reduced and finally results in completely uncorrelated for spacer widths exceeding a few hundred MLs.

The short distance between dots in different layers results in electronic coupling and level splitting of up to a few tens of meV [27]. Carriers can be shown to tunnel coherently between the QDs, resulting in entangled states. These artificial or quantum dot molecules are therefore attractive candidates for quantum gates needed in quantum computing.

It is possible to exploiting the effect of vertical correlation in order to achieve lateral ordering. Recently Mano et al demonstrated for example one-dimensional ordering of (In,Ga)As quantum dots by using quantum wires as templates [28].
Most importantly, though, the use of multiple stacks effectively increases the number of QDs in a given volume, which is crucial for device applications.

### 3.2 Applications

The unique properties of QDs in terms of carrier confinement and delta-function like density of states are very appealing for a large number of applications. Improvements of existing devices are possible as well as the realization of completely new designs. The following subsections list a few of those applications where the use of QDs promises to be beneficial.

#### 3.2.1 Lasers

Using QDs as the gain material in semiconductor lasers was one of the major driving forces for QD research since the discovery of the potential benefits in 1982 by Arakawa and Sakaki [29]. Even though first models considering ideal, completely uniform QD ensembles had to give way for more realistic descriptions (including for example the effects of inhomogeneous level broadening due to a finite distribution of QD sizes [23]), one can still expect new laser structures to perform better than the QW based lasers used today.

The discrete energy levels lead to a significantly lower threshold current density, which in turn results in reduced power consumption and an increase in the dynamic response essential for direct modulation [30]. The threshold is furthermore far less dependent on temperature than for common bulk or QW structures.

Additionally a variation in temperature affects the emission wavelength of QD lasers less than for other devices. This has been attributed to the broad flat gain profile of a QD layer (ultimately originating in the inhomogeneous level broadening) and can be explained as follows [31]: On one hand the bandgap decreases with increasing temperature, resulting in a redshift of the wavelength. At the same time internal losses due to free carrier absorption increase, requiring a higher concentration of injected carriers to maintain the condition for lasing. This in turn leads to an increase of the Fermi level and shifts the gain maximum towards higher energies since transitions from the first excited state become more important. The resulting blueshift compensates the redshift at least partially and thus explains the excellent wavelength stability found in QD lasers.

Selection of the lasing wavelength is achieved by a couple of parameters. An obvious choice is that of selecting different materials. For self-assembled growth, which is driven by strain, there are however limitations in the available material systems. Even so light emission from the visible (e.g. AlInAs/AlGaAs) to the infrared (e.g. InGaAs/GaAs or InAs/InP) can be achieved for III-V semiconductor structures alone. Another key parameter is the amount of strain in the material itself since it determines, to a significant degree, the energy levels in the QDs. Covering the dots with a strain reducing layer allows a fine-tuning of the strain independent of the dot material composition. In such a way, it is possible to tune the emission wavelength over a few hundred nanometers by simple variation of the strain reducing layer thickness.
Of particular interest for fiber communication applications are lasers operating in the 1.3 µm and 1.55 µm regions, where the standard silica fibers have minima in the absorption. Using GaAs-based devices is very appealing, not least of all because of the ability to use high-quality inexpensive GaAs substrates. Therefore significant efforts are made to fabricate and optimize long wavelength GaAs-based QD lasers (for a review of recent advances in the fabrication of QD lasers with excellent characteristics, see Ref. 32 and references therein).

3.2.2 Photodetectors

The most commonly used material for infrared (IR) detectors is Hg_{1-x}Cd_{x}Te. The flexibility in bandgap engineering as well as high optical absorption coefficient are beneficial but the non-uniformity over large areas and the high cost in growth and processing are disadvantageous [33].

Quantum well infrared photodetectors (QWIPs), while based on well-controlled growth mechanisms and successfully used in various device applications, suffer from one major drawback: Because of optical transition selection rules, absorption of light at normal incidence is not possible. Furthermore QWIPs cannot be made sensitive for a broad range of wavelengths since the intrasubband transitions, on which the operating principle is based, are spectrally rather sharp and well defined.

The QDs growth mechanisms, on the other hand, automatically lead to a distribution of island sizes and therefore a rather broad spread of energy levels. This feature - while often detrimental for other applications - can actually be beneficial for quantum dot infrared photodetectors (QDIPs) as it allows the operation of the detector in a rather broad spectral range [34]. Moreover, the selection rules allow detection of normal incident light. Finally, QDIPs are expected to exhibit lower dark current than their QW based counterparts and can feature a greatly improved signal-to-noise ratio since the thermal generation of carriers is significantly reduced owing to the energy quantization. Contrary to HgCdTe detectors and QWIPs, which need to be cooled to around 80 K and 60 K, respectively, QDIPs can operate even at room temperature [33].

Another interesting feature for detectors but also for lasers is the radiation hardness shown for QD devices. Irradiation with protons causes displacement damages in the crystal where free carriers are lost to nonradiative recombination. Electrons and holes in QWs can move in two dimensions. Hence it is possible for them to “find” defects for recombination over significant distances. In QDs, on the other hand, carriers are completely confined in three dimensions. Nonradiative losses can therefore only occur if the defects that cause them are close to or even inside the dots. This makes QD devices considerably less susceptible to performance degradation when operating in hostile environments. It was furthermore found that the photoluminescence of QD structures (contrary to QWs) even increases after irradiation with low to intermediate proton doses. This effect, explored in great detail in paper I, can be explained by increased capture efficiency of carriers into the dots involving the structural defects caused by the protons (see also 4.2.1).
3.2.3 Biological imaging

By far the most important application of quantum dots today is their use in biological imaging [35-37]. In fact it is mature enough to already feature commercially available products on the market.

Commonly light emitting substances (so-called “labels”) are linked to molecules, thus enabling tracking of any development the molecules are participating in. In such a way one can for example study how efficiently the therapeutic molecules contained in drugs can reach the target cells and hence find the means to optimize the drug [35].

Regular dyes, however, exhibit a number of undesirable features: First of all the emitted light is distributed in rather broad spectra. Simultaneous labeling of different molecules or different parts of cells is therefore very limited and can only be done when the respective spectra do not overlap significantly. Typically only two, at most three different labels can be used simultaneously. At the same time the dyes need to be excited with light from a small wavelength region, further restricting the choice of labels that can be used together. Finally their luminescence strongly decreases with time and disappears completely after only a few minutes, an effect known as photobleaching.

Quantum dots, on the other hand, promise to be superior in all the aspects mentioned above. Their photoemission spectra are very narrow and can furthermore be tuned by selecting the appropriate dot size. Moreover, all QDs can be excited by one and the same wavelength, provided that it is shorter than the emission wavelength. QD based labels are also reported to be 100-200 times more resistant to photobleaching than conventional dyes ([36] and references therein).

Early problems of obtaining nanoparticles that are non-toxic and stable in biological environments seem to have been overcome. Already in 2002 Dubertret et al demonstrated the successful use of QD labels for imaging living cells [37]. They used CdS quantum dots covered with a ZnS outer layer to monitor the development of a frog embryo to a tadpole.

To further increase the usability of QD labels, efforts are made to change from the frequently used CdS and CdSe to material systems that emit in the infrared part of the spectrum (e.g. InP or InAs) because tissue is more or less transparent at these wavelengths [35].

3.2.4 Memory, cellular automata, single photon light source, etc.

While most research has been done on the devices described in the previous sections, research is being conducted also on more “exotic” applications.

Optical memories based on QDs, for example, promise to yield ultra-high density storage media [38]. Here, the inhomogeneous broadening of self-assembled QD ensembles is used to achieve persistent spectral hole-burning (PSHB). In PSHB the absorption spectra of materials are modified in such a way as to saturate the absorption for certain wavelengths (so-called spectral holes). These holes correspond to binary “0” while the absence of a hole would be “1”. Using multiple frequencies in one laser beam it is then possible to store multiple bits in the laser focal volume, thus increasing the storage density by several orders of magnitude.
Another concept that uses large spread of optical transitions is a *quantum dot spectrometer* proposed by Jimenez *et al* [39]. Light of different wavelength can be absorbed to generate carriers inside QDs depending on the energy levels and therefore their size. A large inhomogeneous broadening will therefore be necessary for a device detecting broad spectral ranges.

Novel logic circuits utilizing QD *cellular automata* could be the key to increasing the package density on integrated circuits. There the basic cell consists of four QDs arranged in a square. When two excess electrons are introduced, Coulomb repulsion forces them into opposite corners. By choosing which of the corners are occupied, logic states “0” and “1” can be realized [40].

The spin states of coupled single-electron quantum dots can be used for *quantum computation* [41]. In an alternative scheme for quantum computing but also quantum cryptography *single photon light sources* are required, which can again be based on QDs [42].

The list above is of certainly not exhaustive and it remains to be seen what other ideas can be put forward and ultimately be realized in real applications.
4 Carrier dynamics in semiconductors

Electrical, thermal, or optical excitation generates a carrier distribution that differs from the thermal equilibrium. After removal of the excitation source relaxation processes will force the system back into the equilibrium state. Depending on the material this can take anywhere from a few hundreds of femtoseconds to a few microseconds.

Even though the discrete levels in quantum dots increase the complexity of the carrier dynamics, the underlying physical processes are the same as for the bulk case. Therefore in the following chapter fundamentals of the generation and relaxation mechanisms for bulk materials are presented as an introduction.

4.1 Carrier dynamics in bulk semiconductors

Ultrashort optical pulses give raise to a number of dynamic processes of carriers in semiconductors. One can identify two different parts: Carrier excitation (or generation) followed by relaxation. The latter can be further divided into four different regimes – coherent, non-thermal, hot-carrier and isothermal regime - that are not strictly separable and may overlap in time [43]. Figure 4-1 illustrates the carrier distributions in the different regimes.

![Figure 4-1: Temporal development of the energy distribution of the electron population in the conduction band of excited semiconductors. (a) Coherent regime, (b) non-thermal regime, (c) hot-carrier regime, (d) isothermal regime. Details of the different regimes are discussed in the text.](image)

4.1.1 Carrier generation

Shining light on semiconductors causes the following elementary excitations: Interband transitions, excitonic transitions or below-bandgap transitions. These processes are schematically shown in Figure 4-2 for direct bandgap material, i.e. the conduction band minimum occurs at the same position in $k$-space as the valence band maximum.
If the photon energy is larger than the bandgap, interband transitions dominate, exciting electrons from the valence into the conduction band. Following Einstein’s description of stimulated absorption, electron-hole pairs are created with a rate

\[ G = B_{12} p_1 (1 - p_2) \rho(\hbar \nu). \] (4.1)

Here 1 denotes initial state (valence band) and 2 the final state (conduction band). \( B_{12} \) is the Einstein coefficient for (stimulated) absorption, \( p_{1,2} \) the occupation probabilities for electrons in the valence/conduction band and \( \rho(\hbar \nu) \) density of photons with an energy \( \hbar \nu \).

For high excess carrier densities, most of the available states in the conduction band are occupied and \( p_2 \to 1 \). At the same time \( p_1 \to 0 \) because most electrons have been excited over the bandgap. From (4.1) it follows that the absorption will then decrease significantly, an effect called bleaching.

4.1.2 Relaxation

Coherent regime. The electromagnetic field of an ultrashort optical pulse generates a macroscopic polarization in a semiconductor. Carriers have well-defined phase relationships with each other and with the external field. This coherence is lost due to various efficient scattering mechanisms (e.g. momentum, carrier-carrier and hole-optical-phonon scattering) [43]. Phases of the individual carriers are changed randomly within a time range of only a few tens to hundreds femtoseconds, which is referred to as dephasing.
Non-thermal regime. The energy distribution of the carrier population immediately after excitation cannot be described by Fermi-Dirac or Maxwell-Boltzmann distribution with a defined temperature and depends rather on band structure and photon energy. Due to carrier-carrier and carrier-phonon scattering electrons and holes are redistributed throughout the conduction and valence bands.

After a few hundred femtoseconds a Fermi-Dirac distribution is reached. Since the energy exchange via scattering processes is more efficient between carriers of the same type, the characteristic temperatures for electrons and holes are different.

Hot-carrier regime. As the temperatures that describe the carrier distributions are higher than the one for the lattice, the carriers are called “hot”. Thermalization sets in when carriers transfer their excess energies to the crystal lattice through interaction with phonons. In such a way large populations of non-equilibrium (hot) phonons are created and the carriers are “cooled” to the lattice temperature.

The emission rate of longitudinal optical or acoustic (LO or LA) phonons with energy $\hbar \omega_q$ is given by [54]:

$$c_q = \frac{1}{\tau} = \frac{2\pi}{\hbar} \cdot \sum_q \left| M_q \right|^2 \cdot (n_q + 1) \cdot \delta (\Delta - \hbar \omega_q).$$

Here $\Delta$ is the carrier energy difference in energy of initial and final state and $n_q$ the Bose-Einstein distribution function

$$n_q = \left( \exp (\hbar \omega / k_B T) - 1 \right)^{-1}.$$  \hspace{1cm} (4.3)

The matrix element $M_q$ is given by the particular interaction process. Thermalization times depend on many factors such as carrier concentration and lattice temperature but are usually in the range below 100 ps.

Isothermal regime. Carriers, phonons and lattice are now equilibrium, i.e. they can be described by one common temperature. Compared to the thermal equilibrium there are still excess carriers, which are removed both via radiative or nonradiative recombination processes. This is shown in Figure 4-3 and explained in more detail in the following subsections.
4 Carrier dynamics in semiconductors

4.1.3 Radiative recombination

When an electron relaxes from the conduction into the valence band to recombine with a hole, energy is released in form of a photon. This can happen either spontaneously with a recombination rate

\[ R_{\text{sp}} = A_{21} p_1 (1 - p_2) \]  

(4.4)

or due to stimulation by photons (if their energy exceeds the bandgap energy):

\[ R_{\text{st}} = B_{21} p_2 (1 - p_1) \rho (h \nu) . \]

(4.5)

\( I \) and \( 2 \) again denote valence/conduction band, \( p \) the electron occupation probabilities and \( \rho \) the photon densities. \( A_{21} \) and \( B_{21} \) are the Einstein coefficients for spontaneous and stimulated emission. In semiconductors the occupation probabilities can be expressed through electron and hole concentrations, i.e.

\[ p_2 \propto n, \quad 1 - p_1 \propto p \]

(4.6)

It can furthermore be shown that \( A_{21} \) is proportional to the third power of the frequency of the emitted photons \( \nu \) [44]

\[ A_{21} = B_{21} \frac{8 \pi \hbar}{c^3} \cdot \nu^3 . \]

(4.7)

This makes it obvious that radiative recombination is only efficient if the transition energies involved are large.

In an indirect bandgap semiconductor the additional interaction with a phonon, which has to carry the extra momentum, is required. Radiative recombination, which otherwise occurs on nanosecond timescales, is therefore slowed down drastically and can reach characteristic times of several hundreds of microseconds.
4.1.4 Nonradiative recombination

Creating photons is not the only way of releasing energy when electrons and holes recombine. Alternative processes are called nonradiative, since no photons are emitted. They can be categorized into Auger recombination and recombination at defect or surface states, as illustrated in Figure 4-3.

In an Auger process a carrier transfers its momentum and energy to a third carrier. With the usual notation of \( n \) and \( p \) for electron and hole densities, the recombination rate is therefore proportional to

\[
R_{\text{Auger}} \propto n^2 p \quad \text{or} \quad R_{\text{Auger}} \propto np^2
\]

(4.8)

depending on the carriers involved. It is hence obvious that Auger processes will be primarily important for high carrier densities. They are furthermore bandgap dependent and increase exponentially as the bandgap is decreased.

Deviations from a perfectly periodic structure in a crystal lattice result in localized defect energy levels within the forbidden gap. They can be caused either by structural defects in the bulk (such as point defects, dislocations, stacking faults, …) or by the surface itself (so-called surface states). Depending on their energy levels the defects are categorized as either traps or recombination centers.

When the energy difference between defect level and conduction (valence) band is small, an electron (hole) can be captured quickly. The probability of recombination with a carrier of the opposite type is rather small, though, as the energy difference to the corresponding band is large. Consequently, electrons and holes stay at the carrier traps for finite times and can return to conduction or valence bands through thermal excitation.

For defects with energy levels deep within the forbidden gap the situation is quite different. Thermal emission of trapped carriers is significantly reduced (the probability of such an event decays exponentially with the energy difference of defect and band energy). Instead carriers recombine at the defects, which are therefore called recombination centers, nonradiatively via emission of phonons. The statistics of nonradiative recombination at deep levels were first laid out by Shockley, Read and Hall and are explained in all detail in Ref. 45.

4.1.5 Rate equations and carrier lifetimes

In the following, the most important aspects of using rate equations for describing the capture and recombination of carriers at defect levels are presented, leading to the concept of carrier lifetimes.

From the discussion in the previous section it is clear that the change electron concentration in the conduction band is given by (optical) generation rate \( G \), capture rate to the defects \( R_n \) and thermal emission rate from the defects into the conduction band \( G_n \). This can be written in form of a rate equation as
\[
\frac{dn}{dt} = G - R_n + G_n \tag{4.9}
\]

For independently acting capture centers, the capture rate is proportional to the concentrations of both the defects and the carriers:

\[
R_n = c_n \cdot N \cdot n \tag{4.10}
\]

The proportionality factor, which characterizes the trapping to individual capture centers, is called the (electron) capture rate.

Ignoring thermal generation, which is a good approximation for deep levels, one finds the following equation for the decrease of electron concentration in the conduction band after removing the generation source at \( t = 0 \)

\[
\frac{dn}{dt} = -R_n = -c_n \cdot N \cdot n . \tag{4.11}
\]

Integration yields

\[
n(t) \propto \exp\left(-c_n \cdot N \cdot t\right) = \exp\left(-t/\tau_n\right). \tag{4.12}
\]

The introduced electron lifetime \( \tau_n \) therefore represents an average time before an electron stays in the conduction band before it is captured by a defect.

Similar considerations for holes in the valence band lead to expressions for a hole capture rate and lifetime. At steady state, i.e. \( \frac{dn}{dt} = \frac{dp}{dt} = 0 \), one can easily define an effective recombination rate if electrons and holes are captured to the same defects:

\[
R_{\text{def}} \equiv R_n - G_n = R_p - G_p \tag{4.13}
\]

It can be shown that \( R_{\text{def}} \) is given by

\[
R_{\text{def}} = \frac{c_n c_p N (n p - n_1^2)}{c_n (n + n_1) + c_p (p + p_1)} \tag{4.14}
\]

where \( n_1^2 = n_1 p_1 \) is the intrinsic carrier concentration and \( n_1 \) and \( p_1 \) are the equilibrium concentrations of free electrons and holes that would be realized if the Fermi level would coincide with the energy level of the traps.

For the remainder of this chapter, high optical excitation of undoped semiconductors is assumed, i.e. \( n = p \gg n_1, p_1 \). Under these conditions (4.14) reduces to

\[
R_{\text{def}} = \frac{c_n c_p N}{c_n + c_p} \cdot n = \frac{n}{\tau_n + \tau_p} = \frac{n}{\tau_{\text{recomb}}} . \tag{4.15}
\]
By combining the results for the nonradiative (defect, Auger) and radiative (spontaneous and stimulated emission) recombination from (4.4)-(4.6), (4.8) and (4.15) one can find the total carrier recombination rate as

\[
R = R_{\text{def}} + R_{\text{spon}} + R_{\text{Auger}} + R_{\text{stim}} = \left( R_{\text{nonrad}} + R_{\text{rad}} \right)
\]

\[= A \cdot n + B \cdot n^2 + C \cdot n^3 + R_{\text{stim}}\]

which can be expressed in terms of a carrier lifetime \(\tau\)

\[
R = R_{\text{nonrad}} + R_{\text{rad}} \Rightarrow \frac{1}{\tau} = \frac{1}{\tau_{\text{nonrad}}} + \frac{1}{\tau_{\text{rad}}}.
\]

Since the nonradiative processes are much faster than the radiative ones, they will dominate the recombination statistics if either the excitation is very high (Auger processes increase proportional to \(n^3\)) or if the number of defects is appreciable in the material.

In time-resolved photoluminescence experiments samples are excited with ultrashort light pulses and the change of the emitted light as a function of time is monitored. To gain information about the carrier dynamics it is therefore necessary to find the relationship between the photoluminescence decay and the carrier lifetimes.

The light pulse incident on a semiconductor creates initial carrier concentrations \(n(0)\) and \(p(0)\). Considering excited carrier concentrations low enough to disregard Auger effects, one then finds the material response from (4.12) and (4.17) to be determined by radiative recombination and capture to defects as

\[
n(t) = n(0) \cdot \exp \left( -t \cdot \left( \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{n}}} \right) \right)
\]

\[
p(t) = p(0) \cdot \exp \left( -t \cdot \left( \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{p}}} \right) \right)
\]

The photoluminescence intensity, i.e. the light signal emitted by the material due to radiative recombination, is proportional to the product of electron and hole concentrations:

\[
I(t) = I(0) \cdot \exp \left( -t \cdot \left( \frac{2}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{capt}}} \right) \right) = I(0) \cdot \exp \left( -t/\tau_{\text{pl}} \right)
\]

where the following definitions have been used:
\[ I(0) \propto n(0) \cdot p(0) \]
\[
\frac{1}{\tau_{\text{capt}}} \equiv \frac{1}{\tau_n} + \frac{1}{\tau_p}
\]
\[
\frac{1}{\tau_{\text{PL}}} \equiv \frac{2}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{capt}}}
\]

\( \tau_{\text{PL}} \) in this context is then commonly called “decay time”. Thus the capture rates can be extracted from PL transients if either the radiative recombination rate is known or at least much smaller than the capture rate. However it is not possible to distinguish between the influences of electron and hole capture. According to the second equation in (4.20) the total capture rate is unaffected by exchanging electron and hole relaxation times and the faster of the two processes will determine the total capture rate. Additional experiments, either with doped structures or other experimental techniques like deep level transient spectroscopy (DLTS) are necessary to obtain information about the defect character, i.e. whether it preferentially captures electrons or holes.

### 4.2 Carrier dynamics in quantum dots

Due to the hetero-interface of two materials and the discrete nature of the quantum dot levels, carrier dynamics in QD structures are considerably more complex than in bulk materials. Figure 4-4 depicts a simplified band diagram of a semiconductor QD structure under excitation with light, as found for example in photoluminescence experiments.

![Figure 4-4: Schematic representation of possible carrier dynamics in QD structures for nonresonant excitation in the barrier. The different steps are described in the text. For simplicity the quantized level structure in the wetting layer (WL) is not shown.](image-url)
Here the excitation is assumed to occur in the barrier, i.e. the material surrounding the QDs, for example GaAs in the InAs/GaAs system. The wetting layer, on which the QDs form in self assembled growth, acts as an additional quantum well in the structure. The dynamic carrier processes thus include:

1. Excitation of electrons from the barrier valence band into the conduction band, thereby creating free electrons in the conduction band and free holes in the valence band.
2. Relaxation from the barrier to the wetting layer.
3. Capture of the carriers into the quantum dots. The capture can occur either to the ground state or to higher energy states with subsequent relaxation. Capture directly from barrier states is also possible.
4. Carrier relaxation via carrier-carrier interaction (Auger effect) or carrier-phonon interaction.
5. Carrier transfer from the quantum dot to a nearby deep level leading to carrier trapping and/or nonradiative recombination.
6. Radiative recombination, an electron and hole annihilate each other. The energy released in the process is emitted via creation of a photon.

Other possible processes are radiative and nonradiative recombination of carriers in WL and barrier conduction/valence band and (thermal) escape of the electrons and holes from the quantum dots. For simplicity these processes are not included in Figure 4-4.

A more detailed explanation of the mechanisms involved is given in the following subchapters.

4.2.1 Carrier transfer into quantum dots

One of the most important experimental tools to study carrier dynamics in quantum dot structures is photoluminescence. Carriers are either excited nonresonantly into the barrier (from the valence band of the bulk material into the conduction band) or resonantly in the QDs (from a valence band QD level to a conduction band level).

Under nonresonant excitation conditions, electrons and holes, which are created throughout a certain volume determined by focal spot diameter and absorption length, need to be transported to the quantum dot layer before they can be captured. This process is very similar to the trapping of carriers to deep levels and can be studied by the same experimental technique, namely deep level transient spectroscopy (DLTS). Typical capture times are of the order of a few to tens of picoseconds.

As schematically indicated in Figure 4-5, capture barriers can exist between WL and QDs for example due to the strain induced in self-organized systems [46]. These barriers lead to increased capture times [47].
Deep levels close to the QDs, however, can provide an additional pathway for carrier capture. In paper I the impact of proton irradiation on the carrier dynamics – important for applications under hostile environments – is described. It was found that the photoluminescence intensities for low to intermediate proton irradiation doses were increased compared to the unirradiated sample (see also Figure 4-6). This finding is initially surprising because the protons create defects in the crystal structure (and thus deep levels) at which carriers can recombine nonradiatively. One might therefore expect the luminescence coming from the QD ground state transition to be reduced. Instead it was shown in the aforementioned paper that the deep levels may actually increase the capture rate into the dots: First a carrier is captured by the deep level from the WL or barrier states. From there it can tunnel into a quantum dot, provided the distance between is sufficiently small.

**Figure 4-6**: (a) Comparison of QD PL spectra before obtained before and after irradiation of a low density QD sample \(4 \times 10^8 \text{ dots/cm}^2\) with a proton dose of dose \(2.7 \times 10^{12} \text{ cm}^{-2}\). (b) PL peak intensity changes of various InGaAs/GaAs QD structures and a comparable QW.

### 4.2.2 Energy relaxation and nonradiative recombination

After being captured and confined to quantum dots, the carriers, which are typically in higher energy states, will start to relax and recombine similar as they do
in bulk material. There is, however, one fundamental difference: Since the level structure is discrete, interaction with LO phonons, which is the dominant relaxation process in bulk, can only be efficient if the level separation closely matches the energy of one or several phonons. This reduces the average interaction probability dramatically as the energy spectrum of the LO phonons is usually rather narrow.

Instead it was suggested that the intraband (i.e. between two discrete conduction or valence band levels) relaxation had to occur via LA phonon emission. This process, already slow for bulk, was predicted to be even slower in QDs, giving relaxation times of the order of several nanoseconds and therefore longer than radiative recombination times [48]. This phenomenon was called the “phonon bottleneck effect”. It should mainly affect the electrons in the QDs, as the level spacing for holes - because of the shallower potential well and their higher effective mass - is rather small, making fast relaxation possible.

However, the importance of the phonon bottleneck was heavily debated in the literature and both its absence and existence have been reported [49-52, 55]. Summarizing the results it appears that relaxation is slowed down when phonon scattering efficiencies are decreased [53] but not as much as predicted. True observation of a phonon bottleneck effect could only be obtained under special conditions, for example large electron and hole confinement, very low temperatures and low carrier densities. Consequently, various mechanisms were suggested that could explain the breakdown of bottleneck effect [54-60]:

**Multi-phonon emission.** If the interlevel energy difference does not match the LO phonon energy, carrier relaxation can occur via emission and/or absorption of more than one phonon out of several available species.

Theory suggests, for example, efficient simultaneous interaction with LO and LA phonons [54]. The rates of these LO±LA processes (emission of one LO phonon with additional emission (+) or absorption (-) of an LA phonon) are in analogy to (4.2) given by

\[
c_{q,k} \propto \sum_q \sum_k \left(N_q + 1\right) \left(N_k + \frac{1}{2} \pm \frac{1}{2}\right) \delta\left(\Delta - h\omega_q \mp h\omega_k\right).
\]

Even though they exhibit an even stronger dependence on the available phonons, the LO±LA processes were shown to open “energy windows” for efficient relaxation around the LO phonon energy. It is, however, still relatively narrow compared to other mechanisms.

In photoluminescence excitation spectroscopy (PLE) experiments it was found that the phonon bottleneck could be circumvented by simultaneous emission of one, two or three LO phonons [55]. The efficiency is further enhanced and the energy range extended due to the different available phonon “modes” (i.e. phonons in substrate, WL and in the QDs), with which the carriers can exchange energy.

**Relaxation through defect states.** Real structures are never free of defects. If such defects are situated close to QDs, they can provide a relaxation pathway similar to that of deep levels in bulk [56]. As was already pointed out in chapter 4.2.1, carriers
can be captured from the continuous bands but also from higher excited states in the QDs. If, for example, the defect energy level is between two states (e.g. an excited state and the ground state), it can work as a “lift”. First an electron is captured to the defect. Subsequently the carrier relaxes at the defect and can be transferred back into the dot at a lower energy.

Li et al calculated energy windows of several tens of meV for relaxation from a nearby defect state to the QD ground state, consequently providing subpicosecond relaxation times [57].

The transfer probability, however, depends critically on the distance between defect and QD. The transition matrix element describing the transfer is only reasonably large if this distance is less than approximately 10 nm. Thus ultrafast nonradiative recombination channels can be provided by point defects or interface states introduced as a result of the growth process itself.

**LO phonon decay.** In Ref. 58 the coupling of the electronic system to the confined optical phonons in a QD has likened to the coupled atom-photon system in optical microcavities that leads to an enhanced spontaneous emission due to confinement and dissipation of photons. It has been shown that the LO phonons are anharmonically coupled to bulk acoustic phonons which decay, providing a carrier relaxation times of <100 ps for very wide energy windows.

**Auger processes.** The interaction between carriers provides yet another mechanism for relaxation by means of Auger processes [59], some of which are illustrated in Figure 4-7.

For many device applications, high injected carrier densities are needed. Under these conditions Coulomb scattering between confined electrons and high-density electron-hole plasma in the WL is very efficient, resulting in relaxation rates of up to $10^{12} \text{ s}^{-1}$ [60].

On the other hand carrier-carrier scattering may occur even for low electron and hole densities in the WL via interaction of confined carriers. One bound electron can relax by transferring its energy to another one, which does not even necessarily have to be bound to the same level, ejecting it into the WL. Alternatively the electron can make a transition to the ground state by interaction with a hole, which again is excited into the wetting layer continuum. Subsequently the carriers excited to the WL lose their energies via phonon scattering or interaction with other carriers and are re-captured. This relaxation pathway is efficient as long as there is more than one carrier in a QD.
Figure 4-7: Different Auger-like processes in QDs: (a) Scattering of confined electron with continuum electron-hole plasma, (b) electron-electron scattering, and (c) electron-hole scattering (after Ref. 59).

It should be mentioned that there is a finite probability for radiative relaxation, i.e. a carrier loses its energy via spontaneous emission of a photon similar to radiative recombination. From (4.7) it can be seen that this, however, is an inefficient process since the energy separation between two levels is small. Nevertheless midinfrared photoluminescence was found by Sauvage et al as a result of intraband transitions [61].

The mechanisms presented in the section so far consider the relaxation of electrons and holes as separate particles. This is somewhat controversial, though, and it was suggested to consider the relaxation of electron-hole pairs (excitons) instead [62]. Fast relaxation and a breakdown of the bottleneck effect can then be explained by the fact that the energy levels of the excitonic system are much more closely spaced than the levels of the single carriers.

4.2.3 Radiative recombination

The transition probabilities between electron and hole states (with their respective quantum numbers $n, n', m, and m'$) are given by the square of the wavefunction overlap integrals:

$$P \propto \left| \langle \psi_{n,m}^{e} | \psi_{n',m'}^{h} \rangle \right|^2 .$$  (4.22)

It was shown that because of symmetry reasons transitions between equal quantum numbers dominate [63], which is depicted in Figure 4-8.
Denoting the electron energies with $E_0$, $E_1$, $E_2$, … and the hole energies with $H_0$, $H_1$, $H_2$, … one therefore finds peaks corresponding to the $E_0$-$H_0$ (ground state), $E_1$-$H_1$ (first excited state) etc. transitions in photoluminescence spectra.

As mentioned in chapter 2.3, spectra of single quantum dots are subject to homogeneous broadening. The lower limit of the peak width, $\Gamma_{\text{min}}$ is given by the radiative lifetime \([23]\):

$$\Gamma_{\text{min}} \approx \frac{\hbar}{\tau_{\text{rad}}}.$$  \hspace{1cm} (4.23)

A typical value for the radiative lifetime is $\tau_{\text{rad}} \approx 300$ ps and thus $\Gamma_{\text{min}} \approx 2.2 \text{ } \mu\text{eV}$. Measurements of these narrow linewidths, however, are extremely difficult as inhomogeneous broadening dominates in almost all practical situations (except for single QD experiments), giving photoluminescence peak widths of the order of a few to a few tens of meV.
5 Experimental methods

Femtosecond spectroscopy is a very powerful and versatile tool in investigating carrier dynamics in matter. Its usefulness is not limited to the field of semiconductors and indeed in 1999 the Nobel Prize in Chemistry was awarded to Ahmed Zewail “[…] for his studies of transition states of chemical reactions by femtosecond spectroscopy”.

Ultrafast spectroscopy techniques are of interest for a number of reasons: Unlike other measurement methods the samples do not have to be prepared in any special way, for example by etching or introducing electrical contacts. This allows the examination of materials in virgin form as well as ready-made devices. Furthermore, the experiments are non-destructive and by using ultrashort laser pulses provide the means to study very fast processes. Moreover, it is possible to introduce spatial imaging techniques in the setups, which allow the investigation of carrier transport dynamics. With the advent of the scanning near-field optical microscope (SNOM) the spatial resolution was even pushed beyond the diffraction limit [64].

When a light pulse is absorbed in semiconductors, electrons are excited over the bandgap from the valence into the conduction band. If one limits oneself to the study of incoherent effects, ultrafast spectroscopy experiments can be divided in two major groups: Pump-probe and photoluminescence spectroscopy.

**Pump-probe:** In degenerate (i.e. single color) pump-probe experiments the pulse is split in two parts. One part, usually the stronger one, is directed onto the sample to induce a change, which is then probed by the suitably delayed probe pulse. For a sufficiently thin sample the investigated change could for instance be the absorption.

When disregarding the temporal evolution of many-body effects, the change in absorption coefficient at photon energy $h\nu$ is determined by the photoexcited electron and hole distribution functions $f_e$ and $f_h$ as

$$\Delta \alpha(h\nu) = (1 - f_e - f_h) \cdot \alpha_0(h\nu)$$  \hspace{1cm} (5.1)

where $\alpha_0(h\nu)$ is the absorption coefficient of the unexcited semiconductor [43]. It is therefore possible to measure the change in absorption as a function of time delay between the pump and the probe to get an information about the temporal evolution of the dynamics of the sum $f_e + f_h$ in a so-called differential-transmittance spectroscopy (DTS) setup.

For thicker samples where DTS cannot be performed, it is possible to use differential-reflectance spectroscopy (DRS). By using Kramers-Kronig relations one can obtain information about the absorption of the material of interest [44]. The dynamics of $\Delta R$ (the change in reflectance), however, cannot easily be attributed to specific transitions in the semiconductor, making a correct interpretation of the obtained data difficult. It is furthermore difficult to achieve a good signal to noise ratio in the experiments since the changes of $\Delta R$ are usually small.
5 Experimental methods

**Time-resolved photoluminescence (TRPL):** For the simplest case and if the absorption coefficient does not change very much by photoexcitation the luminescence intensity at photon energy $h\nu$ is given by

$$L(h\nu) = \alpha_0(h\nu) \cdot f_e \cdot f_h$$

(5.2)

Thus TRPL allows insight in the development of the product $f_e \cdot f_h$ and is a simultaneous measurement of both $f_e$ and $f_h$.

The luminescence signal is detected by suitable techniques as for example streak cameras or upconversion used in this work. A detailed description of these TRPL techniques as well as a brief introduction to deep level transient spectroscopy (DLTS) follows below.

### 5.1 Streak camera

The experimental setup for time-resolved photoluminescence measurements employing a streak camera as detection instrument is relatively easy to align, has a high sensitivity to light with wavelength shorter than 1200 nm and allows one to obtain results rather quickly. It is therefore the measurement technique of choice for many applications where the requirements on temporal resolution are not extremely high.

Samples are excited with pulses from a Ti:sapphire laser. This self-modelocking laser is often used as the “working horse” in many experimental setups because it provides a wide tuning range (typically from around 700-1000 nm), high pulse repetition rate (several tens of MHz) and average powers exceeding 1.6 W.

Figure 5-1 shows the operating principle of the tube inside a streak camera. The light, which is to be measured, is projected onto the slit and is then focused by a lens on the photocathode of a streak tube. Here the photons are converted into a number of electrons, which is proportional to the intensity of the incident light. The electrons are then accelerated and conducted towards a micro-channel plate (MCP).

As the electrons pass the pair of sweep electrodes, a high saw-tooth voltage is applied, resulting in a high-speed sweep. Electrons created at different times (corresponding to different times of incident light) are therefore deflected in different angles in the perpendicular direction. The electrons are multiplied in the MCP and then directed on the phosphor screen. The brightness of the fluorescence image is proportional to the intensities of the corresponding incident light pulse. The readout section then transfers the signal via a CCD and a frame grabber board to a computer where the streak images can be analyzed.
In our experiments we combine the setup with a 0.25 m spectrometer, which is placed in front of the streak camera. In this way it is possible to convert the spatial (horizontal) axis to a wavelength axis (see Figure 5-2).

To control the timing of the streak sweep, a part of the laser beam is split off and produces the trigger signal to start the high voltage sweep via a photodiode and a delay unit.

Two main limitations are imposed on the detection system. First, its sensitivity is limited by the spectral sensitivity of the photocathode. The spectral characteristic of the photocathode in use is such that the response for light at a wavelength of 1300 nm is 1000 times lower than at 800 nm and it decreases even further for longer wavelengths. For all practical purposes we can therefore not detect any light with a wavelength exceeding 1300 nm. Furthermore one needs to be careful when measuring luminescence with photon energies close to the photon energies of the excitation pulses since scattered light from the laser can enter the spectrometer. A
simple bandpass filter placed in front of the spectrometer entrance slit then significantly improves the performance of the setup.

The second limitation of our system is caused by trigger jitter and results in a temporal resolution of \( \approx 3 \) ps. Moreover, streak cameras are sensitive to temporal and thermal drift. This results in additional broadening for longer integration times (more than a few minutes), which is of course required in the case of weak signals. Correcting for the drift and therefore achieving high temporal resolution even for long measurements can be realized for example by focusing a split off part of the laser beam into the streak camera [66]. Different time frames of streak camera acquisition are then corrected so as to keep the trace of this reference laser locked to a certain pixel position. Streak camera systems used in such a way feature excellent temporal resolutions even after exposure of some hours.

5.2 Upconversion

If the PL signal to be measured is either exhibiting ultrafast dynamics or the wavelength is too long, streak cameras cannot be used and other types of measurement techniques are needed.

One of the possible ways is the so-called upconversion. The basic idea is as follows: The output of an ultrafast laser is split into two beams. One of them is then directed onto the sample. The resulting luminescence is collected and focused on a nonlinear crystal together with the second beam, which is suitably delayed. The angle between the two beams and the angle of the nonlinear crystal are adjusted for phase matched sum-frequency generation at a given luminescence photon energy. In such a way light with a wavelength corresponding to the sum of the frequencies of reference laser and luminescence signal is created.

The laws for the conservation of energy (Eq. (5.3)) and momentum (Eq. (5.4)) describe the conditions for phasematching:

\[
h
\nu_{PL} + h \nu_{P} = h \nu_{S}
\]

\[
h \kappa_{PL} + h \kappa_{P} = h \kappa_{S}
\]

where the subscripts \( PL \), \( P \) and \( S \) denote photoluminescence, pump and sum-frequency signals, respectively. Figure 5-3 shows the schematic diagram.

![Figure 5-3: Sum-frequency radiation generated in a nonlinear crystal.](image)
The sum-frequency (or upconversion) signal is generated only during the time that the delayed laser pulse is present, as illustrated in Figure 5-4. The temporal resolution is then limited by the laser pulse width and the group velocity dispersion (GVD) in the nonlinear crystal. GVD causes a temporal spreading of a pulse because of the different frequency components that the pulse consists of traveling at different velocities.

It can be made small compared to the laser pulse width by choosing a sufficiently thin nonlinear crystal. The time evolution of the luminescence at a given photon energy can be obtained by scanning the relative delay between the two laser beams. The conditions for phasematching can only be obtained by suitably adjusting the angle \( \theta \), which in practice means positioning the crystal correctly.

![Figure 5-4: Schematic on how sum frequency generation acts as a gate](image)

The actual experimental setup used in investigations in this work is shown in Figure 5-5. It is based on a self-mode-locking Ti:sapphire laser with a wavelength tunable from 720-950 nm, a pulse duration of 100 fs and a repetition frequency of 96 MHz. To collect the light and focus it onto the nonlinear crystal two off-axis parabolic mirrors are used since lenses would add GVD and thus decrease the possible temporal resolution.

The beam that serves as gating laser pulse is delayed with a computer controlled delay stage, which allows movements of 0.1 \( \mu \)m resolution, corresponding to a resolution of 0.7 fs in the delay time. The upconverted signal from the 1 mm thick
LiIO₃ nonlinear crystal is dispersed by a 0.25 m monochromator and then detected with a photomultiplier (PM).

This setup allows for a temporal resolution of 130 fs, close to the duration of the laser pulse. A computer connected to the equipment carries out the controlling and signal collection.

Figure 5-5: Experimental arrangement for time-resolved photo luminescence measurements using the upconversion technique

For a complete description of the technique and the theoretical aspects of phasematching, see Ref. 43.

Unfortunately the conversion efficiency is very low (≈ 10⁻⁴) and thus limits the application of this technique to experiments emitting rather high intensity PL. Moreover, due to the experimental setup, only one wavelength can be recorded at a time while a streak camera records the entire spectrum. By replacing the monochromator/photomultiplier with a spectrometer and low-noise high-sensitivity CCD this limitation can be somewhat weakened [51]. Then the bandwidth of the experimental system is given by that of the nonlinear crystal (the upconversion efficiency for light that does not precisely fulfill the phasematching conditions (5.3) and (5.4) is significantly reduced). By either choosing sufficiently thin crystals - at the cost of a lower conversion efficiency - or by continuously rotating the crystal during acquisition, it is possible to measure broader spectra and even achieve an increased signal-to-noise ratio compared to the photomultiplier setup [51].
This limitation cannot be overcome by simply replacing the monochromator/photomultiplier combination with another detection system (for example a low-noise high-sensitivity CCD); at a given angle of the nonlinear crystal the phasematching conditions (5.3) and (5.4) can only be fulfilled for a very narrow luminescence bandwidth.

The upconversion efficiency for light that does not precisely fulfill the phasematching conditions is dramatically reduced and hence only a very narrow spectral range can be upconverted at a time.

5.3 Extracting carrier decay times from photoluminescence transients

In chapter 4.1.5 (equation (4.19)) it was shown how carrier lifetimes determine photoluminescence transients. This, however, is only true for the simple case with infinitely fast carrier generation and single exponential decay, which is only applicable if the recombination rates are independent of time.

One can find a completely different situation when carrier traps are present in the material. It was mentioned before that carrier traps act preferentially on one kind of carrier, i.e. they capture either electrons or holes very fast, while capture rates for the other carrier type are low. Let us consider for example the effects of an electron trap on the PL decay: Initially all traps are empty and electrons are removed from the conduction band efficiently. The PL decay - proportional to the product of both electron and hole densities - is therefore fast. On the other hand, the traps get filled and only after recombination with a hole can they capture another electron. At this point the slow capture of holes determines the shape of the PL decay (neglecting radiative recombination which is assumed to be slower than nonradiative recombination).

In reality carriers do not arrive infinitely fast at the energies that are monitored in PL experiments (typically corresponding to the fundamental transitions from the bottom of the conduction band for electrons and the top of the valence bands for holes). This can be understood from the fact that some carriers are inevitably excited to higher energies because Heisenberg’s uncertainty principle demands short light pulses to have certain energy distributions. The subsequent relaxation and therefore slowed down arrival of carriers results in a finite rise time of the PL signal. For QD structures it also accounts for carrier transport and capture. Analytic expressions for the transient PL intensity are then given by [52]

\[ I(t) \propto \frac{1}{\tau_1 - \tau_{\text{rise}}} \left[ \exp(-t/\tau_1) - \exp(-t/\tau_{\text{rise}}) \right] \] (5.5)

\[ I(t) \propto \left[ \exp(-t/\tau_1) - \exp(-t/\tau_{\text{rise}}) \right] + \text{const} \cdot \left[ \exp(-t/\tau_2) - \exp(-t/\tau_{\text{rise}}) \right] \] (5.6)

for single-exponential and double-exponential decay. Figure 5-6 shows examples for single and double exponential decay, respectively.
5.4 Dependence of luminescence intensity on excitation

Following Marcinkevičius et al., one can derive the dependence of the luminescence intensity on the excitation intensity \([67]\). The rate equations presented in chapter 4.1.5 yield under steady state conditions \((dn/dt = 0)\) and for \(n = p\)

\[
G = R = B \cdot n^2 + \frac{n}{\tau}.
\]  

(5.7)

The rate of carrier generation \(G\) is proportional to the excitation intensity \(I_{ex}\), while the photoluminescence intensity \(I_{PL}\) is proportional to \(n^2\). For a dominant radiative recombination (5.7) reduces to

\[
G \approx B \cdot n^2 \Rightarrow I_{ex} \propto I_{PL}.
\]  

(5.8)

The PL intensity thus increases linearly with excitation intensity. Similarly one finds for a dominating nonradiative recombination

\[
G \approx \frac{n}{\tau} \Rightarrow I_{ex} \propto \sqrt{I_{PL}} \Rightarrow I_{PL} \propto I_{ex}^\alpha.
\]  

(5.9)

Thus in the general case \(I_{PL} \propto I_{ex}^\alpha\) where \(\alpha\) is between 1 and 2. A rough estimation of significance of radiative and nonradiative recombination is therefore possible from plots \(I_{PL}\) vs. \(I_{ex}\).

5.5 Deep level transient spectroscopy

The most commonly used technique for studying defects in semiconductors is deep level transient spectroscopy (DLTS). It was first described in a paper by Lang \([68]\) and allows one to experimentally determine energy level, concentration and capture rates of defects. Furthermore, it is possible to perform depth profiling, thus giving information about the location and distribution of defects in the structure.
Figure 5-7 shows schematically the operating principle of DLTS, which is based on capacitance measurements on \( pn \)-junctions. There and in the following the capture of electrons, which are assumed to be the minority carrier type, is considered.

At a time prior to \( t = 0 \) all traps are empty. Applying a voltage pulse changes the initial depletion layer thickness \( w \) and hence the capacitance, which is inversely proportional to \( w \). Defects that are now outside the depletion region can trap electrons. After turning off the voltage, electrons will be gradually removed from the filled traps via thermal emission at a rate

\[
e_n(t) = \frac{1}{\tau} \approx \sigma_n \exp(-\Delta E/kT) .
\]  

Both the electron emission (or capture) cross section \( \sigma_n \) and the activation energy \( \Delta E \) (the energy difference between defect level and conduction band) are characteristic for the specific trap. The electron emission process can be monitored by measuring the capacitance as a function of time.

In DLTS the capacitance, which often decays exponentially because of the carrier emission from the traps, is measured at two times \( t_1 \) and \( t_2 \). From Figure 5-8 it is obvious that the difference of the signals reaches a maximum when \( \tau \) is of the order of \( t_2 - t_1 \). Since the thermal emission rate is strongly temperature dependent, a thermal...
scan while keeping \( t_1 \) and \( t_2 \) constant will result in a spectrum like the one shown on the right side of Figure 5-8. One can find the value of \( \tau \) that corresponds to the maximum of \( C(t_2) - C(t_1) \) from

\[
\tau = \frac{(t_1 - t_2)}{\ln(t_1/t_2)}.
\]  

(5.11)

By choosing different settings for \( t_1 \) and \( t_2 \) it is possible to obtain points in an Arrhenius plot \( \ln(e_n) \) vs. \( 1000/T \), from which one can then find the capture cross section and activation energy via (5.10). The defect concentration \( N_{\text{def}} \) can be calculated from the maximum of the DLTS signal \( S_{\text{max}} \) using the following expression:

\[
N_{\text{def}} = N_{\text{dop}} \frac{S_{\text{max}}}{F C_0}.
\]  

(5.12)

Here \( N_{\text{dop}} \) is the background doping concentration, \( C_0 \) the capacitance at \( t < 0 \) and \( F \) a correction factor, taking into account the fact that it is not possible to measure the capacitance at \( t = 0 \) but rather always at a finite delay time \( t_1 \).
Figure 5-8: Illustration of how DLTS spectra are obtained. The left-hand side shows the temporal evolution of the capacitance while the right-hand side shows the DLTS signal proportional to $C(t_2) - C(t_1)$ (after [68]).

From Figure 5-7 it is clear that it is possible to determine defect level concentration as a function of depth in the structure by varying the amplitude of the voltage pulse. DLTS is therefore a powerful tool in measuring various aspects of defects in semiconductors but it requires carefully prepared samples that are doped and have electrical contacts.
6 Numerical simulations

Carrier relaxation times are critical for the use of quantum dots in devices. For the quantum dots aligned along dislocation induced surface undulations (paper III) we found extremely fast PL decay corresponding to strong nonradiative recombination, even though transmission electron microscope (TEM) investigations did not show any dislocations close the dot layer. The presence of such a strong nonradiative recombination process could not be explained easily. Moreover, changing the buffer layer thickness did not alter the decay times in a way expected for carriers trapped solely to defects caused by dislocations (papers III & IV).

To develop a better understanding of the physics involved we decided to employ a numerical model to fit our experimental data.

6.1 Rate equation models applied to quantum dot systems: general considerations

In chapter 4.1.5 the concept of using rate equations for the description of carrier dynamics in semiconductors was introduced. While such rate equation models can readily be applied to bulk or quantum well structures, great care needs to be taken when using them to model QD systems. It has been shown that already for rather low excitation intensities higher excited states can get filled [23]. This is a direct result of the fact that the carrier exchange between the quantum dots at low temperatures is very slow. In the limit of a large number of dots the probability of finding $n$ carriers in a QD is governed by Poisson statistics.

In our experiments no light from a transition attributed to higher energy levels in the quantum dot could be detected, which means that the intraband relaxation time constant $\tau_r$ is much smaller than the radiative recombination lifetime $\tau_0$. Under these conditions (when $\tau_0/\tau_r > 1/3$) the rate equation model is still valid. Since, furthermore, no light originating from transitions in the wetting layer could be detected either, we concluded that the carriers were captured by the quantum dots very fast. In the simulations we therefore assumed an initial carrier concentration in the dots, with the exact value depending on the excitation intensity.

6.2 Rate equations, one type of carrier trap

The dynamics of excess electrons and holes (generated at a time $t \leq 0$ with densities $n_1$ and $p_1$ respectively) in a semiconductor where both radiative and nonradiative recombination is present can be modeled using the following set of coupled rate equations:

$$\frac{dn_1}{dt} = -B \cdot n_1 \cdot p_1 - c_{d,e} \cdot n_1 \cdot p_d$$  \hspace{1cm} (6.1)

$$\frac{dp_1}{dt} = -B \cdot n_1 \cdot p_1 - c_{d,h} \cdot p_1 \cdot (N_d - p_d)$$  \hspace{1cm} (6.2)
Equations (6.1) and (6.2) describe the decrease of electron \((n_1)\) and hole \((p_1)\) densities in the quantum dots due to radiative recombination (with a radiative recombination rate \(B\)) and nonradiative recombination. The latter is caused by carrier traps, which in the case at hand are assumed to preferentially capture holes. Their total concentration is given by \(N_d\), the concentration of trapped holes by \(p_d\) and the capture rates by \(c_{d,e}\) and \(c_{d,h}\) for electrons and holes respectively.

The choice of the trap character (electron or hole trap) is completely arbitrary since the only accessible quantity from our experiments is the PL intensity, which is proportional to the product of electron and hole concentrations. Thus the results obtained are independent of the choice of trap character. In a first assumption the traps are assumed to be related to dislocation induced defects.

Due to the many unknown parameters in the rate equation model, it is very tedious to fit the simulated curves to experimental data obtained for different excitation levels. Moreover it is not clear if there might not be more than one solution for the problem. We therefore decided to use a genetic algorithm in our simulations. This is a very powerful technique that can quite generally be applied for finding solutions to complex optimization problems [69]. It got its name from treating a “population” of “individuals” is treated where each individual represents a potential solution to the problem at hand. In an “evolutionary” process the best individuals are allowed to “procreate” and “mutate”. Individuals that do not describe the problem well are disregarded. After many steps in the process the solutions will converge to a certain value and it is then possible to extract the best values for the parameters in question.

Since random processes drive genetic algorithms and since furthermore the initial population consists of random individuals, a comparison of different simulations allows the evaluation if the found solution is a global or local optimum. In our case the values for trap concentration, capture rates etc. could be consistently reproduced between different runs. We thus conclude that the found solution is a global optimum.

The simulations, however, reveal that this simple model does not provide a suitable description of the recombination dynamics involved. While the decay at higher excitation intensities could be fitted somewhat satisfactory, the deviations from the experimentally obtained transients become very obvious for low excess carrier densities.

In particular, we discovered that under low excitation conditions the decay is fast during the first \(\approx\)100 ps and slows down afterwards, a feature typically found for saturation of traps. We therefore concluded that more than one type of carrier trap must be present in our structures.
6.3 Rate equations, two types of carrier traps

The failure to reproduce the experimental data with a simple model involving only one kind of carrier trap meant that we had to include a second type of trap in our rate equation system.

From the shape of the low intensity PL transient shortly after excitation we deduce that there is a quickly saturated recombination channel, which is nevertheless very efficient during the first few tens of picoseconds. Such a nonradiative recombination channel can be provided, for example, by traps close to QDs or even at their interfaces, for instance caused by point defects. For InAs/GaAs and InGaAs/GaAs systems it has been found that such defects indeed introduce deep levels [70, 71]. The capture rate will then be much higher than for the dislocation traps but only those QDs, which actually have a defect in the vicinity, are affected. Figure 6-1 illustrates the model in detail.

As a result we divide the total number of QDs in two parts: A certain percentage of the dots will only be affected by the presence of traps due to dislocations. These trap are numerous and therefore do not saturate but, since they are separated by a couple of nanometers from the QDs, carrier capture will be slow and inefficient. The carriers in the rest of the dots are affected by both the trapping to dislocations and to point defects.

The choice of the trap character is again arbitrary. We thus simply assume the point defects to act as electron traps and the dislocations to act as hole traps as before. Simulations assuming both kinds of traps capturing the same type of carrier were performed as well. The results, however, failed to agree with the experimental findings.

The refined model using the two independently working traps then includes additionally to Eqs. (6.1)-(6.3) the following equations:

![Figure 6-1: Illustration of different possible mechanisms for escape and subsequent nonradiative recombination for carriers inside quantum dots. Solid lines represent carrier trapping to point defects, dashed lines capture to dislocation related centers. With increasing barrier thickness the latter process becomes highly inefficient.](image-url)
In analogy to the previous equations, $n_2/p_2$ denote the electron/hole concentration inside the QDs, $n_t$ is the electron concentration at point defect related traps, $N_t$ the total concentration and $c_{t,e}/c_{t,h}$ the capture rates of electrons/holes to the point traps.

With the help of generic algorithms it is possible to find optimum solutions for our rather complex fitting problem. The simulation results for one trap and two traps models are shown in Figure 6-2 together with the experimental data. From the excellent fits of our refined model to the experimental data we conclude that two independently acting types of traps are necessary to describe the investigated system.
Figure 6-2: Experimental (points) and simulated (lines) results for the PL decay at different excitation intensities. Simulation results obtained considering two different kinds of traps are displayed as continuous lines, the results for considering only one kind of trap with dashed lines. The normalized spectra are shifted along the vertical axis for clarity. The PL transient of the control sample is included for reference.
Figure 6-3: 80K photoluminescence decay times for aligned QD samples with different barrier thicknesses. Since the decay time decreases with increasing barrier layer thickness, carrier capture by dislocation-induced defects cannot be the main cause for nonradiative processes.
7 Summary and conclusions

Photoluminescence was shown to be a powerful tool to study the ultrafast carrier dynamics in semiconductor quantum dot structures. It was explained why the understanding of the underlying physics is important to the optimization and design of future applications. Different experimental photoluminescence setups were shown and compared in terms of their strengths and limitations. Finally it was demonstrated how numerical simulations can help in understanding the carrier trapping and recombination in QDs.

Specific results of this thesis are:

1. The carrier dynamics and photoluminescence intensities of quantum well and quantum dot structures were compared after exposure to proton irradiation. The protons cause structural damage and therefore introduce deep levels, which can act as centers for nonradiative recombination. In QW structures electrons and holes are confined in one direction but free to move in a plane, where they can “find” defects to recombine nonradiatively. Carriers in QDs, on the other hand, are confined in three dimensions and can only be trapped by defects either inside the dots or very close to them. Experiments confirm the increased radiation hardness of QD structures since the carrier lifetimes are not strongly affected by the radiation induced structural defects.

For low to intermediate irradiation doses the photoluminescence intensity instead of decreasing actually increases, which is explained by an increased transfer rate into the QDs. Carriers can be captured by the deep levels caused by proton irradiation and tunnel from there to nearby dots, thus circumventing the potential barriers between QDs and wetting layer.

2. Misfit dislocations deliberately introduced in the substrate were used to achieve lateral ordering of InAs/GaAs QDs. The islands were found to nucleate along lines in trenches in the \{011\} directions, separated by larger “spare” areas without dots.

Photoluminescence spectra were found to be much narrower than for the reference sample grown for comparison, indicating an increased uniformity of the ordered QDs. On the other hand, time-resolved experiments revealed the decreased “quality” of these structures. The photoluminescence decay was found to be very fast, a sign of the presence of nonradiative recombination.

3. The strong contribution nonradiative recombination could be confirmed for spatially ordered InAs quantum dots by additional measurement of the photoluminescence intensity dependence on excitation power.
To develop an understanding for the possible origin and the physical processes involved, three sets of samples were produced. The different thicknesses of the GaAs layer on which the QDs are grown allow studies of the influence of dislocation related traps on nonradiative recombination. The sample with the thickest barrier layer exhibited the shortest decay time, not compatible with the explanation of trapping of carriers to dislocations. Instead point defects close to the dots or at the QD/barrier interface were suggested as to be probable candidates for the fast carrier trapping.

4. A numerical model was developed to verify the findings and simulate the observed PL transients, considering the influence of one or two independently working carrier traps. Point defects were identified as the main contributors to nonradiative recombination. A genetic algorithm was introduced to ensure that the solution (found by simultaneously fitting the data to experimental results obtained for various excitation intensities) was indeed the only one. Thus a qualitative, if not quantitative, explanation of the carrier dynamics could be given.

Suggestions for future work

A complete understanding of the carrier dynamics in semiconductor quantum dots is imperative for the design and development of applications. Hence experiments with different material compositions, dot densities, growth conditions, doping levels etc. need to be performed to obtain this goal. In many of these experiments time-resolved photoluminescence studies will probably be used as characterization method.

Possible extension of the work performed on the structures presented in this thesis is given in the following.

The observed strong nonradiative recombination makes spatial ordering of QDs using misfit dislocations unattractive for many applications. However, it would still be interesting to obtain knowledge about the recombination mechanisms involved by using other experimental techniques, for example deep level transient spectroscopy (DLTS). DLTS could provide information about the location of the carrier traps in the structures and also their characters.

For both the aligned dots and for the irradiated samples it would be of great interest to have the means for investigations with a higher spatial resolution. The possibility to study individual dots separately would give additional insight into which QDs are affected by defects. Currently great efforts are undertaken to include a scanning near-field optical microscope (SNOM) into our experimental setup. This should allow experiments with high temporal and spatial resolution (<200 nm).

Finally, the existing numerical model could be modified to include a random population model as suggested in Ref. 23 instead of rate equations. This would allow considering high-excitation scenarios with several carriers per dot.
8 References


S. Marcinkevičius, A. Gaarder, and R. Leon, “Rapid carrier relaxation by phonon emission in In0.6Ga0.4As/GaAs quantum dots”, Phys. Rev. B 64, 115307 (2001).


