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Magneto-optical properties of dilute nitride nanowires

Mattias Jansson

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Mattias Jansson

Linköping University
Department of Physics, Chemistry and Biology
SE-581 83 Linköping, Sweden

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Nanotrådar av utspädda nitrider för framtidens optoelektronik

Nanotrådar gjorda av utspädda nitrider är ett nytt och spännande material som kan bli användbart i framtidens optoelektronik. Sådana nanotrådar kan nämligen lysa och absorbera ljus mycket effektivt, och i många olika färger. De ger dessutom upphov till exotiska nanostrukturer, så kallade kvantprickar, som spontant bildas i nanotrådarna.

Ett av dagens hetaste forskningsområden är att hitta material som kan omvandla ljus till elektricitet, eller på motsvarande sätt elektricitet till ljus, på ett så effektivt sätt som möjligt. Detta är viktigt inte minst för att förbättra effektiviteten hos solceller, som många tror kommer att bli den dominerande energikällan i framtiden. Det är också viktigt för lysdioder, LED, som i allt större utsträckning används för att lysa upp våra hem och gator. En av utmaningarna som man då ställs inför är att ett givet material bara lyser i och absorberar vissa färger, alltså bara en del av regnbågens spektrum. Nyckeln är att hitta sätt som gör att man kan välja just vilka färger – vilken del av spektrumet – som materialet absorberar eller emitterar ljus i. För det ändamålet passar så kallade utspädda nitrider utmärkt. Utspädda nitrider är legeringar mellan material som galliumarsenid, GaAs, eller galliumarsenid-fosfid, GaAsP, med kväve, där kvävet endast står för några få procent av atomerna i materialet. Genom att välja just hur mycket kväve som finns i legeringen kan man nämligen på ett effektivt sätt ändra vilken färg på ljuset som de utspädda nitriderna lyser i och absorberar.

Genom att välja hur mycket kväve som finns i nanotrådarna kan man ändra vilken färg på ljuset som de utspädda nitriderna lyser i och absorberar

Utspädda nitrider har tillverkats i många år. Till exempel tillverkades några av de första röda lysdioderna av just utspädda nitrider. Däremot har forskare bara nyligen lyckats framställa så kallade nanotrådar gjorda av utspädda nitrider. Nanotrådar är, precis som vanliga trådar, långa och smala strukturer, men de är tusen gånger tunnare

än ett hårstrå. Det har visat sig att sådana nanotrådar är bättre än andra former av material på att absorbera ljus, och de kan också fånga och leda ljus på samma sätt som optiska fiber. Dessutom är det möjligt att tillverka nanotrådar ovanpå kisel, något som är mycket svårt med material i dess vanliga, platta form. Då tenderar materialet nämligen att ta skada, vilket inte händer när man använder nanotrådar. Eftersom kisel, som är grunden för nästan all dagens elektronik, inte absorberar eller emitterar ljus särskilt väl, så är det värdefullt att kunna kombinera kisel med material som kan det, till exempel nanotrådar gjorda av utspädda nitrider.

Elektroner fastnar i defekter

I en perfekt solcell ska allt solljus gå till att skapa en elektrisk ström, det vill säga frigöra elektroner så de kan röra sig fritt i materialet. Likaså vill man i en LED-lampa att all elektrisk ström ska bidra till att skapa ljus. Men på samma sätt som en rullande boll kan fastna i en grop, kan också de fria elektronerna fastna, och därför inte bidra till strömmen eller till ljuset. Sådana gropar, som ofta kallas defekter, kan finnas vid ytskikt mellan olika material, vid materialets yta, eller på platser där materialet inte är perfekt ordnat. För att kunna använda ett material i en solcell eller LED så är det alltså nödvändigt att förstå vilka typer av defekter som finns i materialet, och hur man kan undvika dem. Ju mer man kan minska antalet defekter, desto mer effektivt kommer ljus att kunna omvandlas till elektrisk ström, och vice versa.

I denna avhandling visar jag att kvävet i utspädda nitridnanotrådar har stora konsekvenser för vilka defekter som bildas, och hur de bildade defekterna påverkar materialets ljusegenskaper. I de utspädda nitridnanotrådarna skapas färre av vissa typer av defekter jämfört med liknande nanotrådar utan kväve. Till exempel har vi sett att antalet defekter vid nanotrådarnas yta är lägre än i jämförbara material utan kväve. Det borde göra nanotrådar tillverkade av utspädda nitrider bättre lämpade för användning i exempelvis solceller. Samtidigt ökar antalet av vissa andra typer av defekter. I perfekta material så är atomerna arrangerade fullständigt periodiskt, med jämna mellanrum mellan dem. I utspädda nitridnanotrådar, däremot, så har vi sett att det relativt ofta saknas atomer, specifikt gallium, i den periodiska ordningen. Denna typ av defekt gör de utspädda nitridnanotrådarna mindre effektiva i att omvandla mellan elektrisk ström och ljus. Genom att identifiera vilka defekter som har en effekt på omvandlingen mellan elektrisk ström och ljus blir det också möjligt att veta vilka defekter det är viktigt att försöka eliminera för att göra nanotrådar av utspädda nitrider till ett lovande material för framtida solceller och ljuskällor.

En annorlunda typ av kvantprickar

En intressant upptäckt jag beskriver i denna avhandling är att det uppstår så kallade kvantprickar i de utspädda nitridnanotrådarna. Kvantprickar är, precis som defekter, platser i nanotråden där elektroner fastnar och inte kan röra sig åt något håll. En skillnad mot defekter är att kvantprickarna lyser mycket effektivt, och gör så på ett speciellt sätt. Kvantprickarna lyser nämligen med väldigt specifika färger, eller våglängder på ljuset, där de specifika våglängderna fungerar lite som kvantprickarnas fingeravtryck. Fingeravtrycket kan ge oss mer information om hur kvantpricken är uppbyggd.

En elektron är vanligtvis bunden till en atom, men när den blir fri att röra sig i materialet så lämnar den en tom plats efter sig i atomen, ett så kallat hål. Det finns två olika typer av sådana hål: lätta och tunga hål. Hål kan också fastna i kvantprickarna, och bidrar då till att kvantprickarna lyser. Vanligtvis så är det de tunga hålen som bidrar allra mest till kvantprickarnas ljus, men i de utspädda nitridnanotrådarna så ser vi tecken på en blandning av både lätta och tunga hål i kvantprickarna. Det, i sin tur, betyder att hålen inte är lika starkt bundna till kvantpricken som elektronerna är. Så är inte vanligtvis fallet i andra kvantprickar, där både elektroner och hål är starkt bundna.

Sammanfattningsvis så har vi visat att nanotrådar tillverkade av utspädda nitrider, som är ett nytt och relativt outforskat material, är lovande för att användas i till exempel solceller eller lysdioder. Kvantprickar bildas spontant i nanotrådarna, vilket inte bara är positivt för ljuskällans effektivitet, utan även användbart i mer avancerade tillämpningsområden, som i till exempel kvantdatorer. Vi har dock visat att det uppstår ett antal olika defekter i nanotrådarna, som begränsar deras prestanda. För att utspädda nitridnanotrådar ska vara användbara i exempelvis solceller eller lysdioder så måste sådana defekter effektivt kunna undvikas.

Abstract

Nanostructured III-V semiconductors have emerged as one of the most promising material systems for future optoelectronic applications. While planar III-V compounds are already at the center of the ongoing lighting revolution, where older light sources are replaced by modern white light LEDs, new possibilities for optoelectronic applications are created by fabricating the materials in novel architectures, such as nanowires and quantum dots. Not only do such nanoscale structures allow the optically active III-V materials to be integrated with silicon microelectronics, but they also give rise to new fascinating properties inherent to the nanoscale.

One of the key parameters considered when selecting materials for applications in light-emitting and photovoltaic devices is the band gap energy. While alloying of conventional III-V materials provides a certain degree of band gap tunability, a significantly enhanced possibility of band gap engineering is offered by so-called dilute nitrides, where incorporation of a small percentage of nitrogen into III-V compounds causes a dramatic down-shift of the conduction band edge. In addition, nitrogen-induced splitting of the conduction band in dilute nitrides can be utilized in intermediate band solar cells, belonging to the next generation of photovoltaic devices.

For any material to be viable for optoelectronic applications, detailed knowledge of the electronic structure of the material, as well as a good understanding of carrier recombination processes is vital. For example, alloying may not only cause changes in the electronic structure, but can also induce disorder. Disorder-induced potential fluctuations may alter charge carrier and exciton dynamics, and may even induce quantum confinement. Moreover, various defects in the material may introduce detrimental non-radiative (NR) states in the band gap deteriorating the radiative efficiency. It is evident that, due to their different growth mechanisms, such properties could be markedly different in nanowires as compared to their planar counterparts. In this thesis, I aim to describe the electronic structure of dilute nitride nanowires, and its effects on the optical properties. Firstly, we investigate the electronic structure, and the structural and optical properties of novel GaNAsP nanowires, with a particular focus on the dominant recombination channels in the material. Secondly, we show how short-range fluctuations in the nitrogen content lead to the formation of quantum dots in dilute nitride nanowires, and investigate their electronic structure. Finally, we investigate the combined charge carrier and exciton dynamics of the quantum dots and effects of defects in their vicinity.

Before considering individual sources of NR recombination, it is instructive to investigate the overall effects of nitrogen incorporation on the structural properties of the nanowires. In Paper I, we show that nitrogen incorporation up to 0.16% in Ga(N)AsP nanowires does not affect the overall structural quality of the material, nor does nitrogen degrade the good compositional uniformity of the nanowires. It is evident from our studies, however, that nitrogen incorporation has pronounced and complex effects on the recombination processes. We first show that nitrogen incorporation in GaNAsP nanowires reduces the NR recombination at room temperature as compared to the nitrogen-free nanowires (Paper I). This is in stark contrast to dilute nitride epilayers, where nitrogen incorporation enhances NR recombination. The reason for this difference is that, in nanowires, the surface recombination, rather than recombination via point defects, is the dominant NR recombination mechanism. We suggest that the nitrogen-induced suppression of the NR surface recombination in the nanowires is due to nitridation of the nanowire surface.

Another NR recombination channel common in III-V nanowires is caused by the presence of structural defects, such as rotational twin planes and stacking faults. Interestingly, while nitrogen incorporation does not appear to affect the density of such structural defects, an increasing nitrogen incorporation reduces the NR recombination via the structural defects (Paper II). This is explained by competing trapping of excited carriers/excitons to the localized states characteristic to dilute nitrides, and at nitrogen-induced NR defects. This effect is, however, only present at cryogenic temperatures, while at room temperature the NR recombination via the structural defects is not the dominant recombination channel.

The importance of point defects in carrier recombination is highlighted in Paper III. Using the optically detected magnetic resonance technique, we show that gallium vacancies (V_{Ga}) that are formed within the nanowire volume act as efficient NR recombination centers, degrading optical efficiency of the Ga(N)AsP-based nanowires. Interestingly, while the defect formation is promoted by nitrogen incorporation, it is also readily present in ternary GaAsP nanowires. This contrasts with previous studies of planar structures, where V_{Ga} was not formed in the absence of nitrogen, unless subjected to irradiation by high-energy particles or heavy n-type doping. This, again, highlights how the defect formation is strikingly different in nanowires as compared to planar structures, likely due to the different growth processes.

Potential fluctuations in the conduction band, caused by non-uniformity of the nitrogen incorporation, are characteristic to dilute nitrides and are known to cause exciton/carrier localization. We find that in dilute nitride nanowires, such fluctuations at the short range cause three-dimensional quantum confinement of excitons, resulting in optically active quantum dots with spectrally ultranarrow and highly polarized emission lines (Paper IV). A careful investigation of such quantum dots reveals that their properties are strongly dependent on the host material (Papers V, VI). While the principal quantization axis of the quantum dots formed in the ternary GaNAs nanowires is preferably oriented along the nanowire axis (Paper V), it switches to the direction perpendicular to the nanowire axis in the quaternary GaNAsP nanowires (Paper VI). Another aspect illustrating the influence of the host material on the quan-

tum dot properties is the electronic character of the captured hole. In both alloys, we show coexistence of quantum dots where the captured holes are of either a pure heavy-hole character or a mixed light-hole and heavy-hole character. In the GaNAs quantum dots, the main cause of the light- and heavy-hole splitting is uniaxial tensile strain induced by a combination of lattice mismatch with the nanowire core and local alloy fluctuations (Paper V). In the GaNAsP quantum dots, however, we suggest that the main mechanism for the light- and heavy-hole splitting is local fluctuations in the P/As ratio (Paper VI).

Using time-correlated single-photon counting, we show that the quantum dots in these dilute nitride nanowires are single photon emitters (Paper VI), confirming the three-dimensional quantum confinement of the excitons. Finally, we demonstrate that carrier capture by some quantum dots is strongly affected by the presence of defects in their local surroundings, which alters the charge state of the quantum dot, promoting the formation of the negatively charged exciton at the expense of its neutral counterpart. (Paper VII) This underlines that the local surrounding of the quantum dots may greatly affect their properties, and illustrates a possible way to exploit defects for charge engineering of the quantum dots.

In summary, in this thesis work, we identify several important NR recombination processes in dilute nitride nanowires that can undermine the potential of these novel nanostructures for future optoelectronic applications. The gained knowledge could be useful for designing strategies to mitigate these harmful processes, thereby improving the efficiency of future light-emitting and photovoltaic devices based on these nanowires. Furthermore, we uncover a set of optically bright quantum dot single-photon emitters embedded in the dilute nitride nanowires, and reveal their unusual electronic structure with strikingly different confinement potentials between electrons and holes. Our findings open a new pathway for charge engineering of the quantum dots in nanowires, attractive for applications in e.g. quantum computation and optical switching.

Preface

This thesis summarizes the outcome of Mattias Jansson's doctoral studies, conducted between 2015-2020 at the Department of Physics, Chemistry and Biology at Linköping University. The thesis is divided into two parts: The first part contains an introduction to the research field and of the experimental techniques used in this work. The second part contains the main research results, presented in seven scientific papers.

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*Linköping, 2020
Mattias Jansson*

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List of Abbreviations

BAC	Band anticrossing	ODMR	Optically detected magnetic resonance
bcc	Body-centered cubic	PL	Photoluminescence
BE	Bound exciton	PLE	Photoluminescence excitation
BS	Beam splitter	QD	Quantum dot
CB	Conduction band	RPM	Random population model
CBE	Chemical beam epitaxy	SEM	Scanning electron microscope
CCD	Charge coupled device	SO	Split-off
CL	Cathodoluminescence	SOI	Spin-orbit interaction
cw	Continuous wave	SPE	Single photon emitter
CVD	Chemical vapor deposition	SRV	Surface recombination velocity
DAP	Donor acceptor pair	TA	Transverse acoustic
DOS	Density of states	TCSPC	Time-correlated single-photon counting
EHP	Electron hole pair	TEM	Transmission electron microscope
fcc	Face-centered cubic	TO	Transverse optical
FE	Free exciton	trPL	Time-resolved photoluminescence
FSS	Fine-structure splitting	VB	Valence band
FTB	Free-to-bound	VCA	Virtual crystal approximation
HBT	Hanbury Brown and Twiss	V_{Ga}	Gallium vacancy
HH	Heavy hole	VLS	Vapor-liquid-solid
HMA	Highly mismatched alloy	VS	Vapor-solid
IBSC	Intermediate band solar cell	WZ	Wurtzite
LA	Longitudinal acoustic	X	Single exciton
LE	Localized exciton	X-	Negatively charged exciton
LH	Light hole	X+	Positively charged exciton
LO	Longitudinal optical	XX	Biexciton
LS	Localized state	ZB	Zincblende
MBE	Molecular beam epitaxy	μ PL	Micro-photoluminescence
NR	Non-radiative		

1

An Introduction to Semiconductors

A semiconductor is a material with a higher electrical conductivity than an insulator, but lower than a conductor. Semiconductor materials are used in numerous applications. Perhaps most notably, they are at the heart of the microelectronics industry, where components such as transistors, diodes and complete integrated circuits are generally made from semiconductors. Other applications of semiconductor materials include light emitting diodes, photovoltaic devices and sensors. This chapter gives an introduction to semiconductor materials and some of their properties, with a particular focus on inorganic III-V semiconductor compounds.

1.1 Crystal structure

Crystalline materials, i.e. materials where the atomic positions repeat periodically in space, may be constructed with various crystal structures. Many of the material properties depend on the crystal structure and its symmetry. Here, I will describe two such crystal structures relevant for this thesis, namely the zincblende (ZB) and wurtzite (WZ) structures. They are both very common among inorganic compound semiconductors, where group III-V arsenides and phosphides and also various group II-VI compounds crystallize in the ZB crystal structure, while many wide band gap compounds, such as the group III-V nitrides, ZnO, and SiC, crystallize in the WZ crystal structure.

Both crystal structures have a diatomic base. While the Bravais lattice for ZB crystals is the face-centered cubic (fcc) resulting in a cubic structure, the WZ structure has the body-centered cubic (bcc) lattice and, consequently, a hexagonal structure. Figure 1.1 shows schematically the crystal structures of ZB and WZ crystals. The symmetry of the ZB structure belongs to the T_d point group, while the WZ structure has the symmetry

C_{6v} .

Figure 1.1: Schematic drawings of the crystal structures of ZB (a,c) and WZ (b,d) crystals. The small red and large blue spheres represent different atomic species. The red lines in (a) and (b) show the tetrahedral bonds. The lattice constants, a for the ZB structure, and a and c for the WZ structure, are shown, where c is the lattice constant in the $[0001]$ direction. The stacking order of the bilayers are shown in (c) for the ZB structure in the $[111]$ direction, and in (d) for the WZ structure in the $[0001]$ direction.

The two crystal structures may be differentiated by their stacking order in the $[111]$ (or $[0001]$ in the case of the WZ structure) direction, as shown in Fig. 1.1c and d for the ZB and WZ structures, respectively. While the WZ structure has a stacking period of two bilayers — ABAB — the ZB crystal structure has a period of three bilayers — ABCABC.

1.2 Electronic structure

In individual atoms, the various electron orbitals have discrete energies. In semiconductor crystals, however, countless atoms are bound together in close proximity, allowing the electrons to interact. The Pauli exclusion principle forces the electrons to take slightly different energies, whereby continuous bands of electron states are

formed, as is shown schematically for the outer shell states in Fig. 1.2a, for varying interatomic distances, a . As can be seen from the figure, at the equilibrium interatomic distance, a_0 , a gap of forbidden energies exists, called the *band gap*, between the *valence band* (VB) at a lower energy and the *conduction band* (CB) at a higher energy. The energy difference between the upper VB edge and lower CB edge is the band gap energy, E_g . Generally, for semiconductors at low temperatures, almost all VB states are occupied, while almost all CB states are, correspondingly, empty. Though this is true also for insulators, their band gap energies are larger. The band gap energy for semiconductors generally ranges between approximately 0.2 to 6 eV, though this is by no means an exact definition.

Figure 1.2: The band structure of a semiconductor. (a) shows the evolution from discrete energy levels of atoms with a large interatomic spacing, a , to continuous bands at smaller a . The interatomic spacing a_0 represents the lattice constant of the material, and the energy difference between the CB minimum and VB maximum at a_0 constitutes the band gap, E_g . The gray color represents the CB and VB, where the dashed red and dotted blue lines emphasize the s- and p-character of the band-edge states, respectively. (b) shows a schematic illustration of the energy dispersion of the bands. The solid and dotted lines in the CB represent a direct (solid) and indirect (dotted) band gap semiconductor. The symmetries at the Γ -point represent a ZB crystal structure.

While the electrons can no longer be described by individual orbital states, but rather by extended *Bloch* states, they retain some of their orbital character, as demonstrated by the colors in Fig. 1.2a, where dashed red and dotted blue lines represent states with s- and p-character, respectively. Figure 1.2b shows a schematic drawing of the electron dispersion in a semiconductor, i.e. the relation between the energy and the wave vector (k). The VB of a semiconductor with the ZB crystal structure consists of the heavy hole (HH) and light hole (LH) states, which are degenerate at $k = 0$, and the split-off (SO) band. The CB with minimum at $k = 0$ (the solid red line) corresponds

to a direct band gap semiconductor. A transition between the VB and CB in such a semiconductor can be achieved by an interaction with the electromagnetic field: by the absorption or emission of a photon with energy $\hbar\omega \geq E_g$. For indirect band gap semiconductors, such as GaP, the CB minimum is at $\mathbf{k} \neq 0$, as shown by the dotted line. In this case, a transition between the lowest CB and highest VB states cannot be achieved merely by the absorption or emission of a photon, since the photons have too low momentum to satisfy the momentum conservation requirement. Instead, an additional interaction with a phonon is required for such a transition to occur, which significantly reduces the transition rate.

Temperature dependence of the band gap energy

The band gap energy is an intrinsic property of the semiconductor material, though it varies with e.g. temperature and pressure. For example, the band gap energy of GaAs at ambient conditions is approximately 1.42 eV. For GaP, which is an indirect semiconductor, the indirect (at the X-point) and direct band gaps are 2.26 and 2.78 eV, respectively. The temperature dependence of the band gap energy is usually well described by the Varshni equation,

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta}, \quad (1.1)$$

where $E_g(0)$ is the band gap energy at 0 K, while α and β are material parameters. The Varshni parameters of GaAs and GaP are given in Table 1.1.

Table 1.1: Varshni parameters for GaAs and the indirect band gap of GaP at the X point. The parameters are taken from Ref. [1].

	α (meV/K)	β (K)
GaAs	0.5405	204
GaP	0.5771	372

The temperature dependence of the band gap energy of the direct transition in GaP is not well described by equation 1.1, but rather by

$$E_g[\text{eV}] = 2.886 + 0.1081[1 - \coth(164/T)]. \quad (1.2)$$

Description of the electronic states

The CB states primarily consist of the s-orbitals, where the orbital angular momentum quantum number, $l=0$. They can be described by two basis states, namely the spinors α_{CB} and β_{CB} , where the subscript denotes the CB electrons. These CB eigenstates are degenerate in the T_d symmetry of the ZB crystal structure, and transform as Γ_6 .

For the VB, on the other hand, the states consist primarily of p-type orbitals, where $l = 1$. Three eigenstates of the angular momentum operator, $\mathbf{l}$, exist: $|m_l\rangle = |-1\rangle$, $|0\rangle$, and $|1\rangle$, which when combined with the spinors comprise six basis states: $|-1\rangle \alpha_{VB}$,

$|{-1}\rangle \beta_{VB}$, $|0\rangle \alpha_{VB}$, $|0\rangle \beta_{VB}$, $|1\rangle \alpha_{VB}$ and $|1\rangle \beta_{VB}$. It is usually more convenient, however, to write the states in the combined angular momentum basis, $|j, m_z\rangle$, comprised of the total and z-projection angular momentum quantum numbers. This transformation is done by employing the Clebsch-Gordan coefficients, with $j_1 = 1/2$ and $j_2 = 1$ for the spin and orbital component, respectively, forming the basis states:

$$\begin{aligned} |1/2, -1/2\rangle &= (-|0\rangle \beta_{VB} + \sqrt{2}|{-1}\rangle \alpha_{VB})/\sqrt{3} \\ |1/2, 1/2\rangle &= (|0\rangle \alpha_{VB} - \sqrt{2}|1\rangle \beta_{VB})/\sqrt{3} \\ |3/2, -3/2\rangle &= |{-1}\rangle \beta_{VB} \\ |3/2, -1/2\rangle &= (\sqrt{2}|0\rangle \beta_{VB} + |{-1}\rangle \alpha_{VB})/\sqrt{3} \\ |3/2, 1/2\rangle &= (\sqrt{2}|0\rangle \alpha_{VB} + |1\rangle \beta_{VB})/\sqrt{3} \\ |3/2, 3/2\rangle &= |1\rangle \alpha_{VB} \end{aligned} \quad (1.3)$$

It may be shown[2] that in the T_d symmetry, such a combination of the spin and orbital angular momentum of the VB electrons leads to a Hamiltonian consisting of two components

$$H^{VB} = H_1^{VB} + H_{SOI}^{VB}. \quad (1.4)$$

Here, the first term on the right-hand side of (1.4) is proportional to the unitary matrix and does not cause a splitting between the eigenstates in (1.3). The second term in (1.4), however, splits the VB states into two- and four-fold degenerate levels, where the former contains the $j = 1/2$ states and transforms as Γ_7 , while the latter contains the $j = 3/2$ states and transforms as Γ_8 . This interaction is called the *spin-orbit interaction* (SOI). The magnitude of the SOI varies in different materials, it is a rather strong effect in the materials studied in this thesis. In GaAs, for example, the SOI-induced splitting is approximately 340 meV, where the $j = 3/2$ states reside at higher energy. Due to this large splitting, only the $j = 3/2$ VB states will be considered when discussing the electronic structure of the VB electrons in the following.

Since most of the VB states generally are filled, it is laborious to consider all electrons in the VB. It is instead more convenient to consider the states with *absent* electrons, which may be treated as quasi-particles, usually called *holes*. The holes have opposite charge, wave vector, spin and mass to those of the absent electron, which is easy to understand with the following reasoning: while for a completely filled VB, the net spin is zero, when one electron is removed from the VB, the net spin is reduced by the spin of that electron. The remaining hole must, therefore, have spin opposite to that of the absent electron. Similar reasoning may also be used for the other properties of the hole.

The *effective mass* concept

The behavior of the electrons and holes when subjected to a force is determined by their dispersion. For this reason, it is convenient to introduce the concept of the *effective mass* of electrons and holes, which is defined as

$$\frac{1}{m_{\text{eff}}} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_i \partial k_j}; \quad i, j = x, y, z. \quad (1.5)$$

The acceleration, $\mathbf{a}$, of an electron or a hole with the effective mass, m_{eff} , subjected to a force, $\mathbf{F}$ is then given in the well-known form

$$\mathbf{a} = \frac{1}{m_{\text{eff}}} \mathbf{F}. \quad (1.6)$$

Conveniently, the dispersion of many semiconductors near the VB maximum and CB minimum is quadratic, which through (1.5) leads to a constant effective mass at these points. For semiconductors with anisotropic dispersion, m_{eff} is, however, different in different directions. It should also be noted that the effective mass of electrons and holes are both positive, but are generally not equal, due to the different slopes of the dispersion curves. In the following, the effective mass of the electrons and holes are denoted as m_e and m_h , respectively.

The electron VB states of (1.3), may be rewritten as hole states, $|\phi^h\rangle$ by

$$\begin{aligned} |\phi_1^h\rangle &= -|3/2, -3/2\rangle = -|-1\rangle \beta_h \\ |\phi_2^h\rangle &= |3/2, -1/2\rangle = (\sqrt{2}|0\rangle \beta_h + |-1\rangle \alpha_h)/\sqrt{3} \\ |\phi_3^h\rangle &= -|3/2, 1/2\rangle = -(\sqrt{2}|0\rangle \alpha_h + |1\rangle \beta_h)/\sqrt{3} \\ |\phi_4^h\rangle &= |3/2, 3/2\rangle = |1\rangle \alpha_h, \end{aligned} \quad (1.7)$$

Here, the SO states have been excluded.

1.3 Engineering of the electronic structure

In applications of semiconductors in e.g. optoelectronics, the band gap energy is of vital importance, as it determines the minimum energy of absorbed or emitted photons. One of the key advantages of semiconductors is the tunability of the band gap energy possible through alloying. In a ternary alloy, such as $\text{GaAs}_{1-x}\text{P}_x$, where the relative P (As) content of the group V sublattice is given by x ($1-x$), the band gap energy may take intermediate values between the binary values of GaAs and GaP. Such alloys can be described within the *virtual crystal approximation* (VCA), where the band gap energy is given by *Vegard's rule*. For an alloy $\text{AB}_{1-x}\text{C}_x$, Vegard's rule gives the band gap energy of the alloy:

$$E_g^{ABC}(x) = (1-x)E_g^{AB} + xE_g^{AC} - bx(1-x), \quad (1.8)$$

where b is the so-called *bowing parameter*, which for e.g. GaAsP is $b_{\text{GaAsP}} = 0.19$ eV.[1] The band gap energy of $\text{GaAs}_{1-x}\text{P}_x$ at 4 K, calculated using equation (1.8), is shown in Fig. 1.3 for the direct transition at the Γ -point (the red dashed line) and the indirect transition between the Γ_{VB} maximum and X_{CB} minimum (the blue solid line), respectively. The change from a direct to an indirect band gap semiconductor is marked by the arrow, and occurs approximately at $x=0.45$.

Besides alloying, the electronic structure of semiconductor devices may be engineered by fabricating *heterostructures*, which are structures with regions comprised of different materials, generally with different band gaps. The junction of two such different materials is called a heterojunction, and is generally categorized according to the

Figure 1.3: The band gap energy of $\text{GaAs}_{1-x}\text{P}_x$ as a function of x , calculated using equation (1.8) at 4 K. The red dashed (blue solid) line represents the direct (indirect) transition, and the arrow indicates the transition from a direct to an indirect semiconductor.

alignment of the CB and VB edges of the forming materials. Figure 1.4 shows simplified schematic diagrams of three types of heterojunction band alignments, commonly referred to as types I, II and III. In a heterojunction with the type I band alignment, the VB (CB) edge of material A is below (above) that in material B. In the case of a type II band alignment, the band gaps are staggered, where both the VB and CB edges of material A are below those of material B. Finally, in a type III band alignment the band gap is broken, as the CB edge of material A is below the VB edge of material B. The band diagram may be constructed using the *Anderson's rule*, which says that

Figure 1.4: Simplified energy diagrams of the three types of heterojunctions, type I, II and III. The two different materials are labeled A and B, with band gap energies E_g^A and E_g^B , respectively.

the vacuum levels of the two materials align across the junction. Junctions between regions of the same material but with different crystal structure may also exhibit the different band alignments of Fig. 1.4. Such a junction between GaAs with the WZ and ZB structures, for example, exhibits a type II band alignment. [3]

1.4 Excitons

Since electrons and holes are oppositely charged, they are attracted to each other through the Coulomb potential, V , as

$$V = \frac{-e^2}{4\pi\epsilon|\mathbf{r}_e - \mathbf{r}_h|}, \quad (1.9)$$

where ϵ is the permittivity of the material, e is the elementary charge, and $|\mathbf{r}_e - \mathbf{r}_h|$ is the separation between the charges. Two such interacting electrons and holes forms a quasi-particle called an *exciton*. In the effective mass approximation, the Coulomb potential in (1.9) leads to binding energies of the exciton, E_B , which follow a Rydberg series

$$E_B = -\text{Ry}^* \frac{1}{n_B^2}, \quad (1.10)$$

where $n_B = 1, 2, \dots$ is the quantum number, and Ry^* is the exciton Rydberg energy, given (in eV) by

$$\text{Ry}^* = 13.6 \frac{\mu}{m_0} \frac{1}{\epsilon_r^2}. \quad (1.11)$$

Here, ϵ_r is the relative permittivity, m_0 is the electron mass and μ is the reduced exciton mass,

$$\mu = \frac{m_e m_h}{m_e + m_h}. \quad (1.12)$$

The Coulomb potential also determines the Bohr radius of the exciton,

$$a_B^{\text{ex}} = a_B^H \epsilon \frac{m_0}{\mu} n_B^2, \quad (1.13)$$

where a_B^H is the Bohr radius of a hydrogen atom. The exciton Bohr radius is a measure of the spatial extent of the exciton. If the exciton Bohr radius extends over several lattice constants, the exciton is referred to as a Wannier-Mott exciton. If the extent of the exciton is smaller than the lattice constant, however, it is called a Frenkel exciton. In the latter case, the effective mass approximation is not valid. In the following, we will only consider Wannier-Mott excitons.

The exciton states are formed from the following basis states:

$$\begin{aligned} |\Psi_1\rangle &= |\phi_1^h\rangle \alpha_e & |\Psi_5\rangle &= |\phi_1^h\rangle \beta_e \\ |\Psi_2\rangle &= |\phi_2^h\rangle \alpha_e & |\Psi_6\rangle &= |\phi_2^h\rangle \beta_e \\ |\Psi_3\rangle &= |\phi_3^h\rangle \alpha_e & |\Psi_7\rangle &= |\phi_3^h\rangle \beta_e \\ |\Psi_4\rangle &= |\phi_4^h\rangle \alpha_e & |\Psi_8\rangle &= |\phi_4^h\rangle \beta_e, \end{aligned} \quad (1.14)$$

where the subscript, e , refers to the CB electrons while h refers to the holes. The wavefunction of the excitons consists of the extended (Bloch-) states of the CB and VB, in combination with an *envelope* function, which describes how the electron and hole are spatially correlated. The CB and VB transform as Γ_6 and Γ_8 , respectively,

while the envelope function transforms as Γ_1 . Therefore, the exciton states transform as

$$\Gamma_1 \otimes \Gamma_6 \otimes \Gamma_8 = \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5. \quad (1.15)$$

The full exciton Hamiltonian in T_d symmetry can be written with three components,

$$H^{\text{ex}} = H_1^{\text{ex}} + H_{\text{SOI}}^{\text{ex}} + H_{\text{exchange}}^{\text{ex}}, \quad (1.16)$$

where the first term on the right-hand side is a unitary term, the second term describes the SOI of the VB states, as discussed previously, and the last term arises due to the interaction between the electrons and holes, and is called the *exchange interaction*. The result of the exchange interaction on the exciton states of (1.14) is to split the states of different symmetry, where the eight exciton states are split into two levels of Γ_5 and $\Gamma_3 \oplus \Gamma_4$, respectively. The eigenstates of (1.14) may be adapted to those symmetries by using the $|J, M\rangle$ basis, where J and M denote the total and z-component angular momentum quantum numbers of the exciton. This basis transformation may be obtained similarly to section 1.2 by using the Clebsch-Gordan coefficients. This results in the following eigenstates:

$$\begin{aligned} |1, 1\rangle &= (|\Psi_3\rangle + \sqrt{3}|\Psi_8\rangle)/2 \\ |1, 0\rangle &= -(|\Psi_2\rangle + |\Psi_7\rangle)/\sqrt{2} \\ |1, -1\rangle &= (|\Psi_6\rangle + \sqrt{3}|\Psi_1\rangle)/2 \\ |2, 2\rangle &= |\Psi_4\rangle \\ |2, 1\rangle &= (|\Psi_8\rangle - \sqrt{3}|\Psi_3\rangle)/2 \\ |2, 0\rangle &= (|\Psi_2\rangle - |\Psi_7\rangle)/\sqrt{2} \\ |2, -1\rangle &= (\sqrt{3}|\Psi_6\rangle - |\Psi_1\rangle)/2 \\ |2, -2\rangle &= -|\Psi_5\rangle. \end{aligned} \quad (1.17)$$

Here, the states with $J = 1$ transform as Γ_5 , while the $J = 2$ states transform as $\Gamma_3 \oplus \Gamma_4$.

Interaction with light

The $|J, M\rangle$ basis of (1.17) conveniently also divides the excitons into the dark ($J = 2$) and bright ($J = 1$) categories, where only the latter has a finite electric dipole moment and may therefore make a *radiative* transition, i.e. through the absorption or emission of a photon. The recombination probability of an exciton in a given state is governed by the oscillator strength of the transition, f , which in turn is proportional to the *dipole matrix element*, M^D , squared. For a transition between the initial $|i\rangle$ and final $|f\rangle$ state

$$f_{i,f} \propto |M_{i,f}^D|^2 = |\langle f | \mathbf{Q} | i \rangle|^2, \quad (1.18)$$

where $\mathbf{Q}$ is the electric dipole operator. Therefore, the *relative* recombination probabilities of excitons in the various states are given by $|M_{i,f}^D|^2$, with the empty state of no particles as the final state. Conveniently, the matrix elements also provide information

about the polarization of the emitted photon. By writing the orbital part of the hole angular momentum in its cartesian form

$$\begin{aligned} |-1\rangle &= (x - iy)/\sqrt{2} \\ |0\rangle &= z \\ |1\rangle &= -(x + iy)/\sqrt{2}, \end{aligned} \quad (1.19)$$

and recalling that the spin is conserved during the transition, the dipole matrix elements can be calculated as

$$\begin{aligned} \langle 1, -1 | \mathbf{Q} | 0 \rangle &= -\sqrt{2}(x + iy)M_0 \\ \langle 1, 0 | \mathbf{Q} | 0 \rangle &= -2zM_0 \\ \langle 1, 1 | \mathbf{Q} | 0 \rangle &= \sqrt{2}(x - iy)M_0. \end{aligned} \quad (1.20)$$

Here, (x, y, z) indicate the axes of linear polarization, and M_0 is a constant. While the $|1, 0\rangle$ exciton recombination yields linearly polarized light, recombination of $|1, -1\rangle$ and $|1, 1\rangle$ excitons results in circular polarization.

1.5 Crystal vibrations and phonons

We have seen that the excitons represent excitations of the semiconductor. The semiconductor may also be excited through vibrations of the atoms in the crystal. A simple but instructive way to model vibrations in the crystal is to consider the motion in a linear array of atoms subjected to harmonic potentials, which may be imagined as atoms connected through mechanical springs. The solution to such equations of motion, if the masses and spring constants are all identical, yields the dispersion of the angular frequency, ω :

$$\omega^2(k) = \frac{4C}{M} \sin^2\left(\frac{ka}{2}\right), \quad (1.21)$$

where C and M are the spring constant and mass, respectively, while a is the inter-atomic distance. Equation (1.21) corresponds to the lower, *acoustic*, dispersion branch in Fig. 1.5. Modelling a linear chain with two different atomic masses (M_1, M_2) or spring constants (C_1, C_2), the dispersion becomes

$$\omega^2(k) = \frac{2C_\times}{\gamma M_\times} \left[1 \pm \sqrt{1 - \gamma^2 \frac{1 - \cos(ka)}{2}} \right], \quad (1.22)$$

where $\gamma = (C_\times M_\times)/(C_+ M_+)$, $C_\times = \sqrt{C_1 C_2}$, $C_+ = (C_1 + C_2)/2$, $M_\times = \sqrt{M_1 M_2}$ and $M_+ = (M_1 + M_2)/2$. When the brackets in (1.22) contain a subtraction, the acoustic branch is obtained, while an addition gives the *optical* branch, which is the upper branch in Fig. 1.5. While the acoustic branch is zero at the Γ -point, the optical branch is not. This means that the optical branch may interact more strongly with light, which carries a very small momentum. For the linear chain, each branch contains three states, two transverse and one longitudinal state, where the names refer to the direction of the atomic oscillations relative to the motion of the wave.

Figure 1.5: An example of the dispersion of lattice vibrations in a linear diatomic chain, calculated using (1.22).

The atoms-and-springs model described above may be generalized to three dimensions. Though solving the equations of motion becomes more complicated, the resulting phonon dispersion is similarly divided into transverse and longitudinal modes of acoustic (TA, LA) and optical (TO, LO) branches. For a unit cell with p atoms, there are 3 acoustic and $3(p - 1)$ optical modes. The LO and TO modes are degenerate in materials with the diamond crystal structure, such as Si, but split in materials with e.g. the ZB crystal structure. For materials with the WZ crystal structure, due to the larger unit cell, the number of modes is doubled compared to the ZB case. This can be illustrated through the zone folding approximation, which is shown schematically in Fig. 1.6. The dispersion curves of the ZB material (the black solid curves) are folded at the mid-point between the Γ - and L - points, forming the additional modes (the red dotted curves) for the WZ structure.

In analog to how quantization of the electromagnetic field leads to the concept of the photon, lattice vibrations may also be quantized. A quantum of lattice vibrations is called a phonon, which takes the energies

$$E_{\text{phonon}} = \left(n + \frac{1}{2}\right) \hbar \omega_k \quad (1.23)$$

for the mode ω_k , where n is the quantum number.

Alloys of the form $A(B_{1-x}C_x)$ may, with regards to phonons, show one- or two-mode behavior, which is shown schematically in Fig 1.7a and b, respectively. For alloys with one-mode behavior (Fig. 1.7a), the LO and TO modes shift continuously with changing composition between the values for the binary compounds. For alloys with the two-mode behavior, two sets of branches exist, which are usually said to be AB- or AC-like, where AB and AC are the binary compounds. The GaAsSb alloy is an example of a one-mode alloy, while GaAsP is a two-mode alloy.

Figure 1.6: An illustration of the zone folding scheme which may be used to approximate the phonon dispersion in a WZ crystal, using the phonon dispersion of the ZB structure.

Interaction with light

Interaction between phonons and light can occur in several different ways. Perhaps the most straight-forward interaction is the absorption of a photon to create a phonon. For such a process to occur, the energy and (quasi) momentum need to be conserved,

$$\begin{aligned}\hbar\omega_{\text{photon}} &= \hbar\omega_{\text{phonon}}, \\ k_{\text{photon}} &= q_{\text{phonon}},\end{aligned}\tag{1.24}$$

where k and q are the photon momentum and phonon crystal momentum, respectively. Consequently, only phonon modes near the Γ -point may contribute to such transitions. Since the optical phonon branches generally have energies corresponding to that of an IR photon, this process is usually referred to as IR absorption.

Lattice vibrations may also induce scattering of photons in the material. Such scattering may be divided into elastic (Rayleigh) and inelastic (Raman) scattering, where in the latter case, the incident and scattered photons do not have the same energy. Focusing now on the Raman scattering, the energy and momentum conservation may be written as:

$$\begin{aligned}\hbar\omega_{\text{photon},i} &= \hbar\omega_{\text{photon},s} + \hbar\omega_{\text{phonon}}, \\ k_{\text{photon},i} &= k_{\text{photon},s} + q_{\text{phonon}},\end{aligned}\tag{1.25}$$

where i and s refer to the incident and scattered photons. It should be noted that the scattered photon may have either a lower or a higher energy compared to the incident photon, which occurs either through a generation or annihilation of a phonon during the scattering event. These shifts in energy, which are called Stokes and anti-Stokes

Figure 1.7: The dependency of the LO and TO frequencies at the Γ -point on the composition, x , in the alloy $A(B_{1-x}C_x)$. (a) and (b) show the one- and two-mode behavior, respectively.

shift, respectively, may be used to measure the energies of the different optical phonon modes in a material.

Besides the conservation equations, (1.25), certain Raman scattering selection rules arise from the dependence of the Raman intensity, I , on the Raman tensor, R :

$$I \propto |\hat{e}_i R \hat{e}_s|^2, \quad (1.26)$$

where $\hat{e}_{i,s}$ are the polarization directions of the incident and scattered light. The form of the Raman tensor is governed by the symmetry of the crystal, and the Raman selection rules are thus specific to the crystal structure. The selection rules for Raman scattering and IR absorption are summarized in table 1.2 for the WZ and ZB crystal structures, where the *configuration*, given in standard Raman scattering notation $a(b,c)d$, denotes the direction of the incident (a), and scattered (d) light, and their respective polarization directions (b and c). In particular, two additional Raman-active modes are expected in WZ materials.

Table 1.2: Selection rules for the various modes in ZB and WZ crystals. R and IR indicates that the mode is Raman- and IR-active, respectively. The configuration $a(b, c)d$ denotes the direction of incident (a) and scattered (d) light, and their respective polarization directions (b and c), respectively. The table and the mode labels are adapted from [4].

Mode	ZB	WZ	Configuration
A_1 (LO)	R, IR	R, IR	$z(y, y)\bar{z}$
B_1^H		Silent	
E_2^H		R	$x(y, y)\bar{x}, x(y, y)\bar{z}, z(y, x)\bar{z}, z(y, y)\bar{z}$
E_1^H (TO)	R, IR	R, IR	$x(z, y)\bar{x}, x(y, z)y$
B_1^L		Silent	
E_2^L		R	$x(y, y)\bar{x}, x(y, y)\bar{z}, z(y, x)\bar{z}, z(y, y)\bar{z}$

1.6 Recombination processes

As described earlier, the recombination of an exciton or of an uncorrelated electron-hole pair (EHP) may result in the emission of a photon through radiative recombination. Alternatively, NR recombination, where recombination occurs through phonon generation rather than photon emission, is also possible, and is usually considered a detrimental effect in optoelectronic applications, as it effectively reduces the light emission efficiency.

Radiative recombination

A number of different radiative recombination processes exist. Some of the most common processes are shown schematically in Fig. 1.8.

The EHP-recombination is a recombination between a free electron and a free hole, which generally results in the emission of a photon with the energy corresponding to the band gap energy of the material. The EHP recombination may also involve a phonon, in a so-called phonon assisted recombination process. In this case the energy of the emitted photon is changed by the energy of the involved phonon. This type of recombination process is prominent in indirect band gap semiconductors, where the phonon supplies the momentum required for the indirect transition to occur.

The electron and hole in the CB and VB may, as described previously, form an exciton. When the exciton exists in the band continuum of states, it is said to be a free exciton (FE), and the photon resulting from the FE recombination is lower than the band gap energy by the binding energy of the exciton.

Electrons and holes may be bound to defects or impurities which introduce energy levels within the band gap of the material. A radiative recombination of such a bound electron or hole with a corresponding free charge carrier is called free-to-bound (FTB), or sometimes bound-to-free, recombination. Excitons, too, may be bound to a defect or impurity, which may result in bound exciton (BE) recombination.

Figure 1.8: Schematic illustrations of various radiative recombination processes in semiconductors. The electrons (red) and holes (blue) may either be free carriers in the CB and VB, respectively, correlated through the Coulomb interaction forming a free exciton, or bound to a defect or impurity, with energy levels in the band gap. The dotted ovals indicate the excitons. From left to right, the processes are electron-hole-pair (EHP), free exciton (FE), free-to-bound (FTB), bound exciton (BE) and donor-acceptor-pair (DAP) recombination.

Finally, when both an electron and a hole are bound to adjacent defects (a donor and an acceptor, respectively), the resulting recombination is referred to as donor-acceptor-pair (DAP) recombination. Clearly, when one or both charge carriers involved in the recombination process are bound to a defect or an impurity, the energy of the resulting photon is lowered by the binding energy of the defect or defects. In the case of the DAP recombination, the resulting Coulomb interaction between the charged defects or impurities must also be taken into account.

Non-radiative recombination

Several different NR processes are common in semiconductors. NR recombination may occur at a defect with an energy level within the band gap of the material.[5, 6] Such a recombination process occurs in two steps. In the first step, one charge carrier is captured at the NR center, and in the second step the captured carrier recombines with one of the opposite charge. The energy is transferred to the crystal in the form of phonons. The capture cross section of such NR centers can be different for electrons and holes, meaning that the center may capture one type of charge preferentially, being either an electron- or a hole-attractive center. Another NR recombination process is the Auger recombination. Auger recombination occurs when the recombination energy of a recombination process is transferred to another charge carrier rather than to the lattice.

At the surface of the material the crystal symmetry is broken, resulting in the formation of so-called surface states. Surface recombination, as the name implies, is NR recombination through such surface states, and is often a very pronounced effect in semiconductors. Its effect can, however, be reduced by *passivation* of the surface, through e.g. overgrowth of a large band gap material. In GaAs, for example, over-

growth of AlGaAs on the surface has been shown to significantly reduce the surface recombination.[7] This recombination channel is of special importance in nanostructures, due to the large surface-to-volume ratio.

2

Dilute Nitride Semiconductors

In the dilute nitride material system, a small amount of nitrogen is introduced into the isovalent group-V sublattice of a III-V material, forming a $\text{III-V}_{1-x}\text{-N}_x$ alloy, where x generally is in the order of a few percent or less. Such dilute nitride alloys belong to a wider group of materials usually referred to as *highly-mismatched alloys (HMA)*, in which a minority constituent with a significantly different electronegativity or size is introduced in a conventional III-V or II-VI material.[8, 9, 10, 11] In dilute nitrides, nitrogen has a significantly lower electronegativity and covalent bond length compared to other group-V elements — as shown in figure 2.1 — which leads to several remarkable properties of the alloy. Firstly, the electronic structure of the material is radically altered, through a drastic down shift of the CB edge,[12] reducing the band gap through the so-called *giant band gap bowing effect*. In fact, introducing only 1% of nitrogen in $\text{GaN}_x\text{As}_{1-x}$ reduces the band gap energy by more than 100 meV. Moreover, nitrogen incorporation in GaP leads to a transition from an indirect band gap in GaP to a quasi-direct one in GaNP and, therefore, to a dramatic increase in the luminescence intensity.[13] Incorporation of nitrogen also causes an increase of the electron effective mass[14], and a decrease in the pressure and temperature dependence of the band gap energy.[15, 16] Finally, nitrogen incorporation induces a splitting of the CB into two separate sub-bands.[17]

The highly tunable band gap is of great benefit for possible optoelectronic applications. The band gap of GaNP may, for example, be tuned to reach the amber spectral range, which otherwise has been technologically challenging. In fact, some of the early amber LEDs were fabricated using GaNP as an active material.[20] Similarly, the band gap energy of InGaNs may be tuned to the fiber optics communication windows of 1.3 and 1.55 μm . [21, 22]

Another suggested application of dilute nitrides is in intermediate band solar cells

Figure 2.1: The electronegativity (red squares) and covalent bond radius (blue triangles) of the four first group-V elements. The data is taken from [18, 19].

(IBSC), by utilizing the splitting of the CB.[23, 24] In IBSCs, a larger part of the solar spectrum may be used for charge carrier generation, through additional absorption channels in a three-level system.[25] In fact, the quaternary $\text{GaN}_x\text{As}_y\text{P}_{1-x-y}$ alloy with $x \approx 1\text{-}2\%$ and $50\% < y < 70\%$ fits well to the theoretically calculated optimum material for IBSC.[24]

2.1 N-induced modifications of the electronic structure

When nitrogen is introduced in a III-V compound, such as GaAs and GaP, the host states of the CB are strongly perturbed by the nitrogen incorporation, due to the large mismatch in electronegativity and size between the nitrogen and the host atoms. In the ultra-dilute range, when the nitrogen concentration is much smaller than one percent, highly localized N-related impurity states are formed, with an energy level close to the CB edge. In Ga(N)As, the N-impurity energy level resides above the CB edge,[26] while in Ga(N)P it lies below.[27] Besides the single nitrogen impurity states, various cluster states with different numbers and configurations of nitrogen atoms are also formed, with correspondingly different energy levels. With an increasing nitrogen content, a mixing and an anticrossing interaction between the CB states and the localized N-related states result in a giant band gap bowing characteristic of dilute nitrides[28]. Besides the down-shift of the CB edge, the anticrossing leads to a splitting of the CB into two sub-bands, where the upper sub-band blueshifts with increasing nitrogen content.[17] The VB states, meanwhile, are only weakly perturbed.

A phenomenological description of the shifts of the two CB sub-bands with increas-

ing nitrogen incorporation is provided by the *band anticrossing model* (BAC).[15] In the BAC model, the change in the electronic structure upon nitrogen incorporation is modeled by an anticrossing interaction between the host CB states and a localized nitrogen impurity state. The evolution of the CB dispersion with changing nitrogen concentration (x) can easily be obtained from the BAC model, where the dispersions of the two conduction sub-bands, E_+ and E_- , are given by

$$E_{\pm}(\mathbf{k}) = \frac{1}{2} \left[(E_{\mathbf{k}}^c + E^N) \pm \sqrt{(E_{\mathbf{k}}^c - E^N)^2 + 4V^2x} \right]. \quad (2.1)$$

Here E^N is the energy of the localized N-level, the V parameter describes the interaction between the nitrogen and host CB states, and $E_{\mathbf{k}}^c$ is the host CB energy.[15] Neither E^N nor V are thought to be temperature dependent, so equation (2.1) also gives the temperature dependence of the band gap energies, if the temperature dependence of the host CB energy is known. Table 2.1 summarizes the BAC parameters for the GaNAs and GaNP alloys. For quaternary alloys, such as GaNAsP studied in this thesis, a linear interpolation between the parameters for the ternary compounds in table 2.1 may be used.[24, 29]

Table 2.1: BAC parameters for the GaNAs and GaNP alloys, taken from [30].

	E^N (eV)	V (eV)
GaNAs	1.65	2.7
GaNP	2.18	3.05

The BAC model is remarkably successful in modeling the band gap shift with nitrogen incorporation in dilute nitrides, despite the fact that the model has several shortcomings. For example, dilute nitrides generally exhibit a significant Stokes shift between absorption and luminescence,[31] which is not reproduced in the BAC model. Moreover, experimental evidence for a pinning of the localized N-impurity energy level, which remains fixed with changing nitrogen concentration, has been shown,[32, 33] in contrast to the anticrossing behavior of the N-impurity level in the BAC model.

Localized tail states and quantum dot formation

In semiconductor alloys, disorder due to fluctuations in the alloy composition leads to the formation of localized states (LS), situated below the CB edge. In dilute nitrides, this effect is amplified by the giant band gap energy bowing. The LS form a continuum of tail-states, where the density of states (DOS) is exponential, following

$$N_{\text{DOS}} \propto e^{E/E_0}. \quad (2.2)$$

Here E_0 represents the localization energy of the LS.

In an extreme case of short-range alloy disorder, nitrogen aggregation may lead to quantum dot (QD) formation. Indeed, formation of QDs in dilute nitride quantum wells[34, 35] and nanowires[36, 37, 38] has been observed. The electronic structure of such nanowire QDs is discussed in detail in Papers IV-VI of this thesis.

2.2 Recombination processes in dilute nitrides

General aspects of recombination processes in semiconductors were discussed in Chapter 1. In this section, I discuss recombination processes which are particularly important in dilute nitride alloys.

Radiative recombination

In Ga(N)As, the energy level of an isolated nitrogen atom is above the CB edge. Consequently, the isolated nitrogen atom does not participate in recombination processes. Various nitrogen cluster states, however, have energy levels below the CB edge. In the ultra-dilute range of nitrogen compositions, they give rise to bright, sharp BE lines in photoluminescence (PL) spectra at low temperatures.[39, 40] With a higher nitrogen content, in the alloy range, the dominant low-temperature radiative recombination process in GaNAs is that of excitons localized in the tail states.[41] The PL arising from such localized exciton (LE) recombination has a characteristic asymmetric line shape, where the low energy side is extended in an exponential tail, following the DOS function (2.2). A characteristic feature of the LE is a spectrally dependent PL lifetime, which is drastically longer for excitons in lower energy LS. The spectrally dependent lifetime is a consequence of a temporal redistribution of the excitons within the LS, where excitons are transferred from higher to lower energy LS. Therefore, the lifetime of excitons in the high-energy LS is very short, and is governed by the transfer to lower energy LS and by NR recombination processes[41] while for excitons in low-energy LS, the lifetime is much longer, up to 10 ns,[31] determined by the radiative recombination.

With an increasing temperature, the GaNAs PL exhibits the characteristic *S shape*, due to a thermal redistribution of excitons from the localized to the extended states. This is exemplified in Fig. 2.2a, where PL spectra acquired from GaNAsP nanowires at various temperatures is shown. With increasing temperatures, an initial redshift is observed, corresponding to a reduction of the band gap energy. This is followed by a subsequent blueshift due to the appearance of the FE peak. The peak positions of the deconvoluted FE and LE peaks are shown in Fig. 2.2b, where the transition from LE- to FE-dominated PL is indicated by the dotted line.

In Ga(N)P, the recombination mechanism is the same, though here the energy level of the isolated nitrogen atom is below the CB edge, producing narrow BE emission lines at low temperatures.[42] With an increasing nitrogen composition, emission related to the tail states dominates the radiative recombination. Moreover, mixing between the extended CB states and the N-related LS increases the rate of radiative band-to-band transitions. At higher temperatures, the emission from free charge carriers or excitons may be observed.[43]

Non-radiative recombination

It is well known that the incorporation of nitrogen in dilute nitrides strongly promotes the formation of various defects. This issue is of key importance for applications,

Figure 2.2: Characteristic S shape dependence of the PL from dilute nitrides, in this case a GaNAsP nanowire. (a) shows PL spectra acquired at temperatures ranging from 4.5 to 300 K, displayed in logarithmic scale. (b) shows the peak positions of the deconvoluted LE (blue circles) and FE (red triangles) peaks. The dotted line indicates the transition from LE- to FE-dominated PL. The figure is adapted from Paper I.

due to their often detrimental effects on the mobility and optical efficiency of the material.[44, 45] For example, a very short minority carrier lifetime observed in GaInNAs has been attributed to NR defects.[44] Similarly, an increase in the density of some common defects has been shown to correlate with a decrease in PL intensity, showing that the defects play a crucial role in the recombination processes of dilute nitrides.[46]

One such defect is the gallium vacancy, V_{Ga} . While the V_{Ga} has been observed in nitrogen-free GaAs,[47] its formation has been shown to be significantly enhanced by nitrogen incorporation in GaNAs.[48] This enhancement may be attributed to a binding between the V_{Ga} defect and nitrogen, reducing its formation energy.[49] Though the defect has been shown to act as a NR center, reducing the luminescence efficiency [50], its detrimental impact on the material properties may be remedied through annealing at 700°C, which has been shown to anneal out the V_{Ga} defects.[48] The V_{Ga} defect is most stable in the V_{Ga}^{3-} charge configuration, and forms energy levels near the VB edge [51]. Interaction with nitrogen, while reducing the formation energy of the defect, is not expected to change its dominant charge configuration.[49]

Several other intrinsic defects form NR recombination channels in dilute nitrides. For example, N-interstitial defects are often formed in large concentrations in GaNAs, and contribute to NR recombination.[50]. Other examples of intrinsic defects that act as NR centers are the N-N and N-As split interstitials,[51], complexes involving a Ga_i interstitial atom,[52, 53] and interfacial point defects[54, 55].

3

Nanowires

Nanowires are nanometer-sized structures with a characteristic aspect ratio, where the extent in one dimension is significantly larger compared to the other two. The diameters of the nanowires may range from a few to several hundreds of nm, while the lengths are usually in the μm range, but lengths exceeding 1 mm have also been reported.[56] Besides semiconductor nanowires, growth of e.g. metallic[57] and superconductor[58] nanowires has also been achieved. Clearly, such a span of geometries and materials leads to huge variations in the nanowire properties. Consequently, the task of concisely describing the overall properties of nanowires is all but impossible. Therefore, in this chapter I will focus on semiconductor nanowires with diameters in the 100 nm range.

Nanowires constitute an exciting platform to study fundamental physics at the nanoscale, where phenomena such as light confinement, as well as surface and strain properties, differ from those at the macroscale. Moreover, the nanowire geometry leads to a number of properties which may be useful in various applications. Since nanowires may be grown with diameters similar to the wavelengths of visible light, electromagnetic mode confinement and waveguiding has been demonstrated.[59] Additionally, the end facets of the nanowires may work as partially reflecting mirrors, making nanowire lasing possible.[60] By detecting changes of the evanescent field surrounding the nanowire waveguide, it is possible to use nanowires as sensors for various molecules in their surroundings.[61] The high surface-to-volume ratio of nanowires has also been proven advantageous in various other sensing schemes, such as for gas sensing,[62, 63, 64] pH sensing,[65] and even detection of single viruses[66] and DNA molecules[67].

Numerous applications of nanowires in optoelectronics have also been proposed.[59, 68] For example, the use of nanowire arrays as an active element in photovoltaics has been demonstrated, with a remarkably high absorption using only a small material

volume, demonstrating that nanowire solar cells may be advantageous over planar photovoltaic structures.[69, 70] A promising approach for optoelectronic device design is using the III-V material system, where many of the compounds have a direct band gap, which can be tuned through alloying. [59] Moreover, the III-V nanowires may be grown strain-relaxed on Si due to compensation through expansion in the radial direction,[71, 72] which is not possible in the planar geometry.

3.1 Growth of nanowires

As expected from the existence of numerous types of nanowires, a large number of different growth and fabrication methods exist. The fabrication methods may be divided into two general categories: *top-down* and *bottom-up*, which imply nanowire formation through the removal and addition of material, respectively. As the work presented in this thesis deals exclusively with bottom-up grown nanowires, this section will be devoted mainly to that approach.

Top-down

The top-down approach relies on various lithographic techniques and etching processes. [73, 74] While lithography techniques provide a high degree of control over the sizes and shapes of the fabricated nanostructures, the resolution is inherently limited, which also limits the minimum achievable sizes. The top-down approach is generally also prone to defect formation, though great advances have been made to reduce its severity.[74]

Bottom-up

In bottom-up fabrication, the nanowires are grown by the addition of material which in some way self-assembles to form the desired structure. Several growth techniques exist, such as laser assisted growth,[75] chemical beam epitaxy(CBE), [76] molecular beam epitaxy (MBE), [77] and chemical vapor deposition (CVD).[78]

The nanowire growth is generally achieved through the *vapor-liquid-solid* (VLS) growth mechanism, first described by Wagner and Ellis in 1964.[79] The VLS process is schematically demonstrated in Fig 3.1. The substrate is first prepared with dispersed seed particles, often Au, referred to as the *catalysts* (Fig. 3.1a). Precursor gases are then supplied to the growth chamber (Fig. 3.1b). At the growth temperature, the catalyst forms an eutectic liquid alloy with material supplied from the vapor phase precursors (the straight arrows), which upon supersaturation precipitates, contributing to the nanowire growth. Additionally, adatoms at the substrate surface and nanowire side facets also contribute to the growth, as shown by the wavy arrows in the figure.

While techniques using Au-catalysts have been hugely successful in growth of high-quality nanowires, it also presents drawbacks. Firstly, during the VLS growth, some Au incorporation in the nanowire may occur, which has been shown to severely reduce the minority carrier lifetime and the optical quality of e.g. GaAs nanowires.[80]

Figure 3.1: The VLS growth process. A schematic illustration of the VLS growth mechanism is shown in (a)-(c), where a metal catalyst (a) initiates the growth process (b) by forming a liquid alloy with the precursor material from the vapor (straight arrows) and diffused adatoms (wavy arrows). The catalyst droplet may be completely depleted (c), whereby the VLS growth is terminated. Figures (d) and (e) show TEM micrographs of GaNAsP nanowires without (d) and with (e) tapering. Figures (d) and (e) are adapted from Paper I.

Secondly, integration of III-V nanowires in Si microelectronics, which is a very promising application, may be hampered, since Au is known to create deep-level defects in Si.[81] A solution to these problems is using so-called *self-catalyzed* (or *self-assisted* or *self-seeded*) growth, where the catalyst is one of the constituent elements of the nanowire, for example using a Ga catalyst for GaAs nanowire growth.[82] In this case the catalyst is simultaneously consumed and refilled during the growth, but may be completely depleted, as shown in Fig. 3.1c. In that case, the axial VLS growth stops.

One common side effect in VLS-grown nanowires is tapering, i.e. a non-uniformity of the nanowire diameter, as exemplified in Fig. 3.1e, and contrasted with a nanowire without tapering in Fig. 3.1d. The tapering may be caused by several mechanisms. Firstly, since adatom adsorption may occur during the entire growth process, this type of radial growth will be most prominent near the base of the nanowire simply because the base is grown first. Moreover, the adatom diffusion length is finite, meaning that the range of the adatoms diffusing from the substrate to the nanowire may be limited.[83, 84] Tapering may also be induced by the conditions of the contact angle of the droplet catalyst at the nanowire interface,[85] or, for self-catalyzed growth, a continuous depletion of the catalyst droplet.[86]

Another side effect observed during the growth of III-V alloy nanowires is an unintentional non-uniformity of the composition. For example, a non-uniform radial

composition has been observed in nanowires from several III-V based alloys [87, 88, 89]. Such radial non-uniformity has been attributed to a difference in the diffusion lengths of the different adatoms[87, 88] and to a competing alloying with the metal catalyst[89].

3.2 Crystal structure

Growth in the nanowire geometry may impact the crystal structure of the material. Many semiconductor compounds, such as GaAs and GaP (and their dilute nitride counterparts), crystallize in the ZB structure during bulk and epilayer growth. When grown in the nanowire geometry, however, the WZ structure may form. A lower nucleation barrier for a WZ nucleus at the triple-phase line has been suggested to promote the WZ structure.[90] The influence of the nanowire/catalyst interface geometry has also been established to influence the formed polytype.[91] While growth of pure ZB and WZ nanowires has been demonstrated,[92] both polytypes often coexist in the same nanowire.

The polytypism in nanowires is closely related to the existence of stacking faults and rotational twin planes. To understand the character of such structural defects, we recall that the stacking sequence of bilayers in a ZB crystal along the $[111]$ direction is ABCABC, i.e. it has a period of three bilayers, while the stacking sequence in a WZ crystal along $[0001]$ is ABAB with a period of two bilayers. A stacking fault in such a notation is then, for example, a C bilayer in WZ: ABCBAB. The twin plane, on the other hand, is a mirror plane which reverses the ordering: e.g. ABCABACBA in the ZB structure.

Effects of polytypism on the electronic structure

The crystal structure has a significant impact on the electronic structure of the material. Taking GaAs as an example, the band gap of WZ is reduced by approximately 10 meV compared to that of ZB,[93] and the band alignment with ZB is type II.[3, 94, 95] Therefore, when both ZB and WZ segments are present in the same nanowire, charge separation and quantum confinement of the charge carriers may be observed.[94, 96] In fact, for very thin nanowires (or nanowires with very thin cores), such crystal phase quantum confinement may lead to the formation of QDs.[97, 98]

Changes in the crystalline structure may also affect the nature of the band gap. Taking GaP as an example, the ZB polytype has an indirect band gap while the WZ polytype has a direct band gap.[99, 100]

3.3 Nanowire heterostructures

Due to their ability to withstand strain without the formation of strain-induced defects, nanowire heterostructures are of great interest. Indeed, the nanowire geometry enables the formation of high quality heterostructures involving lattice mismatched

materials, which are not possible to fabricate in the planar geometry, due to the induced defect formation.[72] Two main geometries of nanowire heterostructures exist: axial and radial heterostructures.

Figure 3.2: Nanowire heterostructures. Figure (a) shows a simple axial heterostructure, while (b) and (c) show radial heterostructures of core/shell and core/multishell types, respectively.

Axial heterostructures

In axial heterostructures, the heterointerface is a plane normal to the nanowire axis, as shown in Fig. 3.2a. Such heterostructures have been reported for many different material systems, some with a high degree of lattice mismatch, e.g. GaAs/GaP heterostructures, and are formed by interrupting the supply of one precursor while introducing another during the growth.[101, 102, 103] Not only a single heterointerface is possible, but complex superlattice structures with atomically sharp interfaces have been demonstrated.[104] In thin nanowires (or in nanowires with thin cores) axial heterostructures may even lead to three dimensional quantum confinement, i.e. QDs. Growth of such QD structures have been shown in several III-V material systems, such as AlGaIn,[105] AlGaAs,[106] InAsP[107] and GaAsP[108]. In a similar manner to the formation of heterostructures it is also possible to form p-n junctions by changing the supply of dopant material during the growth.[101]

Radial heterostructures

Another type of nanowire heterostructure is the radial, or core/shell heterostructure, shown in Fig. 3.2b and c for the cases of one and two shells, respectively. The growth process for this structure is markedly different from that of the axial heterostructure. In this case, the inner core of the nanowire is first grown using the VLS technique described previously. The growth mode is then changed to *vapor-solid* (VS) growth, while simultaneously altering the precursors (or dopants for p-n junction formation).

The VS growth mainly occurs in the radial direction. The switch of the growth mode to radial VS growth is generally achieved by increasing the growth temperature. Radial quantum wells have been demonstrated.[109]

Besides the potential uses of the heterostructure itself, the core/shell growth provides an additional benefit to the nanowire performance, namely the passivation of the surface of the inner layers, which may reduce the impact of detrimental surface recombination.

3.4 Recombination mechanisms in nanowires

Due to the specific geometry of nanowires, and to their defect formation mechanisms which are markedly different from those of planar structures, the recombination processes and their relative importance may also differ between nanowires and planar structures. This difference is particularly prominent considering the NR recombination mechanisms in nanowires, as is described in this section.

The termination of the long-range order at the crystalline surface causes the formation of surface defects, such as dangling bonds. This leads to two detrimental effects: (i) NR recombination through the formed deep-level recombination centers, and (ii) Fermi-level pinning, leading to a depletion of carriers near the nanowire surface, which are captured by the surface defects, and to a consequent band bending.[110, 111]

Due to the high surface-to-volume ratio of nanowires, the surface defects may severely affect the overall characteristics of the nanowires. Indeed, in GaAs nanowires a reduction of the exciton lifetime by two orders of magnitude compared to the intrinsic bulk lifetime has been shown.[112] Surface scattering has also been shown to have detrimental effects on the electronic properties of nanowires.[113] The effect of the surface defects on the charge carrier lifetime can be quantified by the *surface recombination velocity* (SRV). GaAs is an example of a material with very severe surface recombination, with a SRV in the order of 10^6 cm/s,[7] whereas it is much smaller in InP, in the order of 10^2 cm/s[114, 115]. In nanowires, the effect of the SRV on the carrier lifetime, τ , can be estimated by

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{vol}}} + \frac{4S}{d}, \quad (3.1)$$

where τ_{vol} is the effective lifetime of the volume, i.e. neglecting the surface recombination. S is the SRV and d is the nanowire diameter.[116]

The surface may be *passivated* to reduce the SRV. One approach, as mentioned previously, is the formation of a radial heterostructure—if an outer shell with a higher band gap energy is grown on top of the core layer, the SRV of the core region is greatly reduced. Surface passivation by an outer shell has been shown to increase the mobility of the carriers,[117] and to greatly increase the optical efficiency of the nanowires.[118] Another approach is to use a chemical process to passivate the surface bonds. An example of such a technique is surface nitridation, where incorporation of nitrogen creates

the strong Ga-N bond at the surface. Interestingly, this process has been suggested to occur spontaneously during the growth of Ga(N,As,P) alloy nanowires, thus making such dilute nitride nanowires less sensitive to surface recombination.[119, 120]

It has been shown that structural defects, such as stacking faults and rotational twin planes may be detrimental for electrical and optical properties of the nanowire.[121, 122] For nanowires successfully grown without such structural defects, an increase in the emission efficiency is correspondingly observed, [123, 124], together with an increase in the photocurrent,[124] and in the charge carrier lifetime [125], confirming that the structural defects function as efficient NR centers. Moreover, an increase in the field effect mobility is also observed upon elimination of the stacking fault density, but the density of rotational twin planes appears to have a limited effect on the mobility.[126]

3.5 Strain in nanowires

One of the main advantages of the nanowire geometry is the possibility of accommodating a large amount of strain without inducing defects.[127] This is evident from the large variety of demonstrated core-shell and core-multishell heterostructures with significant lattice mismatch,[118, 128, 129] and is promising not only for forming high-quality lattice-mismatched heterostructures, but also for use in strain engineering. For example, strain engineering in core-shell nanowires can be used to tune the band gap energy of the material,[129] to alter the energy splitting between the LH and HH states,[130] and to create piezoelectric fields useful for charge carrier separation.[131]

Both numerical[131] and analytic approaches[132, 133] can be used to calculate the effects of strain on the electronic structure of core-shell nanowires. The analytical approach proposed by Ferrand and Cibert,[133] where ZB nanowires with a [111] axis are treated as cylinders, results in approximate expressions for the longitudinal (z) and in-plane (θ, r) strain components for the core (c) and shell (s) regions, where

$$\begin{aligned} \epsilon_{zz}^c &= (1 - \eta)f, \\ \epsilon_{\theta\theta}^c &= \epsilon_{rr}^c = (1 - \eta)(f + B_s), \\ \epsilon_{zz}^s &= -\eta f, \\ \epsilon_{\theta\theta}^s &= B_s \frac{r_c^2}{r^2} - \eta(f + B_s), \\ \epsilon_{rr}^s &= -\eta(f + B_s) - B_s \frac{r_c^2}{r^2}. \end{aligned} \tag{3.2}$$

Here, $f = (a_s - a_c)/a_c$ and η is the ratio of the core to total cross-sectional area. B_s is given by

$$B_s = -f \frac{c_{11} + 2c_{12}}{c_{11} + c_{12} + 2c_{44}}, \tag{3.3}$$

where c_{ij} are the elastic constants. The model may readily be expanded to a nanowire

with several shells.[134] From equations (3.2), it may be shown that the dominant strain component is the uniaxial component along the nanowire axis.[133]

3.6 Dielectric mismatch

The geometry of the nanowire, in combination with the large dielectric constants of semiconductor materials (generally larger than 10), gives rise to polarization dependent absorption and emission in the nanowire. In nanowires, this *dielectric mismatch* leads to the so-called *optical antenna effect*, where the nanowire interacts stronger with light polarized parallel to the nanowire axis rather than light polarized orthogonal to it. A simple description of this phenomenon is given by Ruda and Shik,[135, 136] and is summarized here. A more complex model, taking into account the finite length of the nanowire, is described by e.g. Chen et al.[137].

For an infinitely long nanowire, the electric field parallel to the nanowire axis is constant across the interface with the ambient,

$$E_{\parallel} = E_{0\parallel}. \quad (3.4)$$

Here E and E_0 are the electric fields in the nanowire and the ambient, respectively. For a thin nanowire, with radius $a \ll \lambda$ (λ being the wavelength of the light), the orthogonal component of the electric field inside the nanowire is instead given by

$$E_{\perp} = \frac{2\epsilon_0}{\epsilon + \epsilon_0} E_{0\perp}, \quad (3.5)$$

which is significantly lower than in the ambient. Equations (3.4) and (3.5) lead to a polarization anisotropy of the absorption coefficient, k

$$\frac{k_{\parallel}}{k_{\perp}} = \left| \frac{\epsilon + \epsilon_0}{2\epsilon_0} \right|^2. \quad (3.6)$$

Here $k_{\parallel}$ and $k_{\perp}$ are the absorption coefficients for light polarized parallel and perpendicular to the nanowire axis, respectively. Taking GaAs as an example, $\epsilon = 12.9$, meaning that the ratio in (3.6) is 42.

The PL emitted from the nanowire will be also anisotropic if the radius of the wire, a , is small. Indeed, for a line emitter (where $a = 0$), the ratio of PL intensities with polarization parallel and perpendicular to the nanowire is

$$\frac{I_{\parallel}}{I_{\perp}} = \frac{(\epsilon + \epsilon_0)^2 + \epsilon_0^2}{6\epsilon_0^2}. \quad (3.7)$$

Equations (3.6) and (3.7) are valid only when a is much smaller than the wavelength of light inside the nanowire. For semiconductor nanowires with a in the range of 100 nm, however, the equations need to be modified as

$$\frac{I_{\parallel}}{I_{\perp}} = \frac{d_x^2 + 2d_z^2}{3d_x^2}, \quad (3.8)$$

where d_x and d_z are the *effective dipoles* in the x- and z-directions, respectively. The effective dipoles are given by

$$d_x = d_{0x} \sqrt{\epsilon} \frac{J_1'(ka)H_1^{(1)}(ka) - J_1(ka)H_1^{(1)'}(ka)}{\sqrt{\epsilon_0}J_1'(ka)H_1^{(1)}(k_0a) - \sqrt{\epsilon}J_1(ka)H_1^{(1)'}(k_0a)} \quad (3.9)$$

and

$$d_z = d_{0z} \sqrt{\epsilon} \frac{J_1(ka)H_0^{(1)}(ka) - J_0(ka)H_1^{(1)}(ka)}{\sqrt{\epsilon}J_1(ka)H_0^{(1)}(k_0a) - \sqrt{\epsilon_0}J_0(ka)H_1^{(1)}(k_0a)}. \quad (3.10)$$

Here, $d_{0x/z}$ are the free dipoles, ϵ is the dielectric constant of the semiconductor, $k = \sqrt{\epsilon}\omega/c$, while J_i and $H_i^{(1)}$ are the Bessel and first-kind Hankel functions. From equation (3.8) the maximum ($I_{\parallel}$) and minimum ($I_{\perp}$) PL intensities may be obtained, while the complete angular dependence of the PL is given by

$$I(\theta) = I_{\perp} \sin^2(\theta) + I_{\parallel} \cos^2(\theta), \quad (3.11)$$

where θ is the angle relative to the nanowire axis.

Figure 3.3: The effect of the dielectric mismatch on the PL. The red (black) solid line in (a) and (b) corresponds to the PL spectrum of light polarized parallel (perpendicular) to the axis of a GaNAsP nanowire, while the blue circles show the polarization calculated as in (3.12). In (b), the $\perp$ -spectrum has been adjusted for the dielectric mismatch according to (3.8).

Figure 3.3a shows the strong PL polarization anisotropy of a GaNAsP nanowire with radius $a \approx 50$ nm, where the red (black) solid lines are the PL spectra of the light linearly polarized parallel (perpendicular) to the nanowire axis, while the blue circles show the polarization degree, defined as

$$P_{\parallel} = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}. \quad (3.12)$$

After adjusting the measured PL intensity of light polarized perpendicular to the nanowire axis using equation (3.8) the polarization is almost completely gone (Fig. 3.3b), showing that the strong polarization anisotropy of the detected PL is mainly caused by the dielectric mismatch.

4

Quantum Dots

When the motion of charge carriers is restricted to a small region of space in the semiconductor, quantum confinement causes discontinuities in the DOS. In the extreme case of three-dimensional quantum confinement, a so-called quantum dot (QD) is formed. QDs are sometimes referred to as *artificial atoms*, due to their completely discrete DOS.

Numerous applications of QDs have been proposed. The band gap energy of the QD may be tuned by changing the QD size, which is particularly interesting for light emitting and absorbing applications, such as LEDs, [138, 139] lasers [140] and photovoltaics [141]. QDs may also function as building blocks for novel devices, such as in various quantum computation[142, 143, 144] and quantum communication[145] schemes, in optical switches[146] and in spintronics[147].

QDs may form in many different ways, which, similar to the nanowire growth discussed in Chapter 3, can be broadly divided into top-down and bottom-up approaches. The former method generally involves lithography or etching of a quantum well structure (with one-dimensional confinement of the charge carriers),[148] while bottom-up methods involve ways to grow the QDs through an addition of material. Bottom-up fabricated QDs were first demonstrated in 1981 through the formation of CuCl nanoparticles in a dielectric matrix,[149] and soon thereafter through the formation of CdS colloidal QDs. [150] Another bottom-up QD fabrication method is epitaxial growth using lattice mismatched semiconductors, for example through the Stranski-Krastanov process, which has been studied in detail for III-V semiconductor QDs.[151] Here, the QDs are formed due to plastic deformation of the epitaxial layer, caused by a lattice mismatch with the substrate.

Recently, QDs have also been shown to form within nanowires, which may occur in several different ways. Firstly, for sufficiently thin nanowires (or nanowires with

thin cores), growth of a flat axial heterostructure can cause QD confinement, as has been demonstrated in several different materials, such as AlGaIn[105], AlGaAs[106], InAsP[107, 152] and GaAsP[108]. Interestingly, a similar approach using crystal phase engineering has also been utilized.[97, 98] Secondly, QDs may also form spontaneously, on the surfaces of the nanowires[93, 153, 154], at the core/shell interface[155, 156, 157], or in regions with large alloy fluctuations[36, 158].

4.1 Electronic structure

Arguably the simplest way to model the electronic structure of a QD is using the *particle in a box* model, where a particle is confined in a box with sides L_x , L_y and L_z by infinite energy barriers. The solution to that problem yields the eigenenergies

$$E_{n_x, n_y, n_z} = \frac{\hbar^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right), \quad (4.1)$$

where $n_{x,y,z}$ are the quantum numbers, and m is the mass of the confined particle. This solution highlights the completely quantized energy levels in the QD. Moreover, (4.1) shows that the energy levels depend inversely on the mass of the confined particle, which results in a splitting between the LH and HH states, where the HH is the ground state. While the particle in a box model provides qualitative insights of the electronic structure of a QD, it is incapable of providing a quantitative description, for which more sophisticated models exist.[159]

Now we turn to the problem of describing the electronic states of the QD. A confined charge carrier is no longer described by plane-wave Bloch functions, but rather by a product of the Bloch functions with a so-called envelope function,

$$|\Psi(r)\rangle = |\phi(r)\rangle |u_k(r)\rangle, \quad (4.2)$$

where $|\phi(r)\rangle$ is the envelope function, while $|u_k(r)\rangle$ is the Bloch function. Here, the envelope function describes the confinement of the charge carrier, and is, consequently, non-zero only locally. When the confinement is strong, i.e. the spatial extent of the wavefunction $|\Psi(r)\rangle$ is small, the electronic states become quantized. This is shown schematically in Fig. 4.1a, where the three lowest electron orbital energy levels, and the corresponding three highest hole levels, are shown. The labels indicate the orbital character of the respective envelope functions, where the lowest electron and highest hole state both have s-orbital character.

Focusing on the s-states for the moment, and recalling equation (4.1), confinement of the holes leads to a splitting of the HH and LH states, as shown in Fig. 4.1b (in this discussion, the SO states are neglected). For many common types of QDs, such as Stranski-Krastanov grown QDs, this splitting is often further increased by a compressive strain in the plane of the QD.

However, a LH-HH splitting is not present in all types of QDs. In cases when the hole is only weakly localized in the QD, and when the biaxial compressive strain is not

Figure 4.1: The electronic structure of a typical QD. (a) shows the different envelope function orbitals of the electrons and holes, while (b) shows the electron and hole ground states, which have s-character. The SO states are not included, as they are expected to be energetically well separated from the LH and HH states. In some QDs, the highest p-state may be energetically above the s-orbital LH state, but is not included in (b) for simplicity. (c) shows the optically allowed transitions between states in (b), where the dotted (solid) arrows indicate an absorption/emission of circularly (linearly) polarized light. The states are labeled as $|M\rangle$, where M is the z-projection of the total angular momentum quantum number.

dominating, the splitting between the hole states is reduced. In fact, dilute nitride NW QDs can fall into this category. In dilute nitrides, the electrons are strongly confined in the QD due to the perturbation of the CB states caused by the nitrogen incorporation, whereas the holes can be weakly localized in the QD, through Coulomb interaction with the electron. Indeed, observations of a strong LH-HH mixing in dilute nitride QDs have been reported.[37, 160] The LH-HH mixing may also occur when the shape of the QD is distorted, or when it is highly strained. Interestingly, QDs with a pure LH ground state may be achieved by engineering the strain and shape of the QDs.[130, 161] This type of hole-state engineering may prove vital in various quantum computing schemes. As an example, in electron-spin initialization schemes a LH ground state is preferred.[161, 162]

The orbital character of the electron and hole envelope functions also influences the selection rules for optical transitions in the QD. Optical transitions are only allowed if the parity of the electron and hole envelope functions are equal. Explicitly, an s-character electron may recombine with an s-character hole, but not with one of p-character. An additional set of selection rules also exists, where the difference in the quantum numbers between the initial and final electron states must obey

$$\Delta l = \pm 1, \Delta m_l = 0, \pm 1, \Delta s = 0, \quad (4.3)$$

where l and m_l are the quantum numbers of the orbital angular momentum and its z-projection, respectively, while s is the spin quantum number.

The selection rules are depicted in 4.1c, where the states are labeled in the $|m_j\rangle$ notation, where m_j is the z-projection of the angular momentum quantum number of the single electron. From the $|\pm 3/2\rangle$ valence states only one transition is possible, through the absorption or emission a $\sigma^{-/+}$ photon. The $|\pm 1/2\rangle$ valence states, however, contain both a spin up and a spin down component, whereby two transitions are

possible, through either linearly (π_z) or circularly polarized ($\sigma^{+/-}$) light. The relative strengths of the transitions involving a π_z and a $\sigma^{+/-}$ photon are 2:1.

4.2 Charge configurations

More than one electron and one hole may be confined in the QD at the same time, leading to several possible *charge configurations*. Due to the Pauli exclusion principle, each energy level in Fig. 4.1b may contain a maximum of two electrons or holes, with opposite spin. Considering for the moment only the HH states, as may be done for the QDs where the LH and HH are energetically well separated,[163] nine possible charge configurations exist, including the completely empty QD. The nine possible charge configurations are shown in Fig. 4.2, where the electrons (holes) are represented by the upper red (lower blue) circles. The configurations containing at least one electron and one hole are of special interest, since radiative recombination is possible in these cases. These configurations are indicated with the dotted rectangle, and labeled as X, X-, X+ and XX in the figure. Due to the confined nature of the QDs, the electrons and holes are strongly interacting with each other through the Coulomb interaction, which means that they cannot be described simply as EHPs, but rather as excitons or, more generally, as excitonic complexes. The X configuration is referred to as a single, or neutral, exciton, while X- and X+ denote the negatively and positively charged excitons, sometimes called the negative and positive trions, respectively. Finally, XX denotes the biexciton.

Due to the interaction between the electron and hole of X, its total energy differs from the energy separation between the electron and hole energy levels, by the exciton binding energy. Due to the different charge configurations of the various excitonic complexes, the binding energies of the trions and the biexciton generally differ from that of the single exciton. The binding energies of the excitonic complexes are the difference between the total energy of the complex and of the single exciton. For example, the biexciton binding energy, E_B^{XX} , is given by

$$E_B^{XX} = E_{XX} - E_X. \quad (4.4)$$

When the LH and HH are energetically close, so that both levels may be simultaneously populated, the picture is more complicated. Then, rather than two possible charge configurations of the hole states, nine configurations are possible, leading to a large number of different excitonic complexes.[164]

4.3 Quantum dots as sources of non-classical light

Many light sources can be described by a classical treatment, where the intensity of the light is related to the magnitude of the electromagnetic field. However, QDs are sources of non-classical light and are, therefore, inherently different. To describe the light emitted by a QD, we must consider the quantization of the electromagnetic field — photons. In fact, QDs are so-called *single photon emitters* (SPE), meaning that two

Figure 4.2: The different charge configurations possible in a QD, considering only one energy level for the electrons (the upper, red, circles) and the holes (the lower, blue, circles), respectively. The dotted rectangle shows the excitonic complexes: the single exciton (X), negatively (X^-) and positively (X^+) charged excitons, and the biexciton (XX).

photons cannot be emitted simultaneously. This is because the QD can only bind one exciton (or exciton complex) at a time. The recombination of the single exciton, for example, renders the QD empty. Consequently, there is a delay until the next recombination, related to the capture of an additional exciton. SPEs are gathering much research interest as building blocks for various quantum computation and quantum information schemes.[165]

Figure 4.3: An illustration of a hypothetical experiment to measure the second-order coherence function, $g^{(2)}(\tau)$. A light beam (the solid arrow) is split by a beam splitter into the arms i and ii , whereby the light is detected by photodetectors. The signal from the detector in arm ii is delayed by a time τ . The signals may then be combined according to equation (4.5).

In order to better describe the nature of such non-classical light, it is instructive to consider the *second-order coherence function* (sometimes called the second-order correlation function), $g^{(2)}$. The $g^{(2)}$ function can be visualized by the hypothetical experiment in Fig. 4.3. An initial light beam is split by a beam-splitter, and the detection of

photons in the two arms, i and ii , is performed by two photodetectors. In arm ii , the signal from the detector is delayed by the time τ by a delay-generator, and the $g^{(2)}$ function may be formed from the signals in the two arms as

$$g^{(2)}(\tau) = \frac{\langle n_i(t)n_{ii}(t+\tau) \rangle}{\langle n_i(t) \rangle \langle n_{ii}(t+\tau) \rangle}, \quad (4.5)$$

where n_i and n_{ii} are the numbers of photons detected in the arms i and ii , respectively.

Light may be classified into three categories, depending on the temporal distributions of the photons, as is shown in Fig. 4.4, where the classification is done according to the values of the $g^{(2)}$ function. It can be shown that a classical description of light as electromagnetic waves can result in $g^{(2)}(0) \geq 1$, while antibunched light ($g^{(2)}(0) < 1$) only arises from a quantum mechanical description. Such light is therefore said to be non-classical.

Figure 4.4: Light may be classified into three categories according to the values of the $g^{(2)}$ function: random, bunched and antibunched light. The dots symbolize the temporal distribution of photons in a beam of light.

Specifically, an SPE is an emitter where

$$g^{(2)}(0) < 0.5, \quad (4.6)$$

while for an ideal SPE, the value is zero. For $\tau \neq 0$, the value of $g^{(2)}$ depends on the time between two subsequent photon emission events, which is governed by the charge carrier/exciton capture rate in the QD and the lifetime of the QD exciton. This can be described by the simplified expression

$$g^{(2)}(\tau) = e^{-|\tau|/\tau_c}, \quad (4.7)$$

where τ_c is the characteristic antibunching time, accounting for the QD capture rate and radiative lifetime.[166] A more thorough treatment is possible by a rate-equation analysis taking into account charge carrier and exciton capture and recombination at the QD.

4.4 Random population model

To gain a more detailed understanding of the capture and recombination processes in a QD, it is instructive to model its dynamics through the use of rate equations.

This may be done through e.g. the *Random Population Model* (RPM).[167] In the RPM, the various charge configurations of the QD are represented by *microstates*, where the probability of finding the QD in a certain charge configuration is given by the population of the corresponding microstate, $n_{i,j}$. For example, the probability of finding the QD in the empty state is $n_{0,0}$.

The upper part of Fig. 4.5 is a diagram showing the different microstates of a QD, considering only two electron and two hole states. This diagram is adapted for dilute nitride QDs, where electrons and holes are captured by different processes. Specifically, the holes are localized due to the Coulomb interaction with the captured electrons. Therefore, the number of captured electrons must be greater than or equal the number of captured holes, i.e. $i \geq j$. This is described in detail in Paper VII.

Figure 4.5: A schematic illustration of the RPM. The boxes in the upper panel represent the various charge configurations in a dilute nitride QD, where the upper and lower numbers are the numbers of electrons and holes captured by the QD, respectively. The solid, dotted and dashed arrows represent the capture of an exciton, an electron or a hole, while the wavy lines represent the recombination of an exciton (or an exciton complex). The boxes in the lower panel represent the exciton (N_x), electron (N_e) and hole (N_h) reservoirs, affected by generation (the $G_{x,e-h}$ -terms) and recombination (the $\alpha_{x,e-h}$ -terms) and capture at the QD (the $\gamma_{x,e,h}$ -terms). The reservoirs may also be affected by defects, represented by the horizontal line, which capture electrons and holes with the capture coefficients T_e^D and T_h^D , respectively. The figure is adapted from Paper VII.

The values of the various microstate populations are affected by the capture of electrons (the red dotted arrows), holes (the blue dashed arrows) and excitons (the black solid arrows) from the extended states, and by recombination in the QD (the wavy lines). The extended states in the vicinity of the QD are represented by *reservoirs*. The populations of the electron, hole and exciton reservoirs are N_e , N_h and N_x , respectively, which are affected by carrier/exciton generation ($G_{e-h,X}$), capture at the QD ($\gamma_{e,h,X}$) and recombination ($\alpha_{e-h,X}$), as is depicted in the lower part of Fig. 4.5.

An interaction between the reservoirs and NR defect centers can also be introduced, where the number of defects is N_D^T , of which N_D are occupied with an electron. N_D^0 defects are occupied in the dark. The electron and hole capture coefficients are T_e^D and T_h^D , respectively.

The master equations governing such a system of microstates are

$$\frac{dn_{i,j}}{dt} = C_{i,j}^X N_X + C_{i,j}^e N_e + C_{i,j}^h N_h + R_{i,j}, \quad (4.8)$$

$$\frac{dN_X}{dt} = -N_X \left(\sum_{i,j} D_{i,j} C_{i,j}^X + \alpha_X \right) + G_X, \quad (4.9)$$

$$\frac{dN_e}{dt} = -N_e \left(\sum_{i,j} i C_{i,j}^e + N_h \alpha_{e-h} \right) - T_e^D N_e (N_D^T - N_D) + G_{e-h}, \quad (4.10)$$

$$\frac{dN_h}{dt} = -N_h \left(\sum_{i,j} j C_{i,j}^h + N_e \alpha_{e-h} \right) - T_h^D N_h N_D + G_{e-h}, \quad (4.11)$$

$$\frac{dN_D}{dt} = T_e^D N_e (N_D^T - N_D) - T_h^D N_h N_D, \quad (4.12)$$

$$\sum_{i,j} i n_{i,j} + N_e + N_D - N_D^0 = \sum_{i,j} j n_{i,j} + N_h. \quad (4.13)$$

Here, (4.8) governs the changes of the microstate populations, while equations (4.9)-(4.11) govern the changes of the exciton, electron and hole reservoirs, respectively. Equation (4.12) describes the change of the number of occupied defects, and equation (4.13) is the charge neutrality condition. $D_{i,j}$ is the minimum value of i and j . The C and R parameters represent the capture and recombination at the QD, and are given by

$$\begin{aligned} C_{0,0}^X &= -2\gamma_X n_{0,0}, & C_{0,0}^e &= -2\gamma_e n_{0,0}, & C_{0,0}^h &= 0, \\ C_{1,0}^X &= -\frac{3}{2}\gamma_X n_{1,0}, & C_{1,0}^e &= 2\gamma_e n_{0,0} - \gamma_e n_{1,0}, & C_{1,0}^h &= -\gamma_h n_{1,0}, \\ C_{2,0}^X &= 0, & C_{2,0}^e &= \gamma_e n_{1,0}, & C_{2,0}^h &= -2\gamma_h n_{2,0}, \\ C_{1,1}^X &= 2\gamma_X n_{0,0} - \gamma_X n_{1,1}, & C_{1,1}^e &= -\gamma_e n_{1,1}, & C_{1,1}^h &= \gamma_h n_{1,0}, \\ C_{2,1}^X &= \frac{3}{2}\gamma_X n_{1,0}, & C_{2,1}^e &= \gamma_e n_{1,1}, & C_{2,1}^h &= 2\gamma_h n_{2,0} - \gamma_h n_{2,1}, \\ C_{2,2}^X &= \gamma_X n_{1,1}, & C_{2,2}^e &= 0, & C_{2,2}^h &= \gamma_h n_{2,1}, \end{aligned} \quad (4.14)$$

and

$$\begin{aligned}
 R_{0,0} &= \frac{n_{1,1}}{\tau_X}, \\
 R_{1,0} &= \frac{n_{2,1}}{\tau_{X-}}, \\
 R_{2,0} &= 0, \\
 R_{1,1} &= \frac{n_{2,2}}{\tau_{XX}} - \frac{n_{1,1}}{\tau_X}, \\
 R_{2,1} &= -\frac{n_{2,1}}{\tau_{X-}}, \\
 R_{2,2} &= -\frac{n_{2,2}}{\tau_{XX}}.
 \end{aligned} \tag{4.15}$$

The solutions to the rate equations may be obtained numerically by initiating the system in the empty QD microstate: $n_{0,0} = 1$ and $n_{i,j} = 0$ for all other i, j , and then letting the system evolve according to equations (4.8)-(4.13). Under continuous generation, the microstate populations will converge to their steady-state values, which represent the solutions to the rate equation problem.[168] Figure 4.6a shows an example of the results of such a simulation. The PL intensity from the recombination of a QD exciton is proportional to the total recombination rate, which is given by its corresponding microstate population divided by the radiative lifetime. Taking the single exciton as an example,

$$I_X^{PL} \propto \frac{n_{1,1}}{\tau_X}. \tag{4.16}$$

From (4.16) the relative intensities of the PL peaks corresponding to the various excitonic complexes in the QD may be obtained.

The model can also be used to simulate the PL dynamics under pulsed excitation. In that case, the generation terms are time dependent, and can be implemented as instantaneous pulses,

$$G_{X,e,h}(t) = G_0^{X,e,h} \delta_{t,nt_0}. \tag{4.17}$$

Here, $G_0^{X,e,h}$ are the exciton, electron and hole generation rates during the pulse, and δ_{t,nt_0} is a Kronecker delta function, where T is the pulse period and $n = 0, 1, 2, \dots$. Similarly to the continuous generation simulations, the system is initiated in the empty QD microstate. After a certain number of pulses, the dynamics of the system is identical for each subsequent pulse period, whereby the solution to the problem is found. An example of such a simulation with pulsed generation is given in Fig. 4.6b.

Finally, the model may also be used to simulate the results of (cw) photon correlation measurements, which are described in section 6.4. This type of simulation is performed in a two step process. Firstly, the steady state solution under continuous generation is found, as described above. Secondly, while keeping the steady state values of the reservoir and defect populations fixed, the QD is initiated in the appropriate microstate, depending on the type of auto- or cross-correlation measurement to be simulated. This is best illustrated with an example: In the X,X auto-correlation measurement, after the X radiative recombination (the start signal), the QD is empty.

Figure 4.6: Examples of how the results of the RPM simulation may look for continuous (a) and pulsed (b) generation.

The delay until the next X recombination (the stop signal) occurs depends on the rate at which the QD is repopulated. The corresponding simulation is performed by first finding the steady state values of the reservoir populations, and then initiating the QD in the empty microstate. From (4.16), the probability of a second X recombination is proportional to the single exciton microstate population. In summary,

$$g^{(2)}(t) = \frac{n_{1,1}(t)}{n_{1,1}(t \rightarrow \infty)} \Big|_{n_{1,1}(0)=1}. \quad (4.18)$$

For cross-correlation simulations, separate simulations for the positive and negative delay times are performed. Table 4.1 shows the procedure of performing various auto-

Table 4.1: The table shows in which microstate (A) the QD is initiated at $t = 0$, and which microstate population (B) is monitored to form the simulated $g^{(2)}$ function, when simulating a photon correlation measurement with the Start and Stop signals.

Start, Stop	$t > 0$		$t < 0$	
	A	B	A	B
X,X	$n_{0,0}$	$n_{1,1}$	$n_{0,0}$	$n_{1,1}$
X-,X-	$n_{1,0}$	$n_{2,1}$	$n_{1,0}$	$n_{2,1}$
XX,XX	$n_{1,1}$	$n_{2,2}$	$n_{1,1}$	$n_{2,2}$
XX,X	$n_{1,1}$	$n_{1,1}$	$n_{0,0}$	$n_{2,2}$
X-,X	$n_{1,0}$	$n_{1,1}$	$n_{0,0}$	$n_{2,1}$
XX,X-	$n_{1,1}$	$n_{2,1}$	$n_{1,0}$	$n_{2,2}$

and cross-correlation simulations, where

$$g^{(2)}(t) = \frac{n_B(t)}{n_B(t \rightarrow \infty)} \bigg|_{n_A(0)=1}. \quad (4.19)$$

5

Modelling Excitons in Quantum Dots

In Chapter 1, I discussed the electronic structure of excitons in T_d symmetry of e.g. the ZB crystal structure. In a QD, however, the symmetry is generally reduced, which leads to a change of the electronic structure. In this chapter, I discuss how the Hamiltonian for excitons in QDs of reduced symmetry can be written. Starting with the effects of strain on the electronic structure of QD excitons, I will then discuss the effects of exchange interaction, and their combined effects. Finally, excitons subjected to a magnetic field are considered. With these perturbations, the total Hamiltonian of a QD exciton can be written

$$H = H_0 + H_{\text{strain}} + H_{\text{exchange}} + H_{\text{B}}, \quad (5.1)$$

where H_0 describes the quantized energy levels of the QD arising from the three-dimensional confinement of the excitons, as described in chapter 4, and the exciton binding energy. In the following, the H_0 term is neglected, focusing instead on the last three terms of (5.1), which describe the effects of strain, exchange interaction and magnetic fields on the excitons, respectively. The eigenvalues and eigenstates are obtained by solving the secular equation

$$\det(H - E_j I) = 0, \quad (5.2)$$

where E_j are the eigenvalues of the Hamiltonian.

5.1 Strained quantum dots

Since QDs are generally formed as heterostructures between different materials, a lattice mismatch usually arises as a consequence. Such a lattice mismatch will induce strain in the QDs, which may significantly alter their electronic structure. To model

the effects of strain on the electronic structure of the eight exciton states, the following Hamiltonian (sometimes called the *Bir-Pikus* Hamiltonian) [169, 170] may be used:

$$H_{\text{strain}} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \begin{bmatrix} P+Q & -S & R & 0 \\ -S^* & P-Q & 0 & R \\ R^* & 0 & P-Q & S \\ 0 & R^* & S^* & P+Q \end{bmatrix}, \quad (5.3)$$

which is given in the $|m_z^h, m_z^e\rangle = \{|\frac{3}{2}, \frac{1}{2}\rangle, |\frac{1}{2}, \frac{1}{2}\rangle, |-\frac{1}{2}, \frac{1}{2}\rangle, |-\frac{3}{2}, \frac{1}{2}\rangle, |\frac{3}{2}, -\frac{1}{2}\rangle, |\frac{1}{2}, -\frac{1}{2}\rangle, |-\frac{1}{2}, -\frac{1}{2}\rangle, |-\frac{3}{2}, -\frac{1}{2}\rangle\}$ basis, where $m_z^{e,h}$ are the total angular momentum z-projection quantum numbers for the electron and hole. Here

$$\begin{aligned} P &= a_v(\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}), \\ Q &= b\left(\frac{\epsilon_{xx} + \epsilon_{yy}}{2} - \epsilon_{zz}\right), \\ R &= \frac{\sqrt{3}}{2}b(\epsilon_{xx} - \epsilon_{yy}) - id\epsilon_{xy}, \\ S &= -d(\epsilon_{xz} - i\epsilon_{yz}), \end{aligned} \quad (5.4)$$

where ϵ_{ij} are the strain components and a_v , b and d are the deformation potentials. The x,y-plane is defined as the plane of biaxial strain, and the z-axis as the axis of uniaxial strain. In strained QDs, z often coincides with the high-symmetry (or principal) axis of the QD.

The P component represents the hydrostatic strain. From (5.3) it is clear that while the hydrostatic strain shifts the energies of the exciton states, it does not split them. The Q parameter, however, causes a splitting between the HH ($m_z^h = 3/2$) and LH ($m_z^h = 1/2$) excitons. This occurs in both cases of uniaxial and biaxial strain. In Stranski-Krastanov grown QDs, for example, the strain is predominantly biaxial, and is compressive for the majority of conventional material systems.[171] From equation (5.3), such biaxial compressive strain leads to a HH ground state. In the context of this thesis, however, the uniaxial strain case is more relevant. As discussed in chapter 3, in a radially heterostructured nanowire (a core/shell nanowire), the dominant strain component is the uniaxial strain along the nanowire axis. This uniaxial strain is tensile (compressive) in the regions with a relatively smaller (larger) lattice constant. QDs embedded in a core/shell nanowire will, therefore, experience uniaxial strain. Moreover, QDs formed in GaNAs nanowires experience an additional local strain which is also uniaxial along the nanowire axis.[37] Due to the smaller lattice constant in N-rich regions as compared with their surroundings, the strain experienced by such QDs is tensile, i.e. $\epsilon_{zz} > 0$. The effects of such a uniaxial tensile strain on the electronic structure are shown in Fig. 5.1 (the red lines). The uniaxial tensile strain leads to a HH ground state.

The R and S components in (5.3)-(5.4) represent the in-plane strain anisotropy ($\epsilon_{xx} \neq \epsilon_{yy}$) and shear strain, and may further lift the degeneracy of the exciton states, but will not be discussed here.

Figure 5.1: A schematic diagram showing the electronic structure of excitons when the dominant perturbation is the exchange interaction (the blue lines on the right) and uniaxial tensile strain (the red lines on the left). When the strain is dominating, the evolution of the electronic structure under additional exchange interaction is also shown (the purple lines, left). The coefficients a and b obey $a > b$. The figure is adapted from Paper V.

5.2 Exchange interaction

Here, I will describe the exchange interaction term of the Hamiltonian, H_{exchange} , which is written

$$H_{\text{exchange}} = - \sum_{i=x,y,z} (a_i J_{h,i} S_{e,i} + b_i J_{h,i}^3 S_{e,i}), \quad (5.5)$$

where $J_{h,i}$ and $S_{e,i}$ are the i -projections of the total angular momentum of the hole and electron, respectively. The a_i -terms and b_i -terms describe the isotropic and anisotropic exchange interaction, respectively, where $a_i > b_i$ is generally expected. In the matrix representation, using the basis of the total and z -projection angular momentum quantum numbers: $|j_e, m_z^e\rangle = \{|\frac{1}{2}, \frac{1}{2}\rangle, |\frac{1}{2}, -\frac{1}{2}\rangle\}$, the angular momentum operators for the electrons are given by

$$S_{e,x} = \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad S_{e,y} = \frac{1}{2i} \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}, \quad S_{e,z} = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad (5.6)$$

and in the basis $|j_h, m_z^h\rangle = \{|\frac{3}{2}, \frac{3}{2}\rangle, |\frac{3}{2}, \frac{1}{2}\rangle, |\frac{3}{2}, \frac{-1}{2}\rangle, |\frac{3}{2}, \frac{-3}{2}\rangle\}$ the operators for the holes are

$$J_{h,x} = \frac{1}{2} \begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix}, \quad J_{h,y} = \frac{1}{2i} \begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 2 & 0 \\ 0 & -2 & 0 & \sqrt{3} \\ 0 & 0 & -\sqrt{3} & 0 \end{bmatrix}, \quad (5.7)$$

$$J_{h,z} = \frac{1}{2} \begin{bmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{bmatrix}.$$

To form the Hamiltonian (5.5) in the matrix representation, the operators form a Kronecker product: $S_{e,i} \otimes J_{h,i}$ and $S_{e,i} \otimes J_{h,i}^3$, whereby the 8x8 matrix with the basis $|m_z^h, m_z^e\rangle = \{|\frac{3}{2}, \frac{1}{2}\rangle, |\frac{1}{2}, \frac{1}{2}\rangle, |\frac{-1}{2}, \frac{1}{2}\rangle, |\frac{-3}{2}, \frac{1}{2}\rangle, |\frac{3}{2}, \frac{-1}{2}\rangle, |\frac{1}{2}, \frac{-1}{2}\rangle, |\frac{-1}{2}, \frac{-1}{2}\rangle, |\frac{3}{2}, \frac{-1}{2}\rangle\}$ is formed.

Initially focusing on the case where strain (or hole confinement) is a strong perturbation, whereby the LH and HH are well separated and where the HH is the ground state, the Hamiltonian is simplified by considering only the HH basis states in (5.7). This leads to a Hamiltonian in the explicit form

$$H_{\text{exchange}}^{\text{HH}} = \frac{1}{2} \begin{bmatrix} -\delta_0 & 0 & 0 & \delta_2 \\ 0 & \delta_0 & \delta_1 & 0 \\ 0 & \delta_1 & \delta_0 & 0 \\ \delta_2 & 0 & 0 & -\delta_0 \end{bmatrix}, \quad (5.8)$$

which is given in the $|M\rangle = \{|+2\rangle, |+1\rangle, |-1\rangle, |-2\rangle\}$ basis, where M is the z-projection of the total angular momentum of the exciton. The coefficients δ_i are expressed by the coefficients for the isotropic and anisotropic exchange interactions, a_i and b_i , from equation (5.5) as

$$\begin{aligned} \delta_0 &= \frac{1}{2} \left(3a_z + \frac{27}{4}b_z \right), \\ \delta_1 &= -\frac{3}{4}(b_x - b_y), \\ \delta_2 &= -\frac{3}{4}(b_x + b_y). \end{aligned} \quad (5.9)$$

Conveniently, the pure LH states may be described by a Hamiltonian of the same form as in (5.8), but given in the $|M\rangle = \{|+1\rangle, |0_+\rangle, |0_-\rangle, |-1\rangle\}$ basis and with the coefficients

$$\begin{aligned} \delta_0 &= \frac{1}{8}(4a_z + b_z), \\ \delta_1 &= -(a_x + a_y) - \frac{5}{2}(b_x + b_y), \\ \delta_2 &= -(a_x - a_y) - \frac{5}{2}(b_x - b_y). \end{aligned} \quad (5.10)$$

The electronic structure of the HH and LH states resulting from such exchange interaction is shown with the purple lines in Fig. 5.1. With the isotropic exchange interaction,

the four-fold degenerate HH ground states split into two energy levels containing the dark ($|\pm 2\rangle$) and bright ($|\pm 1\rangle$) states, respectively. For the LH excitons, the isotropic exchange interaction leads to the two-fold degenerate $|\pm 1\rangle$ and to the non-degenerate $|0_+\rangle$ and $|0_-\rangle$ states, where only the latter is dark. As a result of further symmetry reduction by including the anisotropic exchange interaction, the two-fold degenerate levels, $|\pm 1\rangle$ of both the HH and LH states, experience the so-called *fine-structure splitting* (FSS), and split into two levels with states of the form $|1\rangle \pm |-1\rangle$. Recombination of such excitons will result in light linearly polarized in the x,y-plane of the QD (normal to the its principal axis).

If the exchange interaction is the dominant perturbation, the $|J, M\rangle$ basis should be used, where J and M are the total and z-projection angular momentum quantum numbers of the exciton. The eigenstates obtained from equation (5.2) can readily be transformed to this basis by the use of the Clebsch-Gordan coefficients. The transformation of the exciton state Φ in the $|m_z^h, m_z^e\rangle$ basis to the state Ψ in the $|J, M\rangle = \{|1, -1\rangle, |1, 0\rangle, |1, 1\rangle, |2, -2\rangle, |2, -1\rangle, |2, 0\rangle, |2, 1\rangle, |2, 2\rangle\}$ basis is performed using the transformation matrix

$$\Psi = \begin{bmatrix} 0 & 0 & 0 & -\sqrt{3}/2 & 0 & 0 & 1/2 & 0 \\ 0 & 0 & -1/\sqrt{2} & 0 & 0 & 1/\sqrt{2} & 0 & 0 \\ 0 & -1/2 & 0 & 0 & \sqrt{3}/2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1/2 & 0 & 0 & \sqrt{3}/2 & 0 \\ 0 & 0 & 1/\sqrt{2} & 0 & 0 & 1/\sqrt{2} & 0 & 0 \\ 0 & \sqrt{3}/2 & 0 & 0 & 1/2 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \Phi. \quad (5.11)$$

The right-hand side (the blue lines) of Fig. 5.1 shows the impact of a dominant exchange interaction on the exciton states. When the isotropic exchange interaction parameters, a_i , are equal but non-zero, the eight-fold degeneracy is lifted, splitting the exciton states into the $J = 1$ and $J = 2$ levels, with bright and dark excitons, respectively. Often, the exchange interaction in QDs is stronger in one direction, due to the reduced symmetry of the QD. This causes a further splitting of the exciton states into five separate energy levels, as shown in Fig. 5.1. Notably, the $J = 1$ states are now split into two levels, with $M = \pm 1$ and $M = 0$, respectively. Recalling equation (1.20), we note that light emitted by a recombination of the $M = \pm 1$ excitons will result in circularly polarized light, while recombination of excitons with $M = 0$ yields linearly polarized light. Therefore, the origin of the excitonic states participating in light emission can be distinguished experimentally. Moreover, under this reduced symmetry, the $|1, \pm 1\rangle$ and $|2, \pm 1\rangle$ states mix, making the dark states *partially bright*, as shown by the thin lines in the figure. If the in-plane symmetry is broken,[172] the anisotropic exchange interaction parameters, b_i , must be considered. In that case all eight states can be non-degenerate, as shown in Fig. 5.1. The eigenstates are then better described in the Cartesian basis, $|J, M_i\rangle$, where $i = x, y$, as defined in the figure. The light emitted through the recombination of such excitons is no longer circularly polarized, but linearly polarized in the x,y-plane normal to the principal axis of the QD.

5.3 Excitons in a magnetic field

The exciton states are very sensitive to a magnetic field. Therefore, subjecting the QDs to an external magnetic field is a very useful technique to reveal their electronic structure. The Hamiltonian describing the excitons in a magnetic field is written

$$H_B = \mu_B \sum_{i=x,y,z} (g_{e,i} S_{e,i} + K J_{h,i} + L J_{h,i}^3) B_i + \gamma |\mathbf{B}|^2, \quad (5.12)$$

where μ_B is the Bohr magneton, $g_{e,i}$ is the electron Landé g-value, K and L describe the isotropic and anisotropic hole interactions with the field, and γ is the diamagnetic coefficient. [173] To write equation (5.12) in an 8×8 matrix form, a Kronecker product between the angular momentum operator matrices and the 4×4 and 2×2 identity matrices is performed. The last term in equation (5.12), represents the diamagnetic shift, which does not split the exciton states.

Figure 5.2 illustrates how a magnetic field influences excitons in a QD dominated by the isotropic exchange interaction. For a magnetic field in the z-direction (the left panel of Fig. 5.2), the exciton states do not mix (with the exception of the $M = 0$ states), but all degeneracies are lifted. When the magnetic field is applied in the x- or y-directions, all degeneracies are similarly lifted and, in addition, a significant mixing between the various states occurs as shown in the right panel of Fig. 5.2 (the red lines). This mixing has two important consequences: (i) all bright excitons now emit linearly polarized light, and (ii) the $(|2, \pm 2\rangle)$ are now partially bright. In fact, with an increasing B_x or B_y , the oscillator strength of all the four lowest exciton states increases.

It is worth investigating the special case when the HH and LH states are energetically well separated, through e.g. strain or hole confinement. When considering only the HH exciton states, the Hamiltonian of (5.12) can be simplified by replacing the K and L parameters with an effective g-value of the hole, which is

$$\begin{aligned} g_{h,x} &= -\frac{3}{2}L, \\ g_{h,z} &= -3K - \frac{27}{4}L, \end{aligned} \quad (5.13)$$

in the x- and z-directions, respectively, resulting in the Hamiltonians in the explicit forms

$$\begin{aligned} H_B^x &= \frac{\mu_B B_x}{2} \begin{bmatrix} 0 & -g_{h,x} & g_{e,x} & 0 \\ -g_{h,x} & 0 & 0 & g_{e,x} \\ g_{e,x} & 0 & 0 & -g_{h,x} \\ 0 & g_{e,x} & -g_{h,x} & 0 \end{bmatrix}, \\ H_B^z &= \frac{\mu_B B_z}{2} \begin{bmatrix} g_{e,z} - g_{h,z} & 0 & 0 & 0 \\ 0 & g_{e,z} + g_{h,z} & 0 & 0 \\ 0 & 0 & -g_{e,z} - g_{h,z} & 0 \\ 0 & 0 & 0 & -g_{e,z} + g_{h,z} \end{bmatrix} \end{aligned} \quad (5.14)$$

Figure 5.2: A schematic diagram showing the electronic structure of excitons perturbed by isotropic exchange interaction and a magnetic field in the x- (the red lines on the right) and z-directions (the blue lines on the left), where z is the principal axis of the QD. The thick and thin lines represent optically active excitons, where the latter is only weakly active. The dotted lines represent dark states. The figure is adapted from Paper V.

for a magnetic field applied in the x- or z-directions, given in the $|m_z^h, m_z^e\rangle = \{|\frac{3}{2}, \frac{1}{2}\rangle, |\frac{-3}{2}, \frac{1}{2}\rangle, |\frac{3}{2}, \frac{-1}{2}\rangle, |\frac{-3}{2}, \frac{-1}{2}\rangle\}$ basis.

Figure 5.3 shows a schematic diagram of the HH exciton states under the influence of a magnetic field. At $B=0$ the exchange interaction splits the four states into two levels where the higher energy states ($|\pm 1\rangle$) are bright. Similarly to the exchange interaction-dominated QDs in Fig. 5.2, the states become completely non-degenerate upon interaction with the magnetic field. Again, a magnetic field in the z-direction does not induce any mixing between the states, resulting in σ^+ and σ^- polarized emission from the bright excitons. A magnetic field in the x-direction causes a mixing between the exciton states, which results in π_x and π_y linearly polarized emission. Moreover, the formerly dark states become partially bright.

The last term in equation (5.12) represents the diamagnetic shift. This term causes an equal shift proportional to B^2 of all exciton energies. The diamagnetic coefficient, γ , depends on the distribution of the electron and hole wavefunctions, and their effective

Figure 5.3: A schematic diagram of the electronic structure of pure HH excitons perturbed by isotropic exchange interaction and a magnetic field in the x- (the red lines on the right) or z-directions (the blue lines on the left), where z is the principal axis of the QD. The thick and thin lines represent optically active excitons, where the latter is only weakly active. The dotted lines represent the dark states. The figure is adapted from Paper V.

masses. For strongly confined excitons

$$\gamma = \frac{e^2}{8} \left(\frac{\langle r_e^2 \rangle}{m_e} + \frac{\langle r_h^2 \rangle}{m_h} \right), \quad (5.15)$$

where $\langle r_{e,h} \rangle$ represent the extent of the wavefunctions, $m_{e,h}$ are the effective masses, and e is the elementary charge. The γ coefficient, therefore, contains information regarding the sizes of the QDs.

6

Experimental Techniques

This chapter gives an overview of the most important experimental techniques used in the work included in this thesis.

6.1 Electron microscopy

An inherent problem in the investigation of nanostructured materials is that the structures are too small to be easily observed, often smaller than the spatial resolution of optical microscopes, which is limited by the wavelength of the light. Generally, shorter wavelengths of the imaging radiation lead to a better resolution. In light microscopy the wavelengths are relatively large — the wavelengths of visible light ranges between approximately 400 and 700 nm. However, in electron microscopy the wavelengths can be much smaller, meaning that the resolution is generally better. Two of the most common electron microscopy techniques are the *scanning electron microscopy* (SEM) and the *transmission electron microscopy* (TEM) techniques.

Scanning electron microscopy

In SEM, an electron beam is focused and scanned over the sample surface. The signal may be acquired in various ways, for example by detecting so-called secondary electrons, released by the atoms in the sample upon interaction with the electron beam. For a fixed position of the detector, the number of detected secondary electrons will vary depending on the topography of the sample surface, thereby creating the image contrast. Figure 6.1a shows a typical SEM micrograph of an array of approximately 100 nm thin nanowires.

Figure 6.1: Micrographs acquired from GaNAsP nanowires. (a) shows an overview SEM image of as-grown GaNAsP nanowires. (b) shows a TEM micrograph of a single GaNAsP nanowire, with insets showing high magnification images of parts of the same nanowire. Figure (a) is adapted from Paper I, while (b) is adapted from Paper II.

Transmission electron microscopy

In TEM, the electron beam is, similarly, scanned over the sample, but here the transmitted beam is used to form the image. While SEM is a surface and topography sensitive technique, TEM may be used to probe the interior of the structure. In particular, information about the crystal structure and structural defects of the material may be obtained.

Figure 6.1b shows a typical TEM micrograph acquired from a GaNAsP nanowire, where the insets show high magnification images of the same nanowire, where the individual lattice planes are visible.

6.2 Spectroscopy techniques

In a broad sense, spectroscopy encompasses the study of the spectrum of electromagnetic radiation—light, where the studied light generally has interacted with matter through emission, reflection or absorption. By studying the resulting spectrum of the light, properties of the matter may be deduced. Here, several different spectroscopy techniques, which have been employed in this thesis work, are discussed.

Photoluminescence spectroscopy

In PL spectroscopy, the sample is excited with light, often from a laser, whereby charge carriers (and other excitations of the matter) are generated. The light emitted upon recombination by the charge carriers constitutes the signal, which may be analyzed using a monochromator coupled with a light detector, such as a photodiode or a charge coupled device (CCD) camera. The spectrum is acquired by tuning the monochromator to detect the desired range of wavelengths. The analyzed spectrum may provide details about e.g. the electronic structure of the material. PL spectroscopy is a versatile technique, which may be set up in various different ways.

One particular type of PL spectroscopy is micro-PL (μ PL) spectroscopy. A typical μ PL setup is shown in Fig. 6.2. The excitation light beam (the blue, wavy line), generated by a laser, is reflected by a beam splitter, and focused by a microscope lens, providing a spot size which may be less than one μm in diameter. The objective lens also collects the PL emitted from the sample (the red, wavy line in the figure). The collected PL is then guided to the monochromator and detector. For polarization resolved detection or excitation, polarization optics may be placed in front of the laser or monochromator, respectively. Linearly (circularly) polarized excitation/detection is provided by a half (quarter) wave plate in combination with a linear polarizer.

Figure 6.2: A drawing of a typical μ PL setup. The excitation light beam is shown in blue, while the emitted light is shown in red.

Using a cw laser for excitation does not provide any information about the PL dynamics of the sample. This can be obtained by instead employing time-resolved PL (trPL). To measure the trPL signal, a pulsed laser must be used for excitation, while e.g. a streak camera or a time-correlated single-photon counting (TCSPC) unit may be used to reveal the time-resolved signal.

Another variation of PL spectroscopy is photoluminescence excitation (PLE) spectroscopy. In PLE experiments, the excitation wavelength, rather than the detection wavelength, is changed during the measurements, providing insight into the absorption processes in the sample.

Cathodoluminescence spectroscopy

In cathodoluminescence (CL) spectroscopy, the excitation of the sample is done by using a beam of energetic electrons. An advantage of the CL spectroscopy technique is the excellent spatial resolution which may be achieved due to the short wavelength of the electrons. In fact, CL spectroscopy is often performed using a SEM, which makes it possible to correlate spectroscopic properties with structural features.

Raman spectroscopy

In Raman spectroscopy, Raman scattering (which is discussed in Chapter 1) is used to probe the material properties. The spectrum of light scattered in the inelastic Raman scattering process is governed by the Raman scattering selection rules and by the phonon dispersion of the material. The Raman spectroscopy setup is similar to that used for PL spectroscopy (Fig. 6.2), but requires a very sharp edge filter to suppress the much stronger elastic Rayleigh scattering signal.

6.3 Optically detected magnetic resonance

Optically detected magnetic resonance (ODMR) is an electron spin resonance technique that employs optical detection to gain information about the origin of defects and impurities in the material.[174] The optical detection in spin resonance measurements provides several advantages over non-optical spin resonance techniques, where the absorption of microwave radiation is instead measured. For example, while the microwave absorption in nanostructured materials may be too weak to be detected, their luminescence may be strong, facilitating optical detection. Moreover, using ODMR it is possible to determine if the defect functions as a radiative or NR center.

Figure 6.3a shows a schematic drawing of an ODMR setup, where the magnetic field is applied between the N and S poles of the magnet. Optical excitation is generally performed using laser light, and detection is done by a photodiode in phase-lock with the modulation of the microwave radiation.

During an ODMR measurement, the sample is subjected to an applied external magnetic field, which splits the defect energy level into spin sublevels (Fig. 6.3b). At a certain magnetic field strength, the sublevel splitting matches the energy of the microwave radiation, whereby electrons are excited from one sublevel to another. Consequently the PL of the sample may be affected, generating an ODMR signal (Fig. 6.3c).

The ODMR signal may be modeled using the spin-Hamiltonian

$$H = \mu_B \mathbf{B} \mathbf{g} \mathbf{S} + \mathbf{S} \mathbf{A} \mathbf{I}. \quad (6.1)$$

In the first term on the right hand side, representing the Zeeman splitting, μ_B is the Bohr magneton, $\mathbf{B}$ is the applied magnetic field, $\mathbf{g}$ is the electron g-tensor, $\mathbf{S}$ is the electron spin operator. In the second term, representing the hyperfine interaction, $\mathbf{I}$

Figure 6.3: The ODMR setup. (a) shows a schematic illustration of an ODMR setup. (b) shows the magnetic field dependence of two spin sublevels, split by the Zeeman interaction. At a certain magnetic field value, the energy splitting is equal to the energy of the applied microwave radiation, illustrated by the red arrow. (c) shows a possible resulting ODMR spectrum, where the negative signal illustrates the case when the defect is a NR recombination center.

is the nuclear spin operator, and $\mathbf{A}$ is the hyperfine tensor. This term is particularly useful for chemical identification of the defect.

6.4 The Hanbury Brown and Twiss experiment

The Hanbury Brown and Twiss (HBT) experiment measures the time-correlation of photons in a beam of light.[175] Though initially intended for astronomical measurements, the HBT experiment has proven to be a powerful technique to investigate emitters of non-classical light.

Figure 6.4: A schematic drawing of an HBT setup.

A diagram of the setup is shown in Fig. 6.4. The initial light beam (the solid arrow) is split into two beams (the dotted arrows) by a beam splitter (BS). The beams are then

dispersed by two monochromators and detected by two detectors, e.g. avalanche photodiodes. The signals from the detectors (the solid lines) are led to TCSPC electronics, where they constitute the start and stop signals, respectively. The stop signal is delayed by a time τ before reaching the TCSPC electronics. From such measurements, the second-order coherence function, $g^{(2)}$, is measured by creating a histogram of delay times between the arrival of the start and stop signals.

By using separate monochromators in the two detection arms, it is possible to independently select wavelengths of detected light in the two arms. If the two monochromators are set to detect the same wavelength of light, an *auto-correlation* measurement is performed. This is useful when investigating SPEs, e.g. QDs. Since only one photon may be emitted at a time from a perfect SPE, $g^{(2)}(0) = 0$. When the two monochromators are set to detect light of different wavelengths, e.g. the light emitted due to the recombination of two different excitonic complexes in the same QD, a *cross-correlation* measurement is performed. In a cross-correlation measurement, the two emission lines stem from the same quantum emitter if $g^{(2)}(0) < 1$. A cross-correlation measurement between different excitonic complexes may also provide valuable insights into the capture and recombination processes of the QD.

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Publications

List of publications included in the thesis

- I **Effects of Nitrogen Incorporation on Structural and Optical Properties of GaNAsP Nanowires**
M. Jansson, S. Chen, R. La, J. E. Stehr, C. W. Tu, W. M. Chen, and I. A. Buyanova,
J. Phys. Chem. C, **121**, 7047 (2017)
 DOI: 10.1021/acs.jpcc.7b00985
- II **Increasing N content in GaNAsP nanowires suppresses the impact of polytypism on luminescence**
M. Jansson, L. Francaviglia, R. La, R. Balagula, J. E. Stehr, C. W. Tu, A. Fontcuberta i Morral, W. M. Chen, and I. A. Buyanova,
Nanotechnology, **30**, 405703 (2019)
 DOI: 10.1088/1361-6528/ab2cdb
- III **Gallium vacancies — common non-radiative defects in ternary GaAsP and quaternary GaNAsP nanowires**
 J. E. Stehr, **M. Jansson**, R. La, C. W. Tu, W. M. Chen, and I. A. Buyanova,
Submitted manuscript
- IV **Strongly polarized quantum-dot-like light emitters embedded in GaAs/GaNAs core/shell nanowires**
 S. Filippov, **M. Jansson**, J. E. Stehr, J. Palisaitis, P. O. Å. Persson, F. Ishikawa, W. M. Chen, I. A. Buyanova,
Nanoscale, **8**, 15939 (2016)
 DOI: 10.1039/C6NR05168E
- V **N-induced Quantum Dots in GaAs/Ga(N,As) Core/Shell Nanowires: Symmetry, Strain, and Electronic Structure**
M. Jansson, F. Ishikawa, W. M. Chen, I. A. Buyanova,
Phys. Rev. Appl., **10**, 044040 (2018)
 DOI: 10.1103/PhysRevApplied.10.044040
- VI **Formation, electronic structure, and optical properties of self-assembled quantum-dot single-photon emitters in Ga(N,As,P) nanowires**
M. Jansson, L. Francaviglia, R. La, C. W. Tu, W. M. Chen, I. A. Buyanova,
Phys. Rev. Mater. **4**, 056005 (2020)
 DOI: 10.1103/PhysRevMaterials.4.056005
- VII **Generation and recombination dynamics of single-photon emitters embedded in GaNAsP nanowires**
M. Jansson, R. La, C. W. Tu, W. M. Chen, I. A. Buyanova,
Submitted manuscript

Brief summary of the included papers

In the first three papers (I-III), we investigate the structural and optical properties of GaNAsP nanowires, with particular emphasis on the recombination processes in the material. Paper I discusses the effects of nitrogen incorporation on the structural quality, the alloy uniformity, and the overall optical properties of the nanowires. We show that nitrogen incorporation up to 0.16% does not degrade the overall structural quality and compositional uniformity of the nanowires, but has pronounced effects on the recombination processes. Paper II investigates the effects of polytypism and structural defects on the optical quality of the nanowires, and how nitrogen incorporation influences their impact. Interestingly, we see that while the nitrogen content does not affect the density of structural defects, an increasing nitrogen incorporation appears to reduce the rate of non-radiative recombination induced by the defects. Paper III shows the presence of gallium vacancy defects in the nanowires. The defects are shown to act as non-radiative centers, and their formation appears to be promoted by the presence of nitrogen.

In the last four papers (IV-VII) we investigate the properties of self-assembled quantum dots, which form as a consequence of nitrogen incorporation in Ga(N,As,P) nanowires. Paper IV investigates their formation mechanism and optical properties. We show that the quantum dot formation mainly occurs in the bulk of the nanowires, rather than at their surface, and that the formation is promoted by the presence of structural polymorphism. The quantum dots are shown to produce ultra-narrow and highly polarized emission lines. In papers V and VI we investigate the formation mechanism and the electronic structure of quantum dots embedded in GaNAs and GaNAsP nanowires, respectively, and show that the host alloy has a strong impact on their properties. Specifically, the orientation of the quantum dot principal axis and the electronic character of the captured holes is dependent on the host material. Paper VI also shows that quantum dots formed in GaNAsP nanowires are single photon emitters. Finally, paper VII investigates the capture and recombination dynamics of dilute nitride quantum dots. We show that the presence of hole-attractive defect centers in the vicinity of some quantum dots greatly alter their properties. Specifically, the negatively charged exciton is promoted by interaction with the defect.

My contributions to the papers

For paper I and IV, I performed most of the optical measurements, for paper III, I performed the PL measurements and some of the magnetic resonance measurements. For all other papers I performed all optical measurements. For all papers, I performed the SEM imaging, and participated in the TEM imaging.

For all papers, I participated in the data analysis together with my co-authors. I performed all simulations in papers V-VII. For papers I, II, V, VI and VII, I wrote the first version of the manuscript, while for the other papers I contributed to the writing of the manuscripts together with my co-authors.

List of publications excluded from the thesis

- i **Effects of growth temperature and thermal annealing on optical quality of GaNAs nanowires emitting in the near-infrared spectral range**
J. E. Stehr, R. M. Balagula, **M. Jansson**, M. Yukimune, R. Fujiwara, F. Ishikawa, W. M. Chen, I. A. Buyanova
Nanotechnology, **31**, 065702 (2020)
DOI: 10.1088/1361-6528/ab51cd
- ii **Effects of Bi incorporation on recombination processes in wurtzite GaBiAs nanowires**
B. Zhang, **M. Jansson**, P.-P. Chen, X. Wang, W. M. Chen, I. A. Buyanova
Nanotechnology, **31**, 225706 (2020)
DOI: 10.1088/1361-6528/ab76f0
- iii **Effects of thermal annealing on localization and strain in core/multishell GaAs/GaNAs/-GaAs nanowires**
R. M. Balagula, **M. Jansson**, M. Yukimune, J. E. Stehr, F. Ishikawa, W. M. Chen, I. A. Buyanova
Sci. Rep., **10**, 8216 (2020)
DOI: 10.1038/s41598-020-64958-6
- iv **Molecular beam epitaxial growth of dilute nitride GaNAs and GaInNAs nanowires**
M. Yukimune, R. Fujiwara, T. Mita, N. Tsuda, J. Natsui, Y. Shimizu, **M. Jansson**, R. Balagula, W. M. Chen, I. A. Buyanova, and F. Ishikawa
Nanotechnology, **30**, 244002 (2019)
DOI: 10.1088/1361-6528/ab0974
- v **GaAs/GaNAs core-multishell nanowires with nitrogen composition exceeding 2%**
M. Yukimune, R. Fujiwara, H. Ikeda, K. Yano, K. Takada, **M. Jansson**, W. M. Chen, I. A. Buyanova, and F. Ishikawa
Appl. Phys. Lett., **113**, 011901 (2018)
DOI: 10.1063/1.5029388
- vi **Self-catalyzed core-shell GaAs/GaNAs nanowires grown on patterned Si (111) by gas-source molecular beam epitaxy**
R. La, R. Liu, W. Yao, R. Chen, **M. Jansson**, J. L. Pan, I. A. Buyanova, J. Xiang, S. A. Dayeh, and C. W. Tu
Appl. Phys. Lett., **111**, 072106 (2017)
DOI: 10.1063/1.4990821
- vii **Dilute Nitride Nanowire Lasers Based on a GaAs/GaNAs Core/Shell Structure**
S. Chen, **M. Jansson**, J. E. Stehr, Y. Huang, F. Ishikawa, W. M. Chen, and I. A. Buyanova,
Nano Lett., **17**, 1775 (2017)
DOI: 10.1021/acs.nanolett.6b05097
- viii **Characterization of quantum dot-like emission from GaAs/GaNAs core/shell nanowires**
M. Jansson, W. M. Chen, I. A. Buyanova, F. Ishikawa
2016 IEEE 16th International Conference on Nanotechnology (IEEE-NANO), 42 (2016)
DOI: 10.1109/NANO.2016.7751294
- ix **Core-shell and exciton transfer in GaAs/GaNAs coaxial nanowires**
S. Chen, **M. Jansson**, S. Filippov, F. Ishikawa, W. M. Chen, and I. A. Buyanova,
J. Vacuum Sci. and Technol. B, **34**, 04J194 (2016)
DOI: 10.1116/1.4953184
- x **Defect formation in GaAs/Ga_{N_xAs_{1-x}} core/shell nanowires**
J. E. Stehr, **M. Jansson**, F. Ishikawa, W. M. Chen, and I. A. Buyanova,

Appl. Phys. Lett., **109**, 203103 (2016)

DOI: 10.1063/1.4967721

xi **Solar Driven Energy Conversion Applications Based on 3C-SiC**

J. W. Sun, V. Jokubavicius, L. Gao, I. D. Brooker, **M. Jansson**, X. Y. Liu, J. P. Hofmann, E. J. M. Hensen, M. K. Linnarsson, P. Wellmann, I. Ramiro, A. Marti, R. Yakimova, M. Syväjärvi
Materials Science Forum **858**, 1028 (2016)

DOI: 10.4028/www.scientific.net/MSF.858.1028

xii **Cubic silicon carbide as a potential photovoltaic material**

M. Syväjärvi, Q. Ma, V. Jokubavicius, A. Galeckas, J. Sun, X. Li, **M. Jansson**, P. Wellman, M. Linnarsson, P. Runde, B. A. Johansen, A. Thorgeresen, S. Diplas, P. A. Carvalho, O. M. Lovvik, D. N. Wright, A. Y. Azarov, and B. G. Svensson,

Solar Energy Materials and Solar Cells, **145**, 104 (2016)

DOI: 10.1016/j.solmat.2015.08.029

Papers

The papers associated with this thesis have been removed for copyright reasons. For more details about these see:

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-166357>

Ett av dagens hetaste forskningsområden är att hitta material som kan omvandla ljus till elektricitet, eller omvänt elektricitet till ljus, på ett effektivt sätt. För det ändamålet passar utspädda nitrider bra. Utspädda nitrider är legeringar mellan material såsom galliumarsenid med en liten mängd kväve. Genom att välja just hur mycket kväve som finns i legeringen kan man nämligen ändra vilken färg de utspädda nitriderna lyser i och absorberar. Nyligen har man lyckats framställa så kallade nanotrådar gjorda av utspädda nitrider. Nanotrådar är, precis som vanliga trådar, långa och smala strukturer, men är tusen gånger tunnare än ett hårstrå. Sådana nanotrådar har visat sig vara bättre än många andra former av material på att absorbera ljus. Dessutom så är det möjligt att tillverka nanotrådar ovanpå kisel, något som är mycket svårt med material i dess vanliga, platta form.

I denna avhandling undersöker jag sådana nanotråders egenskaper. Jag visar hur det spontant bildas så kallade kvantprickar i nanotrådarna, vilka inte bara är positiva för ljuskällans effektivitet, utan även användbara i mer avancerade tillämpningsområden, till exempel i kvantdatorer. Jag ser dock att det uppstår ett antal olika defekter i nanotrådarna, som begränsar deras prestanda. För att utspädda nitridnanotrådar ska vara användbara i exempelvis solceller eller lysdioder så måste sådana defekter effektivt kunna undvikas.