Study of luminescence properties of single indium phosphide nanowires

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Study of luminescence properties of single indium phosphide nanowires

by

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Abstract

In this study, photoluminescence (PL) measurements are reported on single semiconducting pulsed laser deposition (PLD) grown indium phosphide (InP) nanowires. Luminescence has been performed at room temperature as well as low temperature. PL line shapes, measured with a high excitation intensity, have been investigated and a model, based on the product of a joint density of states and the Fermi-Dirac distribution for characterising the lineshapes is proposed. It shows that at high excitation intensities, the quasi-Fermi level lies in the band-gap due to the Burstein-Moss effect. Furthermore, the temperature in the wire rises significantly due to excitation.

With PL experiments performed at low excitation intensities and low temperatures a distinction can be made between i-InP, n-InP and p-InP. Band-to-band and defect-related emission has been observed for i-InP and n-InP nanowires. In contrast, p-InP shows a completely different spectrum. Besides a larger width, the emission line has been red shifted by 100 meV. These effects can be explained by band bending at the edges of the nanowire due to Fermi level pinning.

Furthermore, luminescence properties have been studied in the presence of an electric field. At room temperature we report a blue shift as well as an intensity increase by applying an electric field. We believe that this effect is due to surface charges compensating the electric field inside the wire. This is confirmed by electric field-effect measurements at low temperature, where the intensity increase is stable.

Finally, we compare the PL properties of PLD-grown InP nanowires and metal-organic chemical vapour deposition (MOCVD) grown InP nanowires. In contrast to the PLD-grown nanowires, bare MOCVD-grown nanowires show no luminescence at all. This is probably due to a large amount of non-radiative recombination. Capping these wires with GaP, a wide-band-gap material, significantly enhances the PL efficiency and takes away the band bending in p-InP nanowires.
Chapter 1

Introduction

This final thesis has been written as the last module to obtain the grade of Master of Applied Physics at the faculty of Applied Physics of Eindhoven University of Technology. The research has been done at Philips Research Laboratories Eindhoven and was supervised by dr. Erik Bakkers, dr. Aarnoud Roest and dr. Olaf Wunnicke and by prof. dr. H.W.M. Salemink at the Eindhoven University of Technology.

In the following sections a brief history and the current situation of the research field will be elucidated. Furthermore, motivations for doing this study will be given. Finally, a brief outline of this thesis will be explained.

1.1 Semiconductor nanowires

Low dimensional systems have attracted much interest, due to the tunability of their fundamental optical and electronical properties. Therefore they might be ideal building blocks for electrical and opto-electronic devices. The zero-dimensional version, nanocrystals or quantum dots, have been widely studied over the past years. However, implementation of nanocrystals into such devices has not yet been achieved, due to the difficulties arising with fabricating electrical contacts to a crystal.

In contrast, nanowires or nanotubes are confined in only two directions. Therefore they can be contacted relatively easily along the third direction. Furthermore, a nanowire by itself can act as an electrical lead. Yet it is clear that the confinement level is smaller in such structures. Carbon nanotubes are such one dimensional structures and they have shown to be potential building blocks for field effect transistors (FET)[1] and single electron transistors. However, the synthesis of carbon nanotubes has met major difficulties, since it is not yet possible to selectively grow semiconducting or metallic tubes[2]. The electrical properties of semiconductor nanowires are,
unlike carbon nanotubes, relatively easy to control. In order to fabricate such structures, two approaches can be followed, the so-called top-down or the bottom-up approach. With the former approach, nanowires are being etched out using standard lithographic techniques. In this way, aspect ratios of 100 can be achieved. With the latter approach nanowires are actually grown bottom-up on a substrate, achieving aspect ratios as high as 1000-10,000. An example of a bottom-up approach is the so-called vapour-liquid-solid (VLS) growth technique. The first VLS whisker growth is dated from 1964[3]. These whiskers had a diameter in the order of 1 μm. Currently the same method is used to grow III-V nanowires as well as nanotubes with a diameter ranging from 5 to 50 nm[4]. Furthermore the nanowires can be n-type or p-type doped with any kind of dopant.

Several devices have already been fabricated using semiconductor nanowires, including room-temperature single-nanowire FETs[5], single electron transistors[6], diodes[7] and logic gates[8]. Furthermore, Doh et al[9] reported supercurrents through InAs nanowires and lasing in ZnO, CdS and GaN nanowires[8, 10, 11] has been demonstrated. In addition, one can think of future devices, such as photonic crystals, by growing the nanowires vertically in a periodic structure, or a single photon source.

Recently all kinds of III-V nanowires have been grown epitaxially on silicon and germanium substrates, including indium arsenide on silicon, which has a lattice mismatch of more than ten percent[12]. This opens up many interesting new possibilities in silicon technology, since the advantages of III-V’s, such as a direct band gap and high mobilities, can be combined with the relatively cheap and highly developed silicon industry.

Of all the different kinds of III-V material, indium phosphide (InP) is especially interesting due to its direct band-gap and its high electron mobility. Therefore it is a realistic candidate for a single photon source or a nanoLED.

1.2 Photoluminescence

Optical spectroscopy is widely used for the study of fundamental optoelectrical properties of materials and for quality control of structures and devices. In contrast to several other techniques, luminescence spectroscopy is a non-destructive technique, often sensitive enough to measure impurity concentrations in parts-per-trillion ranges, which makes it an ideal technique for a quick check on the quality and properties of the semiconducting material. However, in order to get information about impurities, PL measurements have to be done at low temperatures, since at higher temperatures thermal broadening smears out the different emission lines into one broad emission peak.
1.3 Outline

Band-to-band luminescence occurs when an electron in the conduction band recombines with a hole in the valence band, thereby emitting a photon. In this study light is used to excite electrons from the valence to the conduction band and the overall process is therefore called photoluminescence (PL). Electrons and holes could also be injected at the contact and then recombine at a \(pn\)-junction. However, a wire with a \(pn\)-junction has not been grown so far. PL is convenient since a \(pn\)-junction and electrical contacts are not necessary.

There are just a few reports in the literature on PL studies on individual nanowires. Main topics are the giant polarisation anisotropy shown in free standing nanowires. Furthermore, diameter dependences of the luminescence spectra, showing a blue shift, have been shown[13]. These dependences have been attributed to quantum confinement. Another topic is the passivation of the surface of the nanowire. Surface effects play an important role in nanowires due to their small dimensions. The surface states fulfill the role of non-radiative recombination centre, thus decreasing the quantum efficiency of a nanowire significantly. Van Vugt et al[14] showed that InP nanowires can be passivated by a photoetching process.

A major issue in the PL studies on nanowires is the linewidth of the PL spectra. The linewidth in nanowire PL spectra is typically doubled compared to that in bulk PL spectra.

1.3 Outline

This thesis deals with photoluminescence experiments in different regimes. Therefore, the experimental results are split up in several sections. Firstly the high excitation intensity (10 kW/cm\(^2\)) regime is discussed in section 4. In this section room temperature experiments as well as low temperature (1.4 K) experiments are presented. Secondly, the low excitation intensity (10 W/cm\(^2\)) regime is discussed in section 5. This has been done only at low temperatures, ranging from 5 to 70 K. Section 6 discusses the luminescence experiments in combination with applying an electric field perpendicular to the nanowire. Finally, in section 7 the luminescence properties of MOCVD grown InP nanowires are compared with those of PLD grown InP nanowires. A theory and experimental section are included as sections 2 and 3 respectively.
Chapter 2

Theory and background

This chapter deals with a theory which describes the electronic structure of one dimensional semiconductors, or nanowires. Firstly, a brief summary of a theory on semiconductors will be given; the main opto-electrical properties of semiconductors will be explained. The origin of photoluminescence in semiconductors will be explained and some properties of photoluminescence will be elucidated. The third section describes the effect on the electronic properties when the shape of a crystal becomes one-dimensional. Finally, the effect of an electric field on the photoluminescence of individual nanowires is elucidated.

2.1 Energy bands in semiconductors

In order to discuss the properties of energy bands in semiconductor crystals, firstly the density of states and occupation of states will be discussed. Secondly, the nearly free electron model will be explained.

2.1.1 Density of states

Fundamental properties of a crystal can be found by solving the Schrödinger equation $H\Psi = E\Psi$, where $H$ is the Hamiltonian of the crystal, $\Psi$ is the wave vector and $E$ is the eigenvalue. However for a macroscopic crystal this is unsolvable, because for instance, one unit cell of indium phosphide contains four cores and 128 electrons, which are all coupled with each other. To be able to solve it, some approximations must be made. Firstly, the adiabatic approximation or Born-Oppenheimer approximation is applied. This approximation is based on the fact that the mass of the atomic cores is many tens of thousands of times larger than that of the electrons. Furthermore, the kinetic energy of an atomic core in a crystal is much smaller than
Chapter 2. Theory and background

that of a valence electron. In this way, the atomic cores can be separated from the electrons. The second approximation is the one-particle approximation. With this approximation the number of electrons is reduced to one by developing a one-particle Schrödinger equation with an effective periodic potential $V_{\text{eff}}[15]$. The time-independent Schrödinger equation for one electron in spatial representation (as a function of the spatial coordinate $\mathbf{r}$) is given by:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) + V_{\text{eff}}(\mathbf{r}) \psi(\mathbf{r}) = E \psi(\mathbf{r}).$$

(2.1)

Here $\hbar$ is Planck’s constant divided by $2\pi$, $m$ is the mass of the considered particle, $V_{\text{eff}}$ is the effective potential, $E$ is the eigenvalue and $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$. Equation (2.1) can be written as an eigenvalue problem $H \psi(\mathbf{r}) = E \psi(\mathbf{r})$ for the time-independent wave function $\psi$, with $H$ as Hamiltonian, equal to:

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(\mathbf{r}),$$

(2.2)

If we consider an electron in free space, the potential energy $V(\mathbf{r})$ and thus $V_{\text{eff}}(\mathbf{r}) = 0$ everywhere and equation (2.1) becomes

$$-\frac{\hbar^2}{2m_0} \nabla^2 \psi(\mathbf{r}) = E \psi(\mathbf{r}),$$

(2.3)

where $m_0$ is the mass of a free electron. From equation (2.3) can be found that

$$E_k = \frac{\hbar^2 k^2}{2m_0},$$

(2.4)

and the solution for $\psi(\mathbf{r})$ is given by $k$:

$$\psi_k(\mathbf{r}) = Ae^{i \mathbf{k} \cdot \mathbf{r}}.$$  

(2.5)

Here $A$ is a constant due to normalisation of $|\psi|^2$ in a finite volume and $\mathbf{k}$ is the wave vector ($k_x, k_y, k_z$). However, electrons in a crystal do not behave as plane waves, but rather vary periodically due to the periodicity of the crystal. Therefore the Bloch functions must be used instead of equation (2.5):

$$\psi_k(\mathbf{r}) = u_k(\mathbf{r}) e^{i \mathbf{k} \cdot \mathbf{r}}, \quad \text{with} \quad u_k(\mathbf{r}) = u_k(\mathbf{r} + \mathbf{R}).$$

(2.6)
2.1. Energy bands in semiconductors

The functions $u_k(r)$ have the same periodicity $R$ as the crystal. Comparing equation (2.6) with (2.5) shows that the plane wave is a special case of a Bloch function, where $u_k(r) = A$.

In three dimensions the density of states (DOS) as a function of energy can be derived. Consider a system of $N$ free electrons. The system is in the ground state and the occupied orbitals may be represented as points inside a sphere in $k$-space with a volume of $(2\pi/a)^3$. Each state can contain two electrons with opposite spin. The energy at the surface of the sphere is called the Fermi energy $E_F$ and the wave vectors at the Fermi surface have a magnitude of $k_F$. Thus in a sphere with radius $k_F$ the total number of orbitals is equal to:

$$2 \cdot \frac{4\pi k_F^3}{3} = \frac{V}{3\pi^2} k_F^3 = N. \quad (2.7)$$

Using this equation and equation (2.4) a relationship between the Fermi energy and the particle concentration $n = N/V$ can be derived:

$$E_F = \frac{\hbar^2}{2m} \left(3\pi^2 n\right)^{2/3}. \quad (2.8)$$

From this equation the density of states of a three-dimensional system $g_{3D}$ can be derived:

$$g_{3D}(E) = \frac{dn}{dE} = \frac{1}{2\pi} \left(\frac{m}{\hbar^2}\right)^{3/2} \sqrt{E}. \quad (2.9)$$

In one dimension – the case of nanowires –, the density of states $g_{1D}$ shows a different behaviour. In $k$-space, the number of allowed orbitals in a line with length $2k_F$ is given by:

$$2 \cdot \frac{2k_F}{2\pi a} = \frac{a}{\pi} k_F = N. \quad (2.10)$$

Note that there is only one dimension for $k$, so $n = N/R$ represents a line density. Using the dispersion relation (2.4) the density of states for a one-dimensional system $g_{1D}$ becomes:

$$g_{1D}(E) = \frac{dn}{dE} = \sqrt{\frac{2m}{\pi^2 \hbar^2}} \frac{1}{\sqrt{E}}. \quad (2.11)$$

Figure 2.1 shows the one-dimensional and three-dimensional density of states for free electrons. Electrons are fermions and therefore obey the Pauli exclusion principle, which restricts the occupation number of a state to be
either one or zero. The probability that an energy level $E$ is occupied by an electron is then given by the Fermi-Dirac distribution function\[16\]:

$$f(E) = \frac{1}{1 + e^{(E-E_F)/k_BT}},$$

(2.12)

where $k_B$ is the Boltzmann constant, $T$ is the temperature and $E_F$ is the (temperature dependent) Fermi level. In a (non-degenerate) semiconductor, the Fermi level lies in the band gap.

### 2.1.2 The nearly free electron model

In a crystal, the valence electrons are not totally free, instead the valence band electrons are treated as perturbed weakly by the periodic potential of the ion cores and core electrons. This is called the nearly free electron model. In this model the potential energy of an electron is periodic due to a periodic lattice with lattice constant $a$. This periodic potential is considered as an perturbation upon the unperturbed problem, that of a completely free electron. The corresponding Hamiltonian $H_0$ has already been introduced in equation (2.2) with $V = 0$ and the periodic perturbation $V(r)$ can be described as the perturbing operator $H_1$, so the total Hamiltonian becomes $H = H_0 + H_1$. This perturbation results in a change in the dispersion relation $E(k)$, given in equation (2.4). Figure 2.2 shows a plot of the dispersion relation of the nearly free electron model. It is clear that the dispersion relation is almost identical as that described in equation 2.4, except for the wave factors $k = \pm n\pi a$. At these wave vectors the Bragg condition\[16\] applies: the wave functions at these points in $k$-space are standing waves. The physical reason for the forbidden band is Bragg reflection at the lattice for wave functions with a wave vector $k = \pm n\pi/a$. 

![Figure 2.1: Density of states for free electrons in three dimensions (black line) and in one dimension (red line).](image)
2.1. Energy bands in semiconductors

The next stage of sophistication is taking into account that while the electron is on a particular atom, the electron’s wave function must have many of the characteristics of atomic wave functions. Such wave functions must be computed. From these computations the energy band structure can be obtained. The computed band structure of indium phosphide and silicon are shown in figure 2.3.

Figure 2.3: The band structure of (a) indium phosphide with a direct band gap and (b) silicon with an indirect band gap. The $k$-vector varies along the (100) and the (111) high symmetry direction in the first Brillouin zone.

Figure 2.3 can be compared with figure 2.2. In the latter, the second allowed band represents the valence band and the third allowed band represents the
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Conduction band. In between there is a band-gap. When the minimum of the conduction band and the maximum of the valence band are at the same point in k-space, this is called a direct band-gap, which is the case for InP. Close to the minima and maxima, the bands can be approximated by the so-called effective mass theory. With this approximation, it is assumed that near minima and maxima, the bands are parabolic and isotropic in k-space. The effective mass \( m^* \) can then be defined as:

\[
\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2E}{dk^2}. \tag{2.13}
\]

The dynamics of a charged particle in the lattice is then equal to the free particle situation, except for the mass of the particle. This mass is replaced by an effective mass, given by the curvature of the energy band. An energy band can thus be approximated by \( E = \frac{\hbar^2 k^2}{2m^*} \), where \( m^* \) is determined by the curvature of the band. If the energy surface is anisotropic, an effective mass tensor has to be used instead.

As the temperature of a semiconductor increases, the lattice expands and the oscillations of the atoms about their equilibrium lattice points increase. This leads to a decrease of the band-gap. There is also an electron-phonon interaction which depends strongly on temperature. The variation of the band-gap is approximately quadratic at low temperatures and linear at higher temperatures. The temperature dependence of the band-gap of InP is given in figure 2.4.

![Figure 2.4: The temperature dependence of the band-gap of InP on (a) a linear scale and on (b) a logarithmic scale.](image)

2.1.3 Impurities

Several kinds of impurities can be built into the semiconductor. The most important for this study are donors, acceptors and isoelectronic impurities.
If an impurity atom has one valence electron more than the replaced atom, this extra electron stays loosely bound to the impurity atom. This kind of impurity is called a donor, because it can donate an electron to the crystal. The binding energy of this electron, $E_D$, is small. For InP it is typically $E_D \sim 5$ meV (for instance Se on a P-site). If the extra electron acquires an energy of $E_D$, it can leave the impurity atom and enter the conduction band of the semiconducting material. The impurity atom is now called an ionised donor. When the electron does not leave the impurity atom, but stays loosely bound, the impurity atom is called a neutral donor.

However, if an impurity has one valence electron less than the semiconducting material, one covalent bond is incomplete. This vacancy can be seen as a hole. This kind of impurity is called an acceptor, as it can accept an electron from the semiconducting material. The energy needed for an electron at the top of the valence band to become part of the incomplete covalent bond is called $E_A$. For InP the acceptor energies are in the order of $E_A \sim 35$ meV (for instance Zn on an In-site). When an electron actually fills the hole, the impurity is called an ionised acceptor. Otherwise, it is called a neutral acceptor.

These two impurities show up in the energy band diagram as extra energy levels. This is shown in figure 2.6. As long as the density of the impurity atoms is small, the energy levels are sharp. But if the density becomes higher, with an impurity concentration of typically $n \geq 10^{18}$ cm$^{-3}$, the impurity wave functions may overlap each other, creating bands or even overlap the intrinsic electron bands. Semiconductors with such dopant concentrations are called degenerate.

If an impurity has the same amount of valence electrons as the atom it replaces in the semiconducting material, the impurity does not contribute to the electrical conductivity. However, it can affect the luminescence. For example, it can act as a recombination centre in indirect gap semiconductors. For instance, GaP which has an indirect band-gap can be doped with nitrogen in order to improve the luminescence process.

The random distribution of charged impurities leads to spatial potential fluctuations of the band edges. These fluctuations cause the band edge to vary as a function of real space. This effect is shown schematically in figure 2.5. The states below the conduction band edge and above the valence band edge are called tail states. These tail states change the density of states in the vicinity of the band edge. When we consider the conduction band for instance, the density of states of such a perturbed potential can be obtained by a summation over all locations in space, i.e. by an integral over the probability distribution of the conduction band edge[17]:

2.1. Energy bands in semiconductors
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Figure 2.5: The spatially fluctuating band edges (a) due to a random distribution of impurities cause band tails extending into the band-gap. The dashed line represents the density of states of an undoped semiconductor.

\[ g_{Kane}(E) = \frac{1}{2\pi^2} \left( \frac{2m_e}{\hbar^2} \right)^{3/2} \int_{E_C}^{\infty} \sqrt{E - E_C} \frac{1}{\sqrt{2\pi \sigma_E}} e^{-\frac{1}{2} \left( \frac{E - E_C}{\sigma_E} \right)^2} dE, \quad (2.14) \]

where \( \sigma_E \) is the smearing factor originating from the Gaussian distribution of the impurities, \( m_e = m^*_e m_0 \) is the effective mass of the considered particle (in the conduction band this is an electron). This is allowed when the random variation of the number of donor atoms within a spherical volume defined by the screening radius is much smaller than the average number of donors within the sphere[18]. The result for the valence band is similar, except for a different effective mass; furthermore, \( E_V = 0 \) has to be used instead of \( E_C \).

At high doping concentrations the band-gap energy of semiconductors decreases. This is called band-gap narrowing or band-gap renormalisation. Although there are many reasons for this effect, the many-body effects are the most important reason[19]. Many-body effects describe the Coulomb interaction. This interaction becomes important at small carrier-to-carrier distances, i.e., at high carrier concentrations. Electrons interact via their Coulomb potential. When an electron is added to a semiconductor, the other electrons spatially redistribute in order to reduce the long-range Coulomb interaction energy. The energy of the electron added to the semiconductor is reduced by the redistribution of the other electrons. A similar effect takes place with two holes: the repulsive and attractive interactions of holes with like and opposite spin and the long-range Coulomb interactions lead to a net attractive term, i.e., an increase in the valence band edge. The same happens with electron-hole interactions as well as with electron-donor and hole-acceptor interactions.
2.2 Photoluminescence of semiconductors

Photoluminescence is the result of an electronic transition between energy levels of a material. Such emission is characteristic for the material. In paragraph 2.1 the origin of energy bands was discussed. Emission from the transition between the conduction and valence band is called band-to-band emission. However, many other transitions may occur due to excitation[20]. These will be discussed in the following paragraphs.

There are different kinds of luminescence, such as chemiluminescence, cathodoluminescence, electroluminescence and photoluminescence. Chemiluminescence occurs due to excitation by a chemical reaction. With cathodoluminescence, luminescence is achieved by bombarding the material with energetic electrons. If the material is excited by applying a voltage, the process is called electroluminescence. The process used in this study is called photoluminescence and occurs due to excitation with light.

2.2.1 Quantum mechanical description of absorption

The strength of an absorption process is determined by the quantum mechanical probability for the transition rate of a system, changing from an initial electronic state \(i\) to a final electronic state \(f\). The transition probability is proportional to the square of the magnitude of the matrix element \(H_{fi}(0)\), where \(H'\) is the perturbation driving the transition[21]. In this case the perturbation is an electromagnetic radiation with vector potential \(\mathbf{A}(r, t)\). In the following paragraphs a brief derivation of the absorption coefficient using perturbation theory will be given. For a complete derivation, see textbooks such as Kuzmany[21] or Pankove[22].

The interaction energy between radiation field and atomic system can be written as[23]:

\[
H' = \sum_j -\frac{e}{mc} \mathbf{A}_j \cdot \mathbf{p} + \frac{e^2}{2mc^2} \mathbf{A}_j^2,
\]

(2.15)

where the sum is taken over the total amount \(j\) of electrons in the system. In the above equation, \(e\) is the fundamental charge of an electron, \(c\) is the speed of light, \(\mathbf{A}\) is the vector potential of the radiation field and \(\mathbf{p}\) is the momentum operator. Let us reduce the system to one electron and neglect the higher order contributions from the \(\mathbf{A}_j^2\)-term. Equation (2.15) becomes

\[
H' = -\frac{e}{mc} \mathbf{A} \cdot \mathbf{p}.
\]

(2.16)
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The vector potential can be expanded into a set of plane waves. With the time-dependent perturbation theory Fermi’s golden rule can be derived. This rule gives the probability for a transition per unit of time:

\[ P_{fi} = \frac{2\pi |H'_{fi}(0)|^2}{\hbar^2} \delta(\omega_{fi} - \omega), \]  

(2.17)

where \( \omega \) is the frequency and \( \omega_{fi} \) is the characteristic frequency, which is determined by the energy difference of the two states \( \hbar\omega_{fi} = E_f - E_i \). \( H'_{fi}(0) \) represent the matrix elements of the perturbation, which can be derived from the time-dependent matrix element of the perturbation:

\[ H'_{fi} = \langle f|\mathbf{H}'|i \rangle = -\frac{e}{mc} \langle f|\mathbf{pA}|i \rangle. \]  

(2.18)

The time-independent part of the matrix representation can be evaluated by the multipole approximation. Using the dipole representation, thus neglecting all higher order multipoles, the vector potential can be replaced by a plane wave with amplitude \( A_0 \). Equation (2.18) now becomes

\[ H'_{fi}(0) = -\frac{eA_0}{m} \langle f|\mathbf{p}|i \rangle = -\frac{eA_0}{m} p_{fi}, \quad \text{with} \]  

(2.19)

\[ (p_j)_{fi} = -i\hbar \int \psi_f^* \frac{\partial \psi_i}{\partial x_j} d^3x, \quad j = 1, 2, 3. \]  

(2.20)

In this equation \( \psi_i \) and \( \psi_f \) are eigenfunctions of the unperturbed system.

The square of the vector potential of the radiation can be related to the intensity \( I(\omega) = nA_0^2\varepsilon_0c_0\omega^2 \), where \( n \) is the refractive index, \( \varepsilon_0 \) is the dielectric constant in vacuum and \( c_0 \) is the speed of light in vacuum. The square of equation (2.19) can now be rewritten as:

\[ |H'_{fi}|^2 = |\langle f|\mathbf{H}'|i \rangle|^2 = \frac{e^2 I(\omega)|p_{fi}|^2}{m^2\varepsilon_0c_0\omega^2n}. \]  

(2.21)

From equation (2.17) the absorption can be evaluated as the ratio between the rate at which energy is absorbed per volume \( V \) and the rate at which energy is incident per unit area:

\[ \alpha(\omega) = \frac{\hbar\omega P_{fi}}{I(\omega)V}. \]  

(2.22)

Combining this equation with the results from equations (2.17), (2.19) and (2.21) we finally find
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\[ \alpha(\omega) = \frac{2\pi}{V} \frac{e^2 |p_{f_i}|^2}{m^2 \varepsilon_0 \omega} \delta(h\omega_{f_i} - h\omega). \]  
(2.23)

When using the momentum matrix \( p_{f_i} \), the conservation of momentum is automatically fulfilled, in other words \( \sum k_i = 0 \). For absorption as well as luminescence this should be the case, because the wave vector of light is negligible compared to the wave vector of the electrons. For indirect transitions a phonon has to be absorbed or emitted to establish \( k \)-conservation.

We can examine equation (2.23) more closely for interband absorption. In this case the initial and final state are the valence and conduction band state respectively. We thus define a joint density of states \( g_j(E) \):

\[ g_j(E) = \frac{2}{8\pi^3} \int \frac{d\mathbf{k}}{\mathcal{D}_{k}} \delta(E_C(k) - E_V(k) - E). \]  
(2.24)

For a two-band system with isotropic and parabolic bands can now be derived that the joint density of states can be rewritten as:

\[ g_j(E) = \frac{1}{2\pi^2} \left( \frac{2m_r^* \hbar^2}{\hbar^2} \right)^{3/2} (E - E_g)^{1/2}, \]  
(2.25)

which looks similar to the density of states, introduced in equation (2.9), except for the correction for the reduced effective mass \( m_r^* \). This parameter is defined by:

\[ \frac{1}{m_r^*} = \frac{1}{m_C^*} + \frac{1}{m_V^*}, \]  
(2.26)

where \( m_C^* \) and \( m_V^* \) are the effective masses in the conduction band and valence band respectively.

The absorption coefficient \( \alpha(\omega) \) at the band edge, where \( h\omega_{f_i} = E_g \), can be related to the joint density of states \( g_j \) by replacing the \( \delta \)-function in equation (2.23). Assuming again that the band is isotropic and parabolic, equation (2.25) can be used to show that

\[ \alpha(\omega) \propto g_j(E) \propto \sqrt{E - E_g}. \]  
(2.27)

It must be stressed that this relation only holds for direct band-gaps.
2.2.2 Radiative versus non-radiative emission

Luminescence can be seen as the inverse of absorption. Luminescence is a light quantum originating from the radiative recombination of an excited electron, whereas in absorption a light quantum is annihilated in order to excite an electron. In competition with luminescence, other non-radiative processes can take place. The efficiency of luminescence is determined by the ratio of radiative and non-radiative recombination.

The dominant process for the recombination is determined by its lifetime in the excited state, the shorter the lifetime, the more dominant the process becomes. From these lifetimes a quantum efficiency can be defined as:

\[
\eta = \frac{1/\tau_R}{1/\tau_R + 1/\tau_{NR}} = \frac{\tau_{NR}}{\tau_R + \tau_{NR}},
\]

where \(\tau_R\) is the lifetime of a radiative transition and \(\tau_{NR}\) is the lifetime of a non-radiative transition.

Several kinds of radiative processes are illustrated in figure 2.6. Arrow (1) represents absorption. The downwards arrows represent respectively band-to-band emission(2), exciton emission(3) and all kinds of impurity-related emissions(4-8). All these processes will be discussed in the following sections. The most important non-radiative recombination processes are via recombination centers(9) or by Auger processes(10). Recombination centers are usually deep impurity levels close to the center of the band gap. For instance surface states can act as non-radiative recombination centers. Particularly for nanowires the surface states are much more dominant than for bulk material, since the ratio between bulk and surface is much larger. In Auger processes the energy released as a consequence of recombination is transferred to another electron instead of used for the creation of a photon.
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This electron gets excited into a higher state in the band from where it can stepwise return to its ground state emission without radiation by multiple phonon. Auger processes become more significant as the electron density increases. In practice Auger processes are dominant for carrier concentrations of \( n > 10^{18} \text{ cm}^{-3} \).

2.2.3 Band-to-band emission

The band-to-band emission can be derived from Fermi's golden rule, shown in equation (2.17). When using the joint density of states (equation (2.24)), the occupation of states has to be taken into account. The occupation of states is given by the Fermi-Dirac distribution, introduced in equation (2.12). Furthermore, it is assumed that emission takes place at the minimum of the conduction and the maximum of the valence band. The matrix elements \( H'_{fi} \) can be assumed constant, since the variations are very small. From the constant matrix elements, the Einstein coefficient \( A \) for spontaneous emission can be derived. In case of a direct band-gap the joint density of states can be rewritten as has been done in equation (2.25. The probability (in terms of energy) for a spontaneous band-to-band emission is now given by:

\[
P_{CV}(E) \propto f(E)g_j(E).
\] (2.29)

2.2.4 Excitons

When an electron in the conduction band and a hole in the valence band are in the vicinity to each other, a Coulomb interaction occurs between them. Such an electron-hole pair is called a free (Wannier) exciton and has less energy than the two single charges. The exciton can be described as a hydrogen-like atom, except for a much higher dielectric constant and the different mass. Hence, the distance between the electron and the hole, or Bohr radius, is bigger than the Bohr radius of a hydrogen atom \( a_0 \) and is given by:

\[
a_{exc} = \frac{\varepsilon}{\varepsilon_0 m^*_e} \frac{4\pi \hbar^2 \varepsilon_0}{m_0 e^2} = \frac{\varepsilon_r}{m^*_e} a_0. \] (2.30)

Here \( \varepsilon = \varepsilon_r \varepsilon_0 \), and \( \varepsilon_0 \) are the dielectric constants of the semiconducting material and in vacuum respectively and \( m^*_e = m^*_e m^*_h / (m^*_e + m^*_h) \) is the reduced mass, in which \( m_e = m^*_e m_0 \) and \( m_h = m^*_h m_0 \) represent the effective masses of the electron and hole, respectively. The Bohr radius of InP is \( a_{exc} = 9.5 \text{ nm} \). An exciton causes an extra energy level slightly below the band-gap, due to the Coulomb interaction:
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\[ E_{\text{exc}} = -\frac{1}{n^2} \frac{m^* e^4}{2\hbar^2 (4\pi \varepsilon_r \varepsilon_0)^2} = \frac{m^*}{\varepsilon_r^2} E_{\text{Ryd}} \quad n = 1, 2, 3, \ldots \]  

(2.31)

Here \( E_{\text{Ryd}} \) is the Rydberg energy. The largest exciton energy \( (n = 1) \) in InP is equal to \( E_{\text{exc}} = 6 \) meV and can be formed easily only in sufficiently pure material. In less pure or less perfect crystals, local fields tend to break up the exciton into free carriers. Furthermore, they can only be easily formed at low temperatures, because at higher temperatures \((k_B T > E_{\text{exc}})\), the exciton also breaks up into free carriers. The free carriers can then recombine radiatively in a band-to-band transition.

### 2.2.5 Bulk Impurities

Besides band-to-band and exciton luminescence, impurities, as introduced in section 2.1.3, can also produce emission lines upon photoexcitation. The five transitions(4-8) in figure 2.6 show the different recombination processes that can occur due to (deep) donors and acceptors. The DV-line (4) in the figure represents donor-to-valence band emission. In this transition the loosely bound electron of a neutral donor recombines with a hole in the valence band. If the neutral donor has a large ionisation energy \( E_D \), then the donor is called a deep donor. Such a transition is shown as a DD \( \rightarrow V \) process (7) in figure 2.6. Deep levels are more localised due to a larger ionisation energy. The CA-line (6) represents conduction band-to-acceptor emission. In this transition an electron from the conduction band recombines with the hole of a neutral acceptor, thus becoming ionised. Similar to a donor impurity, an acceptor with a large ionisation energy is called a deep acceptor, which gives rise to a C \( \rightarrow DA \) transition (8).

The diagonal DA-line (5) represents donor-to-acceptor emission. If sufficient donors and acceptors are present, an electron from a neutral donor site can decay to a neutral acceptor site. According to Thomas \( et \) al\[24\] after the transition both the donor and the acceptor are ionised with a binding energy of

\[ E_b = \frac{-e^2}{4\pi \varepsilon_r \varepsilon_0 r}, \]  

(2.32)

where \( r \) is the distance between the donor and the acceptor. The energy of this kind of transition is equal to:

\[ E(r) = E_g - E_D - E_A - E_b. \]  

(2.33)

The distance dependence of the transition energy is interesting, because when \( r \) is small, the donors and acceptors will occupy pairs of lattice sites.
with specific crystallographic directions and, since only certain values of $r$ will therefore be allowed, the recombination energies given by equation (2.33) will be discrete. Thus the close pairs will give rise to sharp emission lines. However, when $r$ is distributed, the discrete lines will merge together and form a continuum. As a result, a broad emission band is seen where the highest energy band has a peak energy corresponding to $r \to \infty$ in equation (2.32). Equation (2.32) can also be taken as describing the DA peak energy if $r$ is considered to be the separation at which the DA recombination is largest. This separation will depend on the concentration of neutralised donors, which in turn depends on the excitation intensity. The reported intensity dependent energy shift of a zinc interstitial related DA peak in $p$-doped InP films varies from $10$ meV/decade$^{[25]}$ to $33$ meV/decade$^{[26]}$. This shift depends on for instance doping concentration and homogeneity.

### 2.2.6 Band filling

At high doping concentration ($n \geq 10^{18}$ cm$^{-3}$), e.g. in case of $n$-doping, band filling or the Burstein-Moss effect can take place. The conduction band becomes significantly filled at high doping concentrations due to the finite density of states. As a result, absorption transitions cannot occur from the top of the valence band to the bottom of the conduction band, so the fundamental edge of absorption transitions shifts to an energy higher than that of the band-gap, due to the restriction that the $k$-vector must be conserved. The Fermi-level $E_F$ now lies in the conduction band, as is shown in figure 2.7a.

Band filling cannot only occur at high doping concentrations, but also with high excitation intensities. In the high excitation intensity regime, electrons are optically excited from the valence to the conduction band. When the intensity becomes high enough, more electrons will occupy the conduction band and start to fill up the band to higher energy. This is shown schematically in figure 2.7a.

The curvature of the valence band is small compared with that of the conduction band, due to a large difference in effective mass, $m_h^* = 8m_e^*$, for the band curvature is proportional to the effective mass (see equation (2.4)). Therefore the valence band is assumed flat in this model, so the energy of the released photon is determined solely by the electron energy. The photoluminescence line shape is expected to reflect the joint density of states as a function of energy in the conduction band as shown in equation (2.29). The conduction band is modelled using the dispersion relation stated in equation (2.4), where the mass $m_0$ is replaced by the effective electron mass $m_e^*$, since the valence band is assumed flat.
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Figure 2.7: a) Schematic representation of the valence and conduction band. The valence band is assumed flat, due to the large effective mass of holes compared to electrons. Parabolic band approximation is used to calculate the conduction band. b) An example of a curve predicted by the Fermi-Kane model. The black curve represents an RT spectrum with a band gap of $E_g = 1.35$ eV, while the red curve represents an LT spectrum with a band gap of $E_g = 1.42$ eV.

\[ E_k = \frac{\hbar^2 k^2}{2m^*_e}. \]  

The line shape is now determined by a Kane-type electron density of states, as introduced in section 2.1.3 multiplied by the Fermi-Dirac distribution. Reabsorption has been neglected, since the typical size of a nanowire is smaller than the absorption length of photons in indium phosphide. The PL peak can now be modelled using the following expression:

\[ I(E) = A f(E) \int_{E_C}^{\infty} \sqrt{E - E_C} \frac{1}{\sqrt{2\pi}\sigma_E} e^{-\frac{1}{2} \left( \frac{E - E_C}{\sigma_E} \right)^2} d\tilde{E}. \]  

In this equation $A$ is a scale factor, $\sigma_E$ is the smearing factor, introduced in section 2.1.3 and $E_C$ represents the effective band-gap. The Fermi-Dirac distribution $f(E)$ is given by equation (2.12). In figure 2.7b two example curves predicted by the model are shown, one at room temperature and one at low temperature, which have different band-gaps due to the dependence on temperature. It is clear that the parameter $\sigma_E$ only affects a small part of the spectrum. It broadens the region around the band-gap with a width of $\sigma_E$ (typically $\sigma_E \sim 20$ meV), but leaves the main part of the spectrum unaffected.
2.2.7 Emission intensity dependence on excitation intensity

When the excitation intensity is low enough, no band filling takes place and other transitions can occur. It has been stated by Dean [27] that the underlying recombination process can be identified from the behaviour of the PL intensity as the excitation intensity is varied, according to $I_{out} \propto (I_{in})^k$. These processes can be characterised with a set of rate equations. In order to make a full and detailed characterisation, all transitions must be taken into account, which gives a set of coupled rate equations[28]. As it turns out, it will be sufficient for explaining the results to take into account the following transitions: absorption, band-to-band emission and band-to-acceptor emission (see figure 2.6). However non-radiative recombination is indeed present in nanowires, but these processes are neglected for clarity. The band-to-band emission is described by the recombination rate, explained section 2.2.3. This equation can be rewritten as $R = Bnp$, where $B$ is the transition rate for the band-to-band transition. We can describe the radiative processes by the following coupled differential equations or rate equations in equilibrium:

$$\begin{align*}
\frac{dn}{dt} &= \alpha I_{in} - Bnp - \frac{n}{\tau_R} = 0, \\
\frac{dp}{dt} &= \alpha I_{in} - Bnp = 0.
\end{align*}$$

(2.36)

Here $n$ and $p$ are the electron and hole concentrations respectively, $I_{in}$ is the laser intensity and $\tau_R$ is the lifetime of band-to-acceptor emission. The absorption coefficient $\alpha$ can be found in equation (2.23). We now distinguish three extreme situations:

1. luminescence dominated by band-to-band recombination,
2. luminescence dominated by band-to-acceptor recombination,
3. luminescence where both processes take place.

In the first case the defect recombination is neglected, remaining $\alpha I_{in} = Bnp$. In this case luminescence spectrum yields a dominant peak at the band-gap energy $E_g$. The intensity of luminescence scales linearly with $I_{BB} \propto np$, resulting in

$$I_{BB} \propto (I_{in})^1.$$  

(2.37)

In the second case band-to-band recombination can be neglected, so equation (2.36) becomes $\alpha I_{in} = \frac{n}{\tau_R}$. In this case, the dominant peak in the
luminescence spectrum appears at a lower energy $E_g - E_A$. The intensity of defect luminescence scales with $I_{CA} \propto n N_A$, where $N_A$ is the concentration of neutral acceptors. This gives

$$I_{CA} \propto (I_{in})^1. \quad (2.38)$$

In the third case two processes compete with each other, which makes the problem more complicated. When the luminescence spectrum shows a main peak at $E_g - E_A$ with a shoulder at $E_g$, CA-recombination is dominant, but BB-recombination is present. The latter will behave as $I_{BB} \propto np$, or $n \propto \sqrt{I_{BB}}$, while $\alpha I_{in} = \frac{n}{\tau_r}$ still holds. These two conditions yield

$$I_{BB} \propto (I_{in})^2. \quad (2.39)$$

On the other hand, when the main peak in the luminescence spectrum appears at an energy $E_g$ with a shoulder at $E_g - E_A$, BB-recombination is more dominant, while CA-recombination still takes place. The defect emission in equation (2.36) can be neglected, remaining $\alpha I_{in} = Bnp$. The defect emission scales linearly with $I_{CA} \propto n N_A$, which can be rewritten as $n \propto I_{CA}$. Substituting this formula into the remaining rate equation yields:

$$I_{CA} \propto (I_{in})^{\frac{1}{2}}. \quad (2.40)$$

When a low excitation intensity is used the dominant recombination process is defect transition due to the shorter lifetime. With increasing excitation intensity the defects are becoming more and more filled, which gives band-to-band recombination the opportunity to take place. At relatively high excitation intensity the BB-recombination becomes dominant. The excitation intensity dependence of the two recombination processes are shown schematically in figure 2.8. In reality the different regimes gradually shifts from one to another.

### 2.3 Nanowires versus bulk material

The semiconductor theory given in the previous sections is based upon bulk material. This can be extended to semiconducting nanowires, provided that the following issues must be taken into account. Firstly, dimensions can become so small that particles within that structure start to ‘feel’ the edges of the nanowire and they are confined in two dimensions. In this regime quantum mechanics start to play a role. This will be discussed in short in the first section. Secondly, the ratio between surface and bulk material is much higher for nanowires. As a result surface states start to play an important
2.3. Nanowires versus bulk material

Figure 2.8: Schematic representation of the dependence of the PL intensity on the excitation intensity for defect recombination and band-to-band recombination. The graph is plotted on a double-logarithmic scale, which reveals a linear dependence. The numbers at the lines indicate the power dependence $k$.

part in the luminescence properties. In addition, the oxide at the surface will influence the luminescence properties. Such surface effects will be discussed in the following section. The last section deals with polarisation effects. Due to a large dielectric contrast, one-dimensional structures can have a large polarisation anisotropy. This has a large influence on the luminescence properties.

2.3.1 Quantum confinement

The properties of a semiconductor change as the size of the system decreases. At a certain size quantum confinement occurs. This confinement in one dimension (thin film), two dimensions (wire) or three dimensions (quantum dot), whereas the more dimensions are confined, the bigger the confinement is. In the case of the nanowire, particles are confined in two dimensions, leaving a one-dimensional cylindrical structure. In its simplest form, such a structure can be considered as an infinite potential barrier at the edge of the wire $r = R$. For such a system the Schrödinger equation, by means of the effective mass approximation (see section 2.1.2), can be solved using cylindrical coordinates. It can be shown[29] that the lowest eigenvalue of such a system is given by:

$$E_q = \frac{\hbar^2}{2m^* R^2},$$

where $m^*$ is the effective mass of a free particle in the semiconductor and $R$ is the radius of the nanowire. These two physical parameters determine the size of the quantum confinement energy $E_q$, because $E_q$ is the shift of the
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lowest energy with respect to the bottom of the conduction band in bulk material.

When we consider the case of an InP nanowire with a typical radius $R = 50$ nm and an effective electron mass of $m^* = 0.09m_0$ (the shift of the holes is negligible, because $m^*_h > m^*_e$, the size of the quantum confinement $E_q \approx 0.02$ meV. Comparing this to the band-gap $E_g = 1.344$ eV at room temperature, we can conclude that the shift due to quantum confinement is negligible in this regime. The radius of the nanowire should reach values of $R \sim 5$ nm in order to get a considerable confinement shift of $E_q \sim 10$ meV. Furthermore, when taking (more realistic) finite potential barriers, the effect becomes even smaller. Therefore we can conclude that quantum confinement effects can be neglected when dealing with InP with radii of several tens of nanometers.

2.3.2 Surface effects

The oxide around the surface of a nanowire causes a high density of donor-like states at the surface[30]. These states cause the Fermi level to be pinned at the surface. According to Spicer et al, this Fermi level pinning for bulk InP occurs at around $E_{\text{pinning}} = 0.1$ eV below the bottom of the conduction band. In p-InP holes from the bulk fill up these donor-like surface states until charge neutrality is reached. At the centre of the nanowire the Fermi level will tend to reach bulk values, thus in order to level the Fermi level throughout the whole nanowire ($E_F = \mu(r) - e\phi(r) = \text{constant in the whole crystal}$), the bands will be bent. This band bending will be the largest for p-type nanowires, since in that case the Fermi level in the bulk lies close to the top of the valence band. The band bending can be defined as $\phi_{bi} = E_q - E_{\text{pinning}}$. The situation for a p-type wire with radius $R$ is shown schematically in figure 2.9. Near the centre of the nanowire, within a radius of $0 \leq r < r_c$, the bulk value of the electrostatic potential is reached, while near the edges, with $r_c < r \leq R$, depletion occurs[31]. Here $r_c$ is a critical radius that will be discussed later. The electrostatic potential $\phi(r)$ in the nanowire can be found by solving the Poisson equation. Comini et al[32] have done this in a similar way for tin dioxide two-dimensional nanostructures. The wire is assumed to be cylindrical and infinitely long, so using cylindrical coordinates the Poisson equation can be written in the following form:

$$\frac{\partial^2 \phi(r)}{\partial r^2} + \frac{1}{r} \frac{\partial \phi(r)}{\partial r} = -\frac{\rho(r)}{\varepsilon_0\varepsilon_r}.$$ (2.42)

Here $\rho(r)$ is the charge density and $\varepsilon = \varepsilon_r\varepsilon_0$ and $\varepsilon_0$ are the dielectric constants of the material and in vacuum respectively. Assume that the acceptors are uniformly distributed over the nanowire with a concentration of $N_A$. 

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This is an important assumption, since the diameter of the nanowire is comparable to the distance between the dopants. Also, assume that the radius of the wire is so large, that quantum confinement effect can be neglected. At the centre of the wire, all the ionised acceptors are compensated by holes, while at the edge of the wire the ionised acceptors cannot be compensated by holes due to depletion:

\[
\begin{align*}
\rho(r) &= 0 & \text{for } 0 \leq r < r_c \\
\rho(r) &= -eN_A & \text{for } r_c < r \leq R
\end{align*}
\]  

(2.43)

Here the so-called Schottky approximation is used and it is based on the assumption that there is no intermediate region around \( r_c \), so only full depletion and no depletion at all exists. We now distinguish two situations as a result of the dopant concentration. At relatively high dopant concentrations, there are enough acceptors available to compensate for the surface charge, which will result in a partial depletion of the wire. At low dopant concentrations, all holes from the acceptor sites will be localised in the surface states, resulting in a complete depletion. The two situations are sketched in figure 2.9.

\[\text{Figure 2.9: Schematic representation of band bending in a p-type nanowire due to surface states. In (a) the wire is partial depleted, whereas in (b) the wire is completely depleted.}\]

For both regimes the Poisson equation (2.42) can be solved. In case of partial depletion, the Poisson equation, using the fact that \( \phi \) is continuously differentiable and setting \( \phi(0) = 0 \), yields:

\[
\phi(0 < r < r_c) = 0 \\
\phi(r_c < r < R) = \frac{eN_A}{4\varepsilon \varepsilon_0} \left( r^2 - r_c^2 \right) - 2r_c^2 \ln \frac{r}{r_c},
\]

(2.44)

where \( r_c \) is determined by the boundary condition \( \phi(R) = \phi_{bi} \), which is the built-in potential and has to be solved numerically.
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In the case of complete depletion the Fermi level pinning remains the same as in the former case. However all holes are now localised in the surface states, which gives a charge density of

\[ \rho(r) = -eN_A \quad \text{for } 0 \leq r \leq R. \] (2.45)

The Fermi level pinning determines the Fermi level in nearly the whole nanowire as is shown in figure 2.9b. In this way a p-doped nanowire may not behave as p-type anymore. For complete depletion the Poisson equation (2.42), using the fact that \( \phi \) is continuously differentiable and setting \( \phi(R) = \phi_{bi} \), yields:

\[ \phi(r) = \frac{eN_A}{4\varepsilon_r\varepsilon_0} (r^2 - R^2) + \phi_{bi}. \] (2.46)

In order to show the effect of band bending on the luminescence properties of a p-type nanowire, the situation of complete depletion (figure 2.9b) is examined. Assume that the free carrier concentration due to excitation is several orders lower than the acceptor concentration. In this way the band bending is not influenced by optical excitation. By increasing the excitation intensity, the luminescence properties will be affected as follows. First of all, due to excitation electrons and holes will be concentrating at the edge and in the centre of the wire respectively. The separation in space will result in a diffusion of carriers. The observed luminescence line will start at an energy \( E_{\text{min}} \) and its maximum will occur at \( E_{\text{max}} \) and a schematic representation of the bands with luminescence lines is shown in figure 2.10a. In case of complete depletion, \( E_{\text{min}} \) is completely determined by the acceptor concentration \( N_A \) and is given by:

\[ E_{\text{min}}(N_A) = E_g - (\phi(R) - \phi(0)) = E_g - \frac{eN_AR^2}{4\varepsilon_r\varepsilon_0}. \] (2.47)

\( E_{\text{max}} \) however depends on the excitation intensity, because when the excitation intensity is increased, more free carriers will populate the bands, resulting in a larger diffusion, as is shown in figure 2.10b. Clearly the lowest luminescence energy \( E_{\text{min}} \) remains at the same level. \( E_{\text{max}} \) rises to higher energies with increasing excitation intensities with a maximum at \( E_{\text{max}} = E_g \). Furthermore the overlap of wavefunctions is larger with increasing energy, so the PL-intensity increases with increasing energy. In conclusion, the luminescence intensity as well as the luminescence energy increases with increasing excitation intensity.
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(a) \[ E \]

\[ R \quad R \]

\[ E_{\text{min}} \quad E_{\text{max}} \]

(b) \[ E \]

\[ R \quad R \]

\[ E_{\text{min}} \quad E_{\text{max}} \]

Figure 2.10: The effect of band bending on the luminescence lines. The band bending represents complete depleted p-type nanowire. In (a) the nanowire is excited with a low excitation intensity (the free carrier concentration due to optical excitation is several orders lower than the acceptor concentration) and in (b) the excitation intensity is relatively higher. \( E_{\text{min}} \) and \( E_{\text{max}} \) represent the minimum and maximum luminescence energies respectively.

2.3.3 Polarisation dependence

Another effect of the one-dimensional geometry is the polarisation dependence. According to Wang et al. [33], free standing nanowires have large polarisation anisotropy in photoluminescence measurements due to a large dielectric contrast between the nanowires and the surrounding environment. They have modelled this effect by treating the nanowire as an infinite dielectric cylinder in a vacuum. This is permitted because the wavelength \( \lambda \) of the exciting light is much larger than the wire diameter \( R \) and in turn the length \( L \) of the nanowire is much larger than the wavelength of the exciting light, so \( R \ll \lambda \ll L \). When the incident light is parallel to the nanowire, the electric field inside the cylinder is not reduced. However when the incident light is polarised perpendicular to the nanowire, the electric field amplitude is reduced by:

\[
E_i = \frac{2\varepsilon_0}{\varepsilon + \varepsilon_0} E_e, \tag{2.48}
\]

where \( E_i \) and \( E_e \) are the electric fields inside the cylinder and of the excitation and the dielectric constant \( \varepsilon = \varepsilon_r \varepsilon_0 \). As is shown in equation (2.21), the absorption coefficient \( \alpha \) is quadratically proportional to the amplitude of the electric field \( E_e \). The polarisation ratio \( \rho \) can now be defined as:

\[
\rho = \frac{I_{\|} - I_{\perp}}{I_{\|} + I_{\perp}} = \frac{1 - \left( \frac{2}{1 + \varepsilon_r} \right)^2}{1 + \left( \frac{2}{1 + \varepsilon_r} \right)^2}. \tag{2.49}
\]
In the case of InP, for which $\varepsilon_r = 12.4$, $\rho = 0.96$. The theory described above is a pure classical phenomenon. Persson and Xu[34] showed the giant optical polarisation anisotropy to be an intrinsic band-structure property of free standing semiconductor nanowires.

2.4 Effect of an electric field on the luminescence

Electric and magnetic fields are among the most valuable probes of an electronic system. They can be used to gather useful information of the system or have practical applications. For instance the best known application in semiconducting material, the field effect transistor, uses an electric field to switch. Another example is the Hall effect, which uses a magnetic field to determine the conductivity in semiconducting materials. This section focuses on the effect of a uniform electric field on a semiconducting material, which can lead to the Stark effect and the Franz-Keldysh effect or in low-dimensional systems to the quantum-confined Stark effect. All these effects will be discussed in short in the following sections.

2.4.1 Small electric field

An electric field changes the orientation of elliptical orbits of electrons in a way that the center of gravity of the ellipse and the focus of the ellipse are aligned with the electric field$^1$ $F$. Circular orbits (S-states) are not affected by the electric field. Such an electric field can be interpreted as a perturbation $H_1$ upon the existing Hamiltonian $H_0$. When the electron precesses slowly, its orbit lines up with the weakest field, resulting in an energy shift of $\Delta E \propto F$. This is called the first-order Stark effect and can be calculated with the first-order perturbation theory. When the orbit precesses rapidly, the average position of the electron is centered on the nucleus. Turning on the electric field will gradually displace the average position of the electron in the direction of the field proportionally to the field and induce a dipole. Then the energy shift of this state behaves as $\Delta E \propto F^2$. This is the second-order Stark shift and can be calculated with the second-order perturbation theory. As can be found from perturbation theory, the second-order Stark shift is much smaller than the first-order Stark shift.

$^1$The electric field is denoted with $F$ instead of $E$ in order to avoid confusion with the energy variable.
2.4. Effect of an electric field on the luminescence

2.4.2 Strong electric field

In the presence of a strong electric field, the band edges are tilted. This can be understood by considering a uniform electric field in the $z$-direction. As a result an electron in this field gets an extra potential of $q \phi = eFz$. The tilting of the band edges causes overlap of states across the band-gap, as is shown in figure 2.11, so there are states in both valence and conduction bands at all energies. Their overlap in space depends on the difference in their energies $\Delta E$. If $\Delta E > E_g$, the oscillating part of the wave functions overlap, resulting in a large yield in absorption and luminescence. When $\Delta E < E_g$, only the tails overlap. Therefore the Franz-Keldysh effect appears as a shift to lower energies, while in fact it is a broadening of the absorption edge or band-to-band luminescence peak.

![Figure 2.11: The Franz-Keldysh effect on interband absorption or luminescence due to a strong uniform electric field in the z-direction. The states shown in the valence and conduction bands are separated by $\Delta E < E_g$, but overlap due to the tail that tunnels into the band-gap.](image)

For low-dimensional systems a strong electric field results in the quantum-confined Stark effect. As is shown in section 2.3.1, the transition energy is larger due confinement effects. By applying a uniform electric field, the bottom of the conduction band and the top of the valence band are tilted in the same way as with the Franz-Keldysh effect. As a result the lowest state in the conduction band is shifted to a lower energy and the upper state in the valence band is shifted to a higher energy, thus resulting in a red-shift of the absorption and luminescence.
Chapter 3

Sample preparation and measurement techniques

In this chapter the sample preparation is explained. Firstly, a brief introduction to nanowire growth and deposition techniques will be given. After that the room temperature and low temperature luminescence set-ups will be described. This chapter concludes with a section about the electrical contacting of the nanowires and the electric field set-up.

3.1 Nanowire growth techniques

Numerous techniques can be used to make semiconducting III-V nanowires. A top-down as well as a bottom-up approach can be used. Wagner et al[3] were the first to describe nanowire growth using a bottom-up approach. The measurements discussed in this thesis have been made using two different kinds of bottom-up approaches: the Pulsed Laser Deposition (PLD) and Metal-Organic Chemical Vapour Deposition (MOCVD). Both are Vapour-Liquid-Solid (VLS) techniques. This means that III-V material is offered in the vapour phase to a substrate with metal particles deposited on it. Several metals can be used, such as nickel and copper, but for the wires reported in this study, gold is used as catalyst particle. As a substrate a silicon sample with a native oxide layer is used. This sample is heated to a temperature in the range of 430 – 500 °C, which causes the gold particle to form liquid droplets. These droplets can absorb the III-V material, forming a eutect. Once the metal droplets are saturated, the III-V material will start to condense on the substrate below the eutect and a wire will start to grow. Furthermore the semiconducting nanowires can doped with different materials. In this study, zinc is used as a p-type dopant and sulphur is used as an n-type dopant. Hiruma et al[35] described the VLS growth technique in more detail.
Chapter 3. Sample preparation and measurement techniques

The III-V material can be offered in different ways. As mentioned, the techniques used in this study are PLD and MOCVD. Both are explained in short in the following sections. These sections are specifically about the growth of InP nanowires, whereas this thesis only discusses InP nanowires.

3.1.1 PLD growth

With pulsed laser deposition a ArF laser ($\lambda = 193$ nm, 100 mJ/pulse, 2.5-10 Hz) is focused on either a pressed InP target or on a piece of single crystalline InP. The laser ablates the target, creating In and P species. These are carried through a quartz oven tube by an argon gas flow towards the substrate, where they dissolve in the gold droplets. The substrate is glued on a $\text{Al}_2\text{O}_3$ block at the downstream of the oven. The quartz oven tube is evacuated to a pressure of $10^{-7}$ mbar. A schematic representation of the PLD set-up is shown in figure 3.1.

![Schematic representation of the pulsed laser deposition set-up.](image)

After the wires have been grown, they can be deposited in several ways, of which two will be discussed. Firstly they can be deposited by tissue deposition. In this way a silicon sample with a 120 nm thick silicon oxide layer will be put on top of the as-grown sample. Some of the nanowires will be transferred to the silicon oxide substrate. Due to Van der Waals forces the nanowires will tend to lie flat on the substrate. Another way of transferring the nanowires is by dispersing them in chlorobenzene by low power ultrasonification. A droplet of the dispersion is then deposited onto a silicon oxide sample, causing the nanowires to lie flat on the substrate.
3.2. Luminescence set-ups

3.1.2 MOCVD growth

Another VLS-growth technique is the Metal-Organic Chemical Vapour Deposition (MOCVD). This technique is used to grow thin films of semiconducting material. The mechanism for nanowire growth is the same for this technique as for the PLD technique, except for the supply of III-V material and the carrier gas. With MOCVD growth the III-V material is supplied through extremely poisonous metal-organic precursors. For instance, InP nanowires are grown by supplying tri-methyl-indium (TMI) for indium and phosphine (PH₃) for phosphorous. In the case of GaP, the gallium is supplied by tri-methyl-gallium (TMG). For p-doping zinc is supplied by di-ethyl-zinc (DEZn) and for n-doping sulphur is supplied by H₂S. Instead of argon, H₂ is used as a carrier gas.

This technique has its pros and cons in comparison with PLD growth. The main advantage is that MOCVD techniques are already widely used in industry. Therefore it will be relatively easier to implement nanowire growth into existing industrial processes. The main disadvantage is that the precursors contain carbon. Carbon can be built into the nanowires as an impurity. Therefore it will be more difficult to control the dopant concentration during growth than with PLD techniques.

3.2 Luminescence set-ups

Three different luminescence set-ups have been used in this study. They can be classified by temperature and excitation intensity and will be discussed in the following paragraphs. The first discusses the room temperature (RT) set-up with high excitation intensity \( P \approx 10 \text{ kW/cm}^2 \). The next discusses the low temperature (LT) set-up with high excitation intensity and the last discusses the low temperature set-up with low excitation power intensity \( P \approx 10 \text{ W/cm}^2 \).

3.2.1 RT set-up with high excitation intensity

Room temperature photoluminescence measurements have been carried out using a home-built epifluorescence microscope. In this setup, the wires were excited with a 200 mW 457 nm diode-pumped solid-state (DPSS) laser. A \( \lambda/2 \) wave retardation plate is placed directly after the laser to enable rotation of the polarisation in the specimen plane of the microscope. The linearly polarised laser is reflected from a dichroic mirror and focused through the microscope objective onto the substrate to obtain a spot size with a diameter \( d \approx 5 \mu\text{m} \), corresponding to a power density of \( 10 \text{ kW/cm}^2 \) (after subtracting all losses). The photoluminescence signal is collected by the same objective,
Chapter 3. Sample preparation and measurement techniques

![Schematic representation of the room temperature set-up with a high excitation intensity](image)

Figure 3.2: Schematic representation of the room temperature set-up with a high excitation intensity. See text for details.

passes through the dichroic mirror and an emission filter to filter out the laser light. Then the emission signal is coupled into a glass fiber, dispersed by a grating and recorded by a CCD array spectrometer (Oriel Instaspec IV). The CCD is cooled with ethanol to a temperature of \(-10{\,}^\circ\text{C}\) to get a higher resolution. In order to avoid condensation of water on the CCD, the device is being ventilated by dry air. During measurements, several parameters can be changed, such as the polarisation angle by rotating a polarisation rhomb. Furthermore the intensity of the laser light can be changed by optical density filters. A schematic representation of the room temperature set-up can be found in figure 3.2.

3.2.2 LT set-up with high excitation intensity

Low temperature photoluminescence with high excitation intensity experiments were done with a home-built epifluorescence microscope, that can be either in widefield or confocal mode. The samples are illuminated with a continuous-wave argon laser (514 nm, 400 mW). Low temperature is achieved with a vertical cryostat, where the sample is surrounded by liquid helium. Furthermore, the cryostat is evacuated, resulting in a temperature of 1.4 K. In this set-up, a 514 nm 400 mW linearly polarised laser is used to excite the nanowires. The excitation light passes through through an excitation pinhole and is focused onto the sample by the objective lens inside the cryostat, creating a diffraction-limited excitation volume of less than 1 \(\mu\text{m}^3\). This spot can be scanned over the sample by tilting the direction of the excitation beam with a scan mirror. A pair of telecentric lenses ensures a precise and well-controlled displacement of the focus on the sample while maintaining alignment with the confocal aperture. In between the telecen-
3.2. Luminescence set-ups

A λ/2 plate is used to enable rotation of the polarisation of the laser. The resulting power density in the spot is \( P \sim 100 \text{ kW/cm}^2 \), after subtracting all losses due to lenses etcetera.

![Schematic representation of the low temperature (1.4 K) set-up with a high excitation intensity. See text for details.](image)

The luminescence signal is collected by the same objective lens and focused onto either a single-photon-counting avalanche photodiode (APD), which also fulfills the role of the detection pinhole, or it is focused onto a detection pinhole, after which it is collected by spectrophotometer. With the use of the APD and by scanning the sample with the scan mirror, a widefield image can be taken. Afterwards, with the use of the spectrophotometer a spectrum at a certain position can be taken. The CCD array of the spectrophotometer is cooled with nitrogen to \(-100^\circ\text{C}\). A schematic representation of this low temperature set-up is shown in figure 3.3.

### 3.2.3 LT set-up with low excitation intensity

Low temperature photoluminescence measurements with low excitation intensity were done with Zeiss laser scan microscope. The samples are excited with a continuous HeNe laser (632 nm, 10 μW). Low temperature is achieved by an Oxford cryostat. In this cryostat, the sample is glued onto a copper cold finger with thermal glue. The copper cold finger is cooled with liquid helium. The temperature can be varied from 5-300 K. The laser light is focused onto the sample with an long distance objective, which is placed outside the cryostat. The diameter of the excitation spot is 6 nm, corresponding to an excitation intensity of \( P \sim 10 \text{ W/cm}^2 \). The spot can be scanned over the sample by tilting the direction of the excitation beam with a scan mirror. Furthermore, the cryostat can be moved in three directions with a microcontroller.
Chapter 3. Sample preparation and measurement techniques

The luminescence signal is collected by the same objective lens and is focused onto a spectrophotometer (ARC SpectraPro-300i Spectrograph) with an InGaAs CCD array (Princeton Instruments OMA V). The CCD array is cooled with liquid nitrogen to $-100 \, ^\circ C$. A filter is used for filtering out the laser light before focusing it onto the spectrophotometer. A schematic representation of this low temperature set-up is shown in figure 3.4.

3.3 Electric field dependent luminescence

In order to perform photoluminescence measurements on a nanowire with an electric field, the set-up, shown in figure 3.5 is used. The wire is deposited on a heavily n++ doped silicon substrate, covered with a thermal silicon oxide layer of 120 nm thick. The silicon substrate can be used as a back gate. After deposition of the nanowires on the silicon oxide layer, a patterned metal layer is fabricated on top of it. In this way some nanowires are randomly contacted by the patterned metal. The patterned metal can now be used as top contact (see figure 3.5). For the definition of the patterns photolithography lift-off technology is used. The pattern definition consists of three steps: resist spinning, exposure and development. Firstly, a photo resist layer is spun on the substrate. This photo resist layer contains a polymer solution. The next step is to expose the designed pattern. Then a metallization scheme is evaporated onto the substrate by means of thermal evaporation. After the evaporation, the remaining photo resist is dissolved by an acetone bath, leaving the metal behind.

The choice of the contact material is crucial to make an ohmic contact.
3.3. Electric field dependent luminescence

Figure 3.5: Schematic representation of a sample used for electric field experiments.

to the semiconducting material. Furthermore, besides an ohmic contact, other issues, such as contact stability, metallization adhesion and contact uniformity are of great importance. Therefore a multi-layer metallization scheme is used for making stable ohmic contacts. In this study two of three metal layers are used. The first is the wetting layer and provides a good adhesion of the electrodes. In this study a titanium layer of 20-50 nm thickness is used. The top layer is the capping layer and provides protection from oxidation and other external influences. In this study gold with thickness of 80-100 nm is used as a capping layer. For p-type nanowires an extra metal layer, the so-called doping layer, is used in between the wetting and capping layer. This doping layer provides external doping by diffusion at the interface, improving the contact. For the p-type nanowires, a zinc layer of 20 nm thickness is used.

As already mentioned, the process described above provides a device, shown in figure 3.5, which can be used to perform electrical field measurements. The top contact and back gate can be used to create an electric field perpendicular to the nanowire across the dielectric. The whole set-up can be placed under the microscope objective in order to perform photoluminescence measurements. A block voltage between the top contact and back gate is generated by a block generator. In this way the amplitude of the block voltage can be varied between 0 V and 50 V and the frequency can be varied.
Chapter 4

Measurements in the high excitation power regime

In the following four chapters the experimental results of this study will be presented. This chapter discusses the PL measurements in the high excitation power regime. A simple model to fit the data will be presented, after which the measurements at room temperature and low temperature will be presented respectively. In this regime the excitation power is in the order of $P \sim 10 \text{ kW/cm}^2$. This is called the high excitation intensity regime as the number of charge carriers excited into the bands is in the order of $n_{\text{exc}} \sim 10^{19} \text{ cm}^{-3}$. This number is comparable to or higher than the dopant concentration $N_A$ or $N_D$, which makes it the main supplier of charge carriers. Furthermore, band-to-band emission is the major radiative recombination process in this regime.

4.1 Room temperature measurements

Photoluminescence has been measured as a function of excitation power. This has been performed on several nanowires. The results of a typical measurement are presented in figure 4.1. The different spectra in the figures 4.1a and b represent different excitation intensities, which correspond to 100%, 50%, 25% and 10% of the maximum excitation intensity of 10 kW/cm$^2$, when going from the highest spectrum to the lowest spectrum respectively.

The spectra shown in figure 4.1 were fit using equation 2.35, indicated by the red curves in the figure. They show a reasonable agreement with the PL measurements. Figure 4.1b zooms in on the high energy side of peak. At high energies the Fermi-Dirac statistics dominate over the joint density of
Chapter 4. Measurements in the high excitation power regime

Figure 4.1: (a) Several spectra plotted in counts per second (cps), taken from a Se-doped nanowire excited with different laser intensities at room temperature. The peaks correspond to 100%, 50%, 25% and 10% of the maximum excitation intensity respectively with decreasing PL intensity. The fits from equation (2.35) are indicated by the red curves. (b) The high energy side of the peaks plotted on a logarithmic scale show a linear behaviour. In plot (c) and (d) the spectra of bulk InP are shown as a comparison. The different lines represent excitation intensities of respectively 5%, 10%, 25%, 50% and 100% of the total intensity with increasing PL intensity.
4.1. Room temperature measurements

states term due to the exponential decrease. Furthermore, at high energies the Fermi-Dirac statistics can be approximated by Boltzmann statistics:

$$\log \left( \frac{I}{I_0} \right) \sim -\frac{1}{k_B T} E.$$  \hfill (4.1)

It can be clearly seen that, when plotted on a logarithmic scale, the inverse of the slope determines the temperature. From figure 4.1b it can be concluded that the temperature of the nanowires rises due to the high laser excitation level. The fit results must be investigated to get a more quantitative proof.

![Figure 4.2: Fit parameters as a function of the excitation intensity at room temperature for two different n-InP nanowires (red and green line) and a bulk sample (black line). (a) PL intensity in terms of area versus excitation intensity. The thick black line is a reference line with slope 1. (b) Temperature in meV versus excitation intensity. (c) Conduction band energy $E_C$ relative to the valence band and Fermi-level $E_F$ versus excitation intensity and (d) smearing factor versus excitation intensity. The excitation intensity is plotted on a logarithmic scale.](image)

Using equation (2.35), several parameters can be derived from the data. For instance, $k_B T$, $E_C$, $E_F$ and $\sigma$ can be fit with the equation. These parameters are presented as a function of the excitation intensity in figure 4.2. As a comparison, data on bulk InP are shown in black. The red and green lines are taken from different nanowires. Figure 4.2a shows the PL intensity as
Chapter 4. Measurements in the high excitation power regime

a function of excitation intensity on a double logarithmic scale. In section 2.2.7 it is shown that this should be a linear relationship with slope $k$, since the PL intensity is proportional to the excitation intensity to the power $k$:

$$I \propto P^k. \quad (4.2)$$

The slope of the plots in figure 4.2a is equal to $k = 1.1 \pm 0.2$. As shown in section 2.2.7, such a power dependence indicates that there is one main transition, which could be a defect as well as band-to-band luminescence. However at room temperature the major transition is band-to-band recombination. Therefore we assign this peak to a band-to-band transition.

The temperature dependence is shown in figure 4.2b. It is clear that nanowires behave different than bulk material. The temperature of a nanowire rises significantly with increasing excitation and can reach temperatures as high as 250 °C, whereas in bulk material the temperature remains nearly constant as a function of excitation intensity. Evidently the nanowire cannot lose its heat that well as bulk material, since they occupy a very small volume. Furthermore, due to their cylindrical geometry\(^1\), the thermal contact to the substrate is very poor. In contrast bulk material can transport its heat very easily across the whole material as well as to the substrate.

In figure 4.2c the band-gap or relative conduction band $E_c$ and the (quasi-)
Fermi level $E_F$ are shown as a function of the excitation intensity. Consistent with the model explained in the previous section, for the nanowires the quasi-Fermi level lies in the conduction band. According to this model band filling takes place. However, the band-gap fit with the model is lower than the band gap at room temperature for indium phosphide that is found in literature\(^{[36]}\), which is $E_g = 1.35$ eV. This can be explained by the higher temperature, as the band gap will shrink with higher temperatures. For a nanowire the fit band-gap is $E_g = 1.34$ eV for low excitation intensity and decreases to $E_g = 1.30$ eV for high excitation intensity. According to figure 2.4, these values correspond to 300 K and 450 K. This is in reasonable agreement with the fit temperatures in figure 4.2b. For the bulk sample, no band filling takes place, since the Fermi level lies in the band-gap. Therefore we can conclude that it is easier for band-filling to take place in InP nanowires than in bulk InP. We believe that this is due to a geometrical effect: in a nanowire charge carriers can only diffuse in two directions, or one dimension, while in bulk charge carriers can diffuse in all six directions, or three dimensions.

Finally in figure 4.2d the smearing factor $\sigma$ is shown. As discussed in section 2.1.3, this parameter can be seen as a measure of crystal quality. It depends

\(^1\)Theoretically, semiconducting nanowires grown in the (111) direction, are hexagonal, due to their crystal structure. However, when the nanowire gets thicker, its shape can be approximated by a cylinder.
4.2 Low temperature measurements

on defects, impurities and surface states. A higher smearing factor implies more defects etcetera. It is clear that the crystal quality of nanowires is worse than that of the measured bulk material. However, it is not clear why $\sigma_E$ increases with increasing excitation intensity.

![Graph showing polarisation dependent PL measurements on a p-type nanowire. The lower spectrum is excited with a laser polarisation perpendicular to the nanowire axis, while the upper spectrum is excited with a laser polarisation parallel to the wire. The upper spectrum has been shifted vertically for clarity.](image)

**Figure 4.3:** Polarisation dependent PL measurements on a p-type nanowire. The lower spectrum is excited with a laser polarisation perpendicular to the nanowire axis, while the upper spectrum is excited with a laser polarisation parallel to the wire. The upper spectrum has been shifted vertically for clarity.

Furthermore, polarisation dependent PL measurements have been performed on a p-type InP nanowire. A typical result is shown in figure 4.3. From these measurements we can conclude that we are indeed measuring a nanowire. According to Wang et al [33] nanowires show a large anisotropy in PL intensity recorded parallel and perpendicular to the long axis due to a large dielectric contrast between the nanowires and the surrounding environment, as is explained in section 2.3.3. From the measurements of figure 4.3 a so-called 'on-off' ratio can be calculated with equation (2.49) and is in the order of $\rho = 0.75$. This is a lower value than reported by Wang et al, who reported the theoretical value of $\rho = 0.96$. However, this value depends on the diameter of the nanowire: the larger the diameter of the nanowire, the smaller the anisotropy of the polarisation. This effect could account for the smaller ratio.

4.2 Low temperature measurements

Similar measurements as in the previous section have been done at low temperature, i.e., $T_{\text{substrate}} = 1.4$ K. It has to be stressed that this is the temperature to which the surrounding helium is cooled (see section 3.2.2). The temperature of the wire could differ substantially from the helium temperature due to poor thermal contact. The results from these measurements are shown below. Measurements have been performed on one nanowire.
Chapter 4. Measurements in the high excitation power regime

Firstly, a widefield image is shown in figure 4.4 of the measured wire. This image has been made with an avalanche photo diode and thus reflects PL intensity as a function of position. The figure clearly shows a kink in the wire. The angle of the kink $\theta = 53^\circ$ indicates it is a crystallographic kink. Furthermore an estimation of the length of the wire can be made, which is $l = 15 \ \mu m$. The figure also shows a large non-uniformity in luminescence as a function of position on the wire. This effect will be examined more thoroughly later in this section.

![Figure 4.4](image1.png)

**Figure 4.4:** A widefield image of a nanowire taken at $T = 1.4$ K. Image has been taken with an avalanche photo diode, which reflects the total luminescence at a certain position on the wire.

![Figure 4.5](image2.png)

**Figure 4.5:** a) Several spectra taken from an n-type nanowire excited with different laser intensities at low temperature ($T = 1.4$ K). The spectra correspond to 90%, 58%, 12% and 6% of the maximum excitation intensity respectively with decreasing PL intensity. The fits from equation (2.35) are indicated by the red curves. The grey line corresponds to a room temperature spectrum from figure 4.1a and is plotted as a reference. b) The high energy side of the peaks plotted on a logarithmic scale show a linear behaviour.

Figures 4.5a and b show the low temperature spectra of an n-type InP.
4.2. Low temperature measurements

nanowire for different excitation intensities. The peaks correspond to excitation intensities of 90%, 58%, 12% and 6% respectively with decreasing PL intensity. The red curves in figure 4.5a indicate the fits performed with equation (2.35). The grey line is an RT spectrum taken from figure 4.1a and is shown as a reference spectrum. The fits are not as good as the fits of the RT measurements shown in figure 4.1a, due to the roughness of the peak. This roughness probably originates from the CCD or the set-up. The lowest peak occurs at $E = 1.42$ eV, which is the band gap of indium phosphide at this temperature. Therefore we can conclude that these peaks do not originate from impurities.

Figure 4.5b shows the high energy sides of the LT spectra on a logarithmic scale. According to equation (4.1) the spectrum behaves linearly in this region. The decrease in slope with increasing excitation intensity indicates a temperature rise with increasing excitation intensity. This is also observed in the room temperature measurements (see figure 4.1b).

![Figure 4.6:](image)

In figure 4.6 the fit parameters from equation (2.35) are plotted against the excitation intensity for two different positions on the wire. Figure 4.6a shows the power dependence of the PL intensity in terms of area. It is plotted on
a double logarithmic scale to show the relation expressed in equation (4.2). The slope in this plot is equal to $k = 1.35$, which is too high for a band-to-band transition. A slope higher than 1 can only occur when there are two or more transitions competing. Therefore we must conclude that there are two peaks of equal importance.

From figure 4.6b shows the temperature acquired from the fit. Similar as for the room temperature experiments, the temperature increases rapidly with increasing excitation intensity. In contrast with the RT measurements, the band-gap, shown in figure 4.6c, remains constant while the quasi-Fermi level increases with higher excitation intensities. This difference can be explained due to the fact at low temperatures, the band-gap hardly changes with increasing temperature, while at higher temperatures, the band-gap decreases linearly with increasing temperature. Figure 4.6d shows the smearing factor $\sigma_E$. This factor decreases with increasing excitation intensity, which is the opposite of the result found with RT experiments. An explanation for this decrease could be lying in the fact that there are in fact two or more transitions. At low excitation intensity a defect emission is relatively important, while at higher intensities the band-to-band transition becomes the dominant emission.

Secondly, polarisation-dependent measurements have been performed. The results are shown in figure 4.7. From these data it can be concluded that we are indeed measuring a nanowire, for there is a large polarisation anisotropy. The ratio of PL intensities, calculated with equation (2.49), is $\rho = 0.7$, which is not as high as reported in literature. This could be due to the geometry of the wire. As can be seen in figure 4.4 a kink in the wire is observed, which could lower the on-off ratio. In addition, as discussed with the RT
4.2. Low temperature measurements

polarisation dependent experiments, the lower ratio could also be due to a
diameter dependence.

![Figure 4.8: PL intensity in terms of area of the spectra as a function of time. Measurements have been performed at T = 1.4 K on an n-type nanowire. Every five seconds a spectrum is taken with continuous excitation.](image)

Measurements as a function of time have been performed. The results are shown in figure 4.8. In this figure the PL intensity in terms of area of the spectra are shown as a function of time. Firstly, the position of the emission peak stays constant as a function of time. Besides the long term degradation of the intensity, small emission intensity fluctuations in the range of 10% are observed. This could be due trapping and detrapping of (surface) charges, causing similar effects in quantum dots. According to Shimizu et al[37], trapping and detrapping of charges causes a quantum dot to blink. This can happen in time scales of microseconds as well as seconds. In a nanowire, only two dimensions are confined, which could result in partial blinking: electrons and holes can diffuse through the wire in one dimension, which can compensate for the (de)trapping. When the excitation and detection spot becomes larger, the blinking effect in a nanowire becomes less visible due to spatial averaging.

Furthermore, measurements as a function of position on the wire have been performed. The results are shown in figure 4.9. In this figure the PL intensity in terms of area of the spectra are shown in (a) and the positions of the spectra are shown in (b) as a function of the position on the wire. The position of the peak remains nearly constant as a function of position on the wire, except for one point, where the intensity is very low. This point could be due to the kink in the wire, which is also observed in the widefield image, shown in figure 4.4. The fluctuations as a function of position, which are also visible in the widefield image in figure 4.4, are much larger than the time fluctuations. Therefore we can conclude that these position fluctuations are real fluctuations. Such fluctuations could be due to defects, such as trapping centres or twinning planes.
Chapter 4. Measurements in the high excitation power regime

Figure 4.9: PL intensity in terms of area (a) of the spectra and peak positions (b) of the spectra as a function of position. Measurements have been performed at $T = 1.4 \text{ K}$ on an n-type nanowire of about 15 $\mu\text{m}$ long. The measurements are equally spaced over the wire.
Chapter 5

Measurements in the low excitation intensity regime

This chapter discusses the low excitation intensity regime. It is split up in two sections: first the measurements on intentionally undoped InP nanowires, which should be intrinsic, and on selene-doped nanowires. Selene acts as a donor in indium phosphide, so these wires should be n-type. Secondly the measurements of zinc-doped nanowires are presented. Zinc acts as an acceptor, which makes the wires p-type.

The maximum excitation intensity is $P \sim 10 \text{ W/cm}^2$. This is a factor 1000 less than in the high excitation regime. Due to the low excitation intensity, these measurements can only be done at low temperatures. At higher temperatures phonon-assisted transitions, which are non-radiative, quench the signal below noise level. For most measurements the substrate temperature is held constant at $T = 5 \text{ K}$ except when stated otherwise. Strong thermal radiation through the glass plate may heat up the wire in the excitation spot.

5.1 Intrinsic & n-type nanowires

The results of the low excitation intensity measurements on intrinsic and n-type nanowires are shown in figure 5.1. Here the excitation intensity is varied from 100% to 2% of the total excitation intensity of 10 W/cm$^2$.

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1 Zinc is usually built in substitutionally, which makes them a shallow acceptor, with $E_A = 35 \text{ meV}$. However, when built in interstitially, it acts in combination with a vacancy as a deep level complex. Annealing in an H$_2$ plasma will electronically passivate all zinc defects. Then an extra annealing step will only reactivate the substitutional zinc. However an annealing step causes extra difficulties for indium phosphide due to the high vapour pressure of phosphide.
Around half of all intrinsic wires show a spectrum similar to that as shown in figure 5.1a. The other half and all of the n-type wires show a spectrum as shown in figure 5.1b. This is reasonable, because indium phosphide without intentional doping tends to be n-type due to shallow donor sites, such as silicon and carbon, which are both present in the system, or due to phosphorous vacancies in the crystal. The emission lines of both types show similar behaviour at higher temperatures ($T \sim 5 - 45$ K): the peak positions remain the same, while the PL intensities decrease with increasing temperature, due to electron-phonon interactions.

Firstly, the spectra of Se-doped n-InP will be discussed. The main luminescence peak (1) in n-type nanowires can have several origins. Firstly, it could
Intrinsic & n-type nanowires

be the band-to-band transition, since its energy is $E = 1.42$ eV (indicated with the vertical dotted line (1)). Another origin could be a donor-valence band (DV) transition due to selene, since the ionisation energy for selene in InP is $N_{D,sc} \approx 5$ meV. Due to the relatively large FWHM of the peaks it is difficult to distinguish a donor-valence band (DV) transition from the band-to-band (BB) transition. The linewidths of the peaks remain constant at around 30 meV with varying temperatures as well as with varying intensities. This is relatively broad for these temperatures and is a common feature of PL spectra of single nanowires. Van Vugt et al.[14] attributed this broadening to Coulomb interactions of the exciton electron and hole with charges or dipoles distributed on the surface of the nanowire. Spatial inhomogeneities in the effective charge density on the surface of the wire could account for the broadening.

The emission line (1) seems to occur slightly below the band-gap. Therefore it is more likely that the emission line is due to a DV-transition. However, in n-InP nanowires band bending takes place, which can account for a small decrease of the BB-transition. As shown in section 2.3.2 the band bending in n-doped and intrinsic nanowires is relatively small, so it has little influence on the energy of the BB-transition. Another reason for the lower BB transition is heating of sample, which decreases the band-gap. Finally, the emission line could be an exciton line. Assuming the nanowire has a diameter in the order of $d = 50$ nm, quantum confinement plays no role (see section 2.3.1), so the exciton energy is $E_{exc} = 6$ meV. However excitons can only exist in extremely pure material, which is not the case with the nanowires. Though, it is believed that excitons are more easily formed when dimensions decrease, due to less scattering modes. Nevertheless, the diameter $d$ of the nanowire is still larger than the Bohr radius of an exciton $a_{exc} = 9.5$ nm. In order to get a decisive answer, more experiments must be performed. For now, the most likely origin of emission line (1) in figure 5.1 is a DV-transition involving selene.

The spectrum of n-InP shows an extra peak (2) at 45 meV below the band-gap. This indicates an acceptor-related transition, because in indium phosphide acceptors are a bit less shallow ($N_A \sim 40$ meV) than donors ($N_D \sim 5$ meV). Although it is an n-doped nanowire, the acceptor-related transition could be due to the presence of carbon (in the glue) or due to silicon, which is present in the substrate and could be diffused into the nanowire during growth. However carbon is more likely, since the acceptor energy of carbon is $E_A = 40$ meV and that of silicon is $E_A = 30$ meV.

Figure 5.1a shows the results of an i-InP nanowire. There are three peaks visible. Peak (1) and (2) occur at the same energies as the peaks (1) and (2) in figure 5.1b. Therefore it is likely that these are similar transitions as discussed above. In contrast to the intrinsic nanowires, the assumed CA-emission is dominant. In peak (2) a small shift as a function of excitation
Chapter 5. Measurements in the low excitation intensity regime

intensity is observed (approximately 10 meV/decade). Therefore, it could be a DA-emission line instead of a CA-emission line. However, an n-dopant is not available in the system. Furthermore, the emission lines are somewhat more red shifted than those of the n-InP nanowires. This could be explained by the fact that the band bending is larger for intrinsic wires than for n-type wires. In figure 5.1a a third peak (3) is present at 85 meV below the band-gap. This emission line could be assigned to a surface state-related transition.

![Figure 5.2](image)

Figure 5.2: PL intensity in terms of area as a function of the excitation intensity for the intrinsic wire (a) and the n-type wire (b), shown in figure 5.1. The different lines represent different substrate temperatures: the squares represent 5 K, the circles represent 10 K, the up-triangles 15 K, the down-triangles 25 K and the diamonds 40 K. For the intrinsic wire the dependence of the dominant peak (2) is shown, whereas for the n-type wire the dependence of the two peaks is shown: the red lines represent the PL intensities of the BB-emission (1) and the black lines represent those of the smaller defect emission (2). The straight lines are reference lines and indicate different slopes as given in the plot.

In order to make a more quantitative analysis of the luminescence, the PL intensity is plotted as a function of excitation intensity. This has been done for the main peak (2) in intrinsic wires (figure 5.1a) as well as for the two peaks (1) and (2) in n-type wires (figure 5.1b). The other emission lines have a too small PL intensity. The results are shown in figure 5.2. The left figure shows the excitation intensity dependence of an intrinsic wire and the right figure the dependences of the n-type wire. According to equation (4.2) the PL intensity versus excitation intensity on a double logarithmic scale should yield a linear relationship with slope $k$. In the case of the intrinsic wires a slope of $k = 1$ is found, corresponding to one transition, either a band-to-band transition an impurity-related defect. In the case of the n-type nanowire, the lower peak starts with a slope of $k = 1$, similar to the case of the intrinsic wire. However when the band-to-band peak starts to rise, the slope of the lower peak drops back to $k = 0.5$, as shown in section 2.2.7. According to the theory explained in this section, such a peak originates from
5.2 Zn-doped nanowires

A defect transition. The upper peak starts to rise superlinear with a slope of \( k = 2 \). This can only be the case with a band-to-band transition. According to the theory, it is expected that the slope should eventually converge to \( k = 1 \) for higher excitation intensities. However, in these measurements this point has not yet been reached.

5.2 Zn-doped nanowires

Similar PL measurements have been performed on several zinc-doped, i.e., p-type InP nanowires. A typical result of these measurements is shown in figure 5.3. The data is plotted on the same energy scale as for the other types of nanowires. In comparison with other types of nanowires some clear differences can be pointed out with regard to the position as well as the shape of the spectrum. Firstly, the energy of the luminescence peak is much lower: \( E \) varies from 1.15 eV to 1.35 eV in contrast with constant peak positions for intrinsic and n-type nanowires. Furthermore, the peak position shifts to higher energy with increasing excitation intensity. The third major discrepancy with the other types is the linewidth of the peak: the full width at half maximum (FWHM) of 70 meV is more than two times larger than the FWHM of intrinsic and n-type nanowires, which is typically 30 meV.

Figure 5.3: PL spectra of a p-type nanowire, measured at low temperature (15 K) and low excitation intensity. The different lines represent excitation intensities of 5%, 10%, 20%, 50% and 100% of the maximum excitation intensity with increasing emission intensity respectively. The spectra have been shifted vertically for clarity.

One explanation could be that the luminescence peak is made up of sev-
eral peaks superposed onto each other. This would account for the larger linewidth as well as the shift with increasing excitation intensity. However, since the peak shifts gradually towards higher energy rather than in steps, we believe that the luminescence peak is one individual transition. Another explanation for the shift as a function of the excitation intensity could be that the emission line originates from a DA transition. As explained in section 2.2.5 such a peak could give rise to excitation intensity dependent shift. In section 2.3.2 the effect of band bending on the luminescence peak is shown. All the effects mentioned above, can be explained by band bending if the band bending is large enough. It is shown that the band bending is the largest for p-type nanowires, since an oxide layer pins the Fermi level around 0.1 eV below the conduction band[30], as discussed in section 2.3.2. As can be seen in figure 5.3 the energy at which the peak starts \( E_{\text{min}} \) remains constant at 1.2 eV as a function of excitation intensity. Furthermore, the lower energy side remains the same for all excitation intensities, so increasing the excitation intensity only affects the high energy side of the spectrum.

The behaviour of the emission lines as a function of excitation intensity is examined. The excitation intensity dependence of the PL intensity, which is shown in figure 5.4, yields a slope of \( k = 0.9 \). This is not in agreement with the theory explained in section 2.2.7, but in the case of band bending, the theory from section 2.2.7 cannot be used anymore. The emission intensity and emission energy (as a function of position \( r \) in the wire) are strongly dependent on the electron and hole concentrations and thus on the excitation intensity. Therefore these two intensities cannot be separated anymore.

Figure 5.4: PL intensity in terms of area as a function of the excitation intensity for a p-type nanowire. The different lines represent different substrate temperatures: the squares represent 5 K, the circles represent 15 K, the up-triangles 25 K, the down-triangles 35 K, the diamonds 45 K, the left-triangles 55 K and the right-triangles 70 K. The thick black line is a reference line, which indicates different slopes.

The blue shift as a function of excitation intensity is examined more closely in figure 5.5. In the left figure the peak energy is plotted as a function of
excitation intensity for different substrate temperatures. In the right figure the peak energy is plotted against the substrate temperature for different excitation intensities. The observed shift is about 75 meV/decade, which is much larger than the shifts reported due to DA transitions, since all reported DA-shifts are between 10 and 50 meV. For instance, Montie et al. [25] and Sieg et al. [26] reported DA shifts of 10 meV/decade and 33 meV/decade respectively for p-InP films. Therefore the more plausible explanation is the one of band bending.

The minimum energy $E_{min}$, introduced in section 2.3.2, can be calculated with equation (2.47). Assuming a wire radius of $R = 50$ nm and $\varepsilon_r = 12.4$, $E_{min}$ is only dependent on the acceptor concentration $N_A$. This dependence is shown in figure 5.6. The model of complete depletion is only valid for low acceptor concentrations. Fortunately, maximum realistic values for electrically active acceptor concentrations are $N_A \sim 1 \cdot 10^{18}$ cm$^{-3}$, which is within the range of correctness of the complete depletion model. From figure 5.5a a value of $E_{min} \approx 1.15$ eV can be found, corresponding to an acceptor concentration of $N_A = (2.5 \pm 0.5) \cdot 10^{17}$ cm$^{-3}$, as indicated with the dashed and dotted lines in figure 5.6b. This is a realistic value for the acceptor acceptor concentration.

In figure 5.5b the temperature dependence of the peak position for a p-InP nanowire is shown. The plot clearly shows a decrease of emission energy with increasing temperature. This effect is too large to be explained just by the temperature dependence of the band-gap, as in this temperature range the band-gap decreases with only 7 meV, while the observed decrease in this
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![Figure 5.6: The minimum energy $E_{\text{min}}$ for photoluminescence (as defined in figure 2.10) as a function of the acceptor concentration $N_A$ on (a) a logarithmic scale and (b) a linear scale. In this figure the radius of the nanowire is assumed to be $R = 50$ nm and the dielectric constant of InP is $\varepsilon_r = 12.4$. The dashed line is a reference line at $E_{\text{min}} = 1.2$ eV, corresponding to an acceptor concentration of $N_A = 2.5 \cdot 10^{17}$ cm$^{-3}$. Temperature range is ten times larger.](image-url)

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Chapter 6

Electric field measurements

This chapter is the third part of the results sections. It discusses the photoluminescence measurements in combination with applying an electric field across the nanowire. Such measurements have been done at room temperature as well as at low temperature (5 K), which will be discussed in the following two sections.

6.1 Room temperature measurements

Room temperature photoluminescence experiments have been performed on the system as described in figure 3.5. The measured nanowires are intentionally n-type. The applied gate voltage is $V_{\text{gate}} = 25$ V and is a block voltage with period $T = 2$ s. It is applied to the silicon back gate, while the top contacts with the wire is kept grounded. The excitation intensity is 10 kW/cm$^2$, which is the same as in the high excitation intensity regime.

A typical result from these measurements is shown in figure 6.1. The different PL measurements in figure 6.1b are taken at the points in time which correspond to the vertical dotted lines in figure 6.1a. So the spectrum labelled with 1 is the spectrum without an applied electric field. The spectrum labelled 2, which is taken right after the voltage is turned on, shows a large increase in intensity as well as a blue shift. When time passes (spectra 3 and 4) the PL signal decreases to its original value coupled with a back shift to its original peak wavelength. When the voltage is turned off – corresponding to spectrum 5 – the PL signal decreases below the value without an applied electric field and with a small red shift. The PL intensity and peak position are extracted from the spectra shown in figure 6.1b and are plotted as a function of time in figure 6.2.

Clearly the appliance of a gate voltage (+25 V) yields a higher PL intensity ($\times3$) as well as a blue shift (6 meV). However this increase is not stable in
Chapter 6. Electric field measurements

Figure 6.1: (a) A block voltage is applied on the back gate. Luminescence spectra (b), plotted in counts per second (cps), were taken at the different times which are indicated in the plot by vertical dotted lines. The numbers of the lines correspond to the numbers in the luminescence spectra in (b). The spectra are shifted vertically for clarity.

Figure 6.2: The PL intensity in terms of area (a) and the peak position (b) versus time while applying a block voltage of 25 V and 0.5 Hz on the back gate.
6.2 Low temperature measurements

The sign of the gate voltage does not have any influence on the effect, i.e., when applying a negative gate voltage (-25 V) a decrease in intensity (\(\times 2\)) as well as a small red shift (3 meV) is observed, and when the voltage is turned off a much larger increase in PL intensity (\(\times 3\)) accompanied with a larger blue shift (6 meV) is observed. Furthermore the voltage can be applied to the nanowire instead of to the back gate. In this case, similar results are found with opposite sign.

The decay has a rather slow decay time in the order of \(\tau = 1\) s. A possible explanation for this slow decay is compensation of the charges on the wire, possibly due to water molecules at the surface of the nanowire. In order to avoid this effect, the same measurements can be done at low temperature, since water molecules are frozen at such circumstances, so they cannot align their dipole to compensate the electric field. Similar effects occur in electrical gate measurements on nanowires. At room temperature such gate experiments show a large hysteresis when sweeping from negative to positive gate voltages or vice versa. This hysteresis is much reduced at low temperatures[38].

6.2 Low temperature measurements

The low temperature (5 K) PL measurements combined with the appliance of a gate voltage have been performed with low excitation intensity (10 W/cm\(^2\)). The contacting of the nanowire has been done in a similar way as for the room temperature measurements. The measurements and are performed on a p-type nanowire. The gate voltage has been varied from -30 V to +30 V. The spectra measured with gate voltages of 0 V, -20 V and +25 V are shown in figure 6.3. Since the data shows a main peak with one smaller shoulder at a lower energy, the spectra have been fitted with a superposition of two Gaussians, which are shown in red in the figure.

At zero gate voltage the spectrum clearly shows a main peak at \(E = 1.36\) eV with a shoulder at \(E = 1.34\) eV. This is a much lower energy than the bandgap. As discussed in section 5.2, this could be due to band bending, since the measured nanowire is zinc-doped. The difference in peak position between the two \(p\)-InP wires could be explained by a difference in acceptor concentration. Contrary to the room temperature experiments, the overall PL intensity increasing with a positive gate voltage as well as with a negative gate voltage. Furthermore, a small blue shift is observed in the main peak.

When applying a negative gate voltage the main peak intensity increases while the shoulder remains constant at the original level. Clearly a negative gate voltage only influences the main peak while a positive voltage influences both. Before analysing this effect by examining the Gauss parameters, first the time dependence of the PL signal is discussed. For this purpose a con-
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![Figure 6.3: Low temperature (5 K) PL spectra, plotted in counts per minute (cpm), of p-type nanowires with gate voltages of (1) 0 V, (2) -20 V and (3) +25 V. The spectra are fitted with two Gaussians, indicated by the thicker red lines. The spectra are shifted vertically for clarity.](image)

A constant positive gate voltage of $V_{gate} = 25V$ is applied and every three seconds a spectrum is taken. The PL intensity of the measured spectra are plotted as a function of time in figure 6.4. The vertical dotted red lines indicate when the gate voltage is turned on and off. Besides the fluctuations in the order of 10%, which have also been observed at high excitation intensity (see section 4.2), the increase due to the gate voltage is stable over time. Furthermore, the effect is reproducible. This supports the idea that this is the same effect as observed in the electrical gate experiments[38].

![Figure 6.4: Time dependence of the luminescence peak while applying a gate voltage of +25V. The gate voltage is turned on at $t = 6$ s and turned off at $t = 136$ s, indicated with the red dotted vertical lines.](image)

Now we can take a closer look at the fit parameters found from figure 6.3.
6.2. Low temperature measurements

The double Gaussian fit provides two peaks with two peak intensities and two peak positions. Measurements have been performed for different gate voltages ranging between -25 V and +25 V. The results from the double Gaussian fit are shown in figures 6.5 as a function of gate voltage. The left figure gives the peak intensities of the two Gaussians and the right figure gives the peak energies. Evidently the main peak behaves symmetrically around $V_{\text{gate}} = 0$ V, whereas the shoulder behaves similar as the main peak for positive gate voltages and remains unaffected when a negative gate voltage is applied.

![Figure 6.5: The peak intensities (a) and peak positions (b) of the two peaks fitted with a double Gaussian as a function of gate voltage. The black and red curves indicate the upper and lower energy peak respectively.](image)

The appliance of a gate voltage can be interpreted as supplying extra charge carriers, i.e. electrons or holes. When a negative gate voltage (or positive wire voltage) is applied extra holes are available in the nanowire. When a positive gate voltage (or negative wire voltage) is applied the nanowire gets more electrons. Apparently the main peak intensity $I_{\text{main}}$ is indifferent for the type of charge carrier supply while the shoulder peak intensity $I_{\text{shoulder}}$ increases solely when the concentration of electrons is increased. In formula it can be written as:

$$ I_{\text{main}} \propto n \cdot p $$

$$ I_{\text{shoulder}} \propto n \cdot N_A. $$

(6.1)

According to the rate equations, introduced in section 2.2.7, the main peak can now be assigned to a band-to-band transition and the shoulder peak can be assigned to an acceptor-related transition. Equation (6.1) shows that for the shoulder peak the hole concentration $p$ does not influence the intensity, while it does for the main peak intensity. With regard to the electron concentration $n$, the emission intensities of both the main peak and the shoulder peak is influenced.
Chapter 7

MOCVD nanowires versus PLD nanowires

This chapter deals with the PL experiments on nanowires grown with metal-organic chemical vapour deposition (MOCVD) techniques and in particular, the difference between MOCVD-grown nanowires and PLD-grown nanowires. The previous chapters all dealt with PLD-grown InP nanowires, which gave a reasonable PL intensity. In contrast, MOCVD InP nanowires showed no luminescence at all. This could be explained in several ways.

First of all, it should be stressed that MOCVD nanowires are much shorter \( (l \sim 2\mu m) \) than PLD nanowires \( (l \sim 10\mu m) \). This is shown in the figures 7.1a and b, which are photos of MOCVD nanowires and PLD nanowires respectively, taken with a scanning electron microscope (SEM). Clearly, the typical length of an MOCVD nanowire is smaller than the diameter of the excitation spot \( (R_{\text{spot}} \sim 5\mu m) \). The thickness of the wires however is comparable. Therefore this effect could cause a factor 5 decrease in PL signal,
but cannot completely quench the luminescence.

Secondly, the MOCVD nanowires could easily be burnt away while exciting them with a high excitation intensity. This is also not the case with the PLD nanowires. This is shown in the SEM images in figure 7.2. The upper image shows clear traces where the laser (10 kW/cm²) scanned the surface. As shown in the lower left image, the nanowires are melted by the laser, leaving damaged wires mixed up behind, while before laser scanning, the wires were more or less positioned in the same direction (due to epitaxial growth). This is shown in the lower right image. This effect could be explained by assuming that a lot of (phonon-assisted) non-radiative processes are taking place. These processes convert the excitation intensity into heat. The nanowires cannot lose its heat to the substrate due to bad thermal contact. As a result, the temperature in the nanowire rises rapidly, reaching values of more than 500 K. Eventually the nanowire could evaporate. All this means that the crystal quality of the nanowires grown with MOCVD is worse than those grown with PLD. Maybe this is due to side growth, present in MOCVD but not in PLD, causing a bad crystalline quality at the edges of the nanowires. This problem has been overcome with success by putting a wider band-gap material around the nanowire. Figure 7.3 shows the cross section of an
InP nanowire with a GaP capping layer grown coaxially around it. The hexagonal structure is the $p$-InP nanowire. The GaP layer surrounding it has a thickness of approximately 5 nm (see detailed image 7.3b). The larger dark grey layer is SiO$_2$ and is deposited after growth and is needed for sample preparation. On top of it, a platinum layer (in white) is deposited in order to avoid charging by the electron beam. GaP has a wider bandgap than InP, which causes the free carriers to stay inside the InP core. These nanowires indeed showed luminescence. The results of a zinc-doped MOCVD-grown InP nanowire are presented in figure 7.4. As a comparison, a (scaled) PL spectrum of a PLD-grown $p$-doped InP nanowire is shown in grey. The spectra exhibit a peak (1) around 30 meV below the bandgap and a peak (2) around 45 meV below the bandgap (indicated with the dotted reference lines in figure 7.4). The higher peak (1) could be an acceptor-related transition, for instance due to zinc, which is present in the nanowire. The ionisation energy of zinc is $E_A = 35$ meV, which is in reasonable agreement with the experiments. The lower peak (2) could be due to another acceptor-related transition, for instance carbon. Carbon has an ionisation energy of $E_A = 40$ meV. Moreover it seems that no band bending takes place in MOCVD-grown $p$-InP nanowires, since the red shift in the emission lines has vanished completely. This could be due to the GaP capping layer, which reduces the Fermi level pinning. Or it could be due to the large width ($d = 150$ nm) of the nanowire. It is obvious that the band bending is of less importance with increasing diameter. Another explanation could be that the acceptor concentration is so high, that the nanowire is not completely depleted anymore. This causes the Fermi level to
Chapter 7. MOCVD nanowires versus PLD nanowires

reach bulk values in the core of the nanowire.

![Graph showing PL spectra (counts per minute) of a p-InP nanowire with a GaP capping layer grown around it coaxially. The spectra were measured at low temperature (5 K) and low excitation intensity. The nanowire has been grown with MOCVD techniques. The different lines correspond to 100%, 50%, 20%, 10%, and 5% of the maximum excitation intensity respectively with decreasing PL intensity. The spectra are shifted vertically for clarity. The grey line represents a spectrum from a PLD-grown p-InP nanowire. The three vertical dotted lines are reference lines at the band-gap ($E_g$), (1) at $E_g - 30$ meV and (2) at $E_g - 45$ meV.](image)

Figure 7.4: PL spectra, in counts per minutes (cpm) of a p-InP nanowire with a GaP capping layer grown around it coaxially. The spectra were measured at low temperature (5 K) and low excitation intensity. The nanowire has been grown with MOCVD techniques. The different lines correspond to 100%, 50%, 20%, 10%, and 5% of the maximum excitation intensity respectively with decreasing PL intensity. The spectra are shifted vertically for clarity. The grey line represents a spectrum from a PLD-grown p-InP nanowire. The three vertical dotted lines are reference lines at the band-gap ($E_g$), (1) at $E_g - 30$ meV and (2) at $E_g - 45$ meV.
Chapter 8

Conclusions and outlook

In this study microphotoluminescence experiments on single InP nanowires have been performed. Measurements have been done on wires with and without intentional electrical doping in the high excitation regime as well as the low excitation regime. Furthermore PL experiments have been done in combination with an electric field. This thesis has attempted to explain the results from the experiments with several models. The conclusions are summarised below.

- Semiconducting InP nanowires grown with PLD show luminescence at room temperature (RT) as well as at low temperature (LT), i.e., $T = 1.4 - 5$ K.

- Semiconducting InP nanowires grown with MOCVD techniques show no luminescence. Instead (in the high excitation regime), due to a large amount of non-radiative recombination, the nanowires heat up and eventually evaporate. However, when the nanowires are being capped with a larger band-gap material, such as GaP, the InP nanowires do show luminescence at low temperature (5 K) and with low excitation intensity (10 W/cm$^2$).

- With low excitation intensities and low temperature half of all the intrinsic InP nanowires have a dominant defect emission line 40 meV below the band-gap, whereas the other half show a similar spectrum as that of the $n$-type InP nanowires with a dominant peak at the band-gap energy.

- The PL spectra of $p$-InP nanowires show a large red shift (100 meV) as well as a broadening. This can be explained by band bending due to Fermi pinning caused by the oxide at the surface. This band bending seems to vanish when $p$-InP are capped with wider band-gap material, such as GaP.
• When exciting the nanowires with a high excitation intensity (10 kW/cm²), the luminescence spectra show a Burstein-Moss effect: the quasi-Fermi level lies in the conduction band resulting in a broadening of the peak.

• The measured nanowires show a large polarisation anisotropy $\rho = 0.7$ at RT as well as LT, as reported in literature. However it is not as large as the expected theoretical value of $\rho = 0.96$. This could be caused by a diameter dependence. As the diameter increases, the polarisation anisotropy becomes smaller.

• From the fits can be concluded that the temperature in the nanowire rises significantly with increasing excitation intensity. In this way, for RT experiments the temperature within the wire can get as high as $T = 700$ K and for LT experiments the temperature within the wire can reach values of $T = 120$ K.

• The emission intensity is strongly dependent on the position and moment of excitation of the nanowire. The emission intensity is thus sensitive to uniformity and stability. This could be due to inhomogeneities or local defects or electrostatic charges on the surface of the nanowire.

• At RT an electric field causes a blue shift and an increase of PL intensity. It is proposed that this is due to charges on the surface, e.g. water molecules, which compensate the electric field inside the wire. At RT this effect decays in the order of $\mu$s’s. At LT, also a large increase of PL intensity is observed. This effect is stable, which confirms the model of surface charges.
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Bibliography


