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Growth and characterization of Mn-doped InAs quantum dots on GaAs (001)

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Report of a graduation project from October 2006 to August 2007, carried out at the NEXT-NS spintronics group of the Interuniversity Micro-Electronics Center (IMEC), Leuven and the Photonics and Semiconductor Nanophysics (PSN) group at the Eindhoven University of Technology (TU/e) at the department of applied physics.

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Abstract

In recent years, the interest in semiconductor spintronics in research has grown significantly. In diluted magnetic semiconductors (DMS), electrical, optical and spin-properties can be integrated into one material system. Semiconductor quantum dots (QDs) are considered to be important candidates for the realization of q-bits, and also for single photon emission. In this project, manganese doped InAs/GaAs QDs were grown by molecular beam epitaxy (MBE) and the growth procedure was optimized in order to obtain QDs containing one single manganese atom. The samples were characterized using AFM, photoluminescence (PL), Hall effect measurements and cross-sectional STM (X-STM). The interaction of manganese with the exciton in the QDs was studied by performing PL-measurements in a confocal microscope setup. Emission lines from single quantum dots were observed, but no coupling of the exciton with manganese could be detected so far.
1. Introduction

In recent years, semiconductor quantum dots (QDs) have attracted much attention in research. They are the textbook example of a particle in a box in quantum mechanics, in which electrons and holes are confined in all three spatial directions, resulting in discrete energy spectra. These discrete energy states are very similar to molecular orbitals, which is why semiconductor quantum dots are also referred to as artificial atoms.

The interest in semiconductor quantum dots is mainly due to their optical properties. For indium arsenide (InAs) quantum dots within a gallium arsenide (GaAs) matrix, the emission wavelength can be tuned in a large range, covering both the 1300 nm and 1550 nm wavelength which are important for data transport through optical fibers. Therefore, the most important applications are light emitting diodes (LED) and lasers, but also more advanced applications, such as (polarized) single photon emitters.

The single photon emitters are used in quantum cryptography, where the polarization of the photon is used as an information carrier. When an eavesdropper is to intercept part of the transmitted signal, the wavefunction of the system will be altered, so the receiver will detect that something is wrong. The photon can not be divided, so therefore it is the ultimate information carrier for optical data transmission. The polarization of the emitted photon depends on the spin state of the recombining charge carriers. This brings us into the field of spin-dependent electronics, or spintronics.

For realizing the emission of single photons, semiconductor QDs are being investigated. The polarization of the emitted light can be controlled by influencing the spin states of the confined charge carriers. One way to do this is by inserting a single magnetic impurity such as manganese in the QD. The wavefunction of the manganese couples with the excitons which are confined within the QD, which results in a splitting of the PL energies for the different excitons. This splitting is related to the spin state of the manganese, which can be changed by applying magnetic fields in order to obtain the required polarization state for the emitted photon.

For quantum dots, the introduction of magnetic dopants was realized recently in II/VI materials, by doping cadmium telluride quantum dots within zinc telluride matrix with a single manganese atom [1]. The coupling between the manganese spin and the quantum dot wave functions can be probed in photoluminescence measurements on single quantum dots, as illustrated in figure 1.1.
Figure 1.1: Photoluminescence from CdTe/ZnTe quantum dots in a Schottky structure. (a) Undoped QD; (b) Mn-doped QD. The splitting in 6 and 11 states is due to the coupling with the Mn-spin. [1]

Similar results are expected within III/V quantum dots, which can be tuned to match the telecommunication wavelengths, opening up many opportunities for device applications. The major difference is that manganese acts as an acceptor in a III/V material system, whereas it acts as a neutral impurity for a II/VI material system. Therefore, in a doped III/V-dot, one is more likely to find positively charged excitons than neutral excitons, due to the acceptor behavior of manganese.

In this thesis, MBE grown manganese doped InAs QDs are studied within a GaAs matrix. The coupling between the manganese and the confined excitons in the QD are investigated by photoluminescence (PL) in a confocal microscope setup.

In order to be able to address single dots, the density of the QDs has to be sufficiently low. Therefore, the quantum dot growth is first optimized using AFM and bulk photoluminescence as characterization steps. Subsequently, the doping of the QDs with manganese is performed by both direct and indirect doping methods.

In chapter 2, the theoretical framework of this thesis is outlined, starting from MBE growth of quantum dots, going to exciton complexes within these dots and dealing with the coupling between the exciton and the manganese wavefunction. In the third chapter, the experimental setups and procedures are described, with the main focus on photoluminescence (PL) measurements in a confocal microscope setup, providing the ability to collect the PL signal from single quantum dots. The fourth chapter gives an overview of the experimental results and provides explanations for them. In the fifth chapter, the conclusions from this project are outlined, and an overview of possible future work is provided.
2. Theory

2.1. Molecular Beam Epitaxy (MBE)

Since its invention in the 1970’s, the technique of molecular beam epitaxy (MBE) has been widely used for the fabrication of high-quality single crystalline semiconductor structures, both for industrial and research applications. MBE is an ultra-high vacuum (UHV) growth method which allows layer-by-layer growth of semiconductor structures, with sub-monolayer control on layer thicknesses.

2.1.1. General outline

In MBE growth, molecular beams are directed onto a heated single crystalline substrate, where the atoms can be incorporated into the crystal lattice. The schematic overview of an MBE chamber in figure 2.1 gives insight in the process of MBE growth.

The source materials are evaporated from effusion cells (1) which are heated resistively. The molecular flux from the cells is controlled through the cell temperature, which is monitored using a thermocouple. Each cell can be shielded by a cell shutter, and the entire block of cells can be separated from the rest of the chamber by closing the main shutter (3). In order to maintain an ultra-high vacuum, the entire chamber is cooled with cryo-panels (2) using liquid nitrogen. The sample is mounted on a block which is clamped into the sample holder (4), which can be resistively heated (5). The sample holder is mounted on the manipulator unit, together with an ion-gauge used for flux measurements. This manipulator unit can be rotated into different positions for sample loading (substrate holder facing the transfer system (7)), flux calibration (ion-gauge facing the effusion cells) and growth (sample holder facing effusion cells).
facing the effusion cells). During the growth process, the sample is heated, in order to increase the mobility of the deposited atoms, while the sample holder is rotated in order to obtain better uniformity in the layer structures (since all cells face the sample under slightly different angles, and the flux of the molecular beam is not homogenous). The substrate temperature is monitored using a thermocouple which is positioned in the center of the sample holder. The structural quality of the sample is monitored during growth by Reflection High Energy Electron Diffraction (RHEED), which will be discussed in detail in 2.1.2. An electron beam is generated by the electron gun (9), which hits the sample under a grazing angle, generating a diffraction pattern on a phosphorus screen (10). This pattern provides information about the growth and the sample quality. The quality of the UHV is monitored using a pressure gauge and a quadrupole mass spectrometer (11) for determining the composition of the background.

2.1.2. Reflection High Energy Electron Diffraction (RHEED)

RHEED allows in-situ characterization of the crystal structure and its quality, and is therefore an indispensable tool for MBE growth. The power of RHEED lies in the fact that one obtains real-time in-situ information on the growth process, while it does not interfere with the growth process. The most important types of information one can extract from RHEED are the quality of the surface preparation, the orientation of the crystal, the crystal morphology during growth and the number of deposited layers in layer-by-layer growth.

In RHEED, high energy electrons are generated from an electron gun with typical energies in the range of 5 to 100 keV. These electrons hit the sample under grazing incidence with an angle in the order of only 1 degree. The sample influences the beam in two ways: it acts both as a reflector (figure 2.2) and as a diffraction grating for the incoming beam of electrons.

Both elastic and inelastic scattering events take place when the electron beam interacts with the sample. The elastic scattering events can be described using a one-body Schrodinger equation. Quasi-elastic scattering events can also be accounted for within this framework, using perturbation theory.

The incoming beam is represented by a plane wave with the corresponding wave vector $\vec{k}_0$ (see figure 2.2). The wave vector $\vec{g}_n$ represents the momentum imparted by the crystal onto the wave. The final wave vector $\vec{k}_f$ is found by looking for the intersection of $\vec{g}_n$ with the Ewald sphere, the sphere in k-space consisting of wave vectors allowed by conservation of energy.
On the left-hand-side in figure 2.2, the diffraction approach is illustrated in reciprocal space, while on the right-hand-side the reflector approach is illustrated in real space. The diffracted beams can only excite phosphorus atoms on the RHEED screen in positions above the shadow edge \( y_2 \).

The rows of atoms on the surface act as a series of line scatterers for the incoming beam, forming a diffraction grating. Two particular cases are of interest when considering the sample as a diffraction grating. One case is where the electron beam is perpendicular to the line scatterers, and the other case is where the electron beam is parallel to the line scatterers.

When the incident beam is perpendicular to the line scatterers, each line is the source of a wave, of which the phase is determined by the incoming wave, as described by the grating formula (equation 2.1).

\[
k_0 \cos \theta_n = k_0 \cos \theta_0 + nG
\]  
(2.1)

Where \( k_0 \) is the magnitude of the incoming wave vector; and since the scattering is assumed to be elastic, it is also the magnitude of the outgoing wave vector; \( \theta_0 \) is the angle of grazing incidence, whereas \( \theta_n \) is the n-th order diffracted beam; \( G \) is given by the periodicity of the crystal lattice \( a_0 \), such that \( G = 2\pi/a_0 \).

An instructive way of looking at the diffraction phenomena is by using the Ewald construction, which was already mentioned in figure 2.2. For the case of line scatterers perpendicular to the incoming beam of electrons, this construction is illustrated in figure 2.3, in which the diffraction angles are given by the grating formula (equation 2.1).
Figure 2.3: Ewald sphere for diffraction with a grating perpendicular to the incoming beam of electrons [2]

In figure 2.3, the allowed diffraction angles for a given incident wave vector $k_0$ are given. All real wave vectors have the same magnitude, due to conservation of energy. Next to the real solutions, scattering to imaginary wave vectors is also possible, in the form of evanescent waves. The origin for the construction of the Ewald sphere is the beginning of the incident wave vector, whereas the end of the incident wave vector forms the origin for the k-space description of the grating. The lines intersecting the tips of the grating vectors are the diffraction rods, which are perpendicular to the plane of the grating. Scattering to the evanescent wave cannot be seen, but it can be diffracted again by the crystal. In a scattering event into the evanescent wave, momentum is extracted from the grating.

Important to note is that for small angles of incidence, the angle of reflection for the specular beam is also small, while the angle for the first order reflection at $-G$ is sufficiently large for having a much larger momentum transfer in the $z$-direction compared to the specular beam. The intensity of the reflection decreases with increasing momentum transfer in the direction perpendicular to the surface, and hence, with increasing orders of diffraction. For small angles, the first order diffraction is given by equation 2.2.

$$\theta_n = \sqrt{\theta_0^2 - \frac{2nG}{k_0}}$$  \hspace{1cm} (2.2)

Substituting with the typical numbers which were listed before, one obtains a typical first order diffraction angle of 0.3 rad for an incident beam of 10 keV electrons under grazing incidence at 0.02 rad. In that case, the intensity of this reflection would be a factor 8 lower than the specular spot, if the scattering from the lines would be
isotropic, which is not the case for 10 keV electrons. According to the uncertainty principle (equation 2.3), with $\Delta x$ of the order of the Bohr radius, most of the scattering for 10 keV electron volts will be within 0.1 rad.

$$\Delta p \Delta x \sim h$$  \hspace{1cm} (2.3)

For larger periodic blocks as compared to the periodicity of the lattice, for example surface reconstructions such as the 2x4 reconstruction in GaAs, the diffraction angles are still within 0.1 rad for 10 keV electrons. These reconstructions are discussed at the end of this paragraph.

For line scatterers parallel to the incoming beam, more interesting effects are going on. In this case, the action is taking place in the $k_y$ direction. The reflection from a grating with lines parallel to the incoming beam becomes a 3D diffraction, with the beam in the x-z plane being diffracted in the positive and negative y-direction, which is illustrated in figure 2.4. The transmitted beam vector represents the incoming momentum, and all the other vectors on the same Ewald sphere are the refracted beams in k-space. The scattering vectors have a momentum of $\pm nG\hat{y}$ in the y-direction, together with a momentum in the x-direction as described above. The number of refracted beams depends on the line spacing of the grating, denoted by G. A larger spacing results in more refracted beams within the Ewald sphere.

![Figure 2.4: Scattering for grating parallel to the incident beam of electrons][2]

When the sample is rotated, the specular beam will remain on the same position, whereas the other diffraction spots will move. This will cause spots from above the shadow line to move until they disappear below the shadow line, while spots on the other side of the specular beam will move from below and end up above the shadow line. By combining the patterns as illustrated in figures 2.3 and 2.4, and all the patterns corresponding to positions in between these two, one can assemble a picture of the diffraction patterns as a function of sample rotation, as illustrated in figure 2.5. It can be seen that the subsequent spots for the different angles all lay on one line, in that way producing a “streaky” pattern, which is characteristic for a flat surface.
Figure 2.5: Formation of a streaky RHEED pattern as a function of changing sample position. On the left, new spots appear from below the shadow line, while on the right spots disappear below the shadow edge with increasing angle.

Next to the quest for "streaky" RHEED patterns, the experimental MBE grower also makes use of another very useful property: RHEED oscillations. During the deposition of new layers in layer-by-layer growth, the intensity of the streaks oscillates, with one deposited monolayer corresponding exactly to one oscillation. By monitoring the intensity of the specular spot during deposition without substrate rotation, the growth rate can easily be calibrated, with accuracy better than 2 percent. Two different explanations for the RHEED oscillations are generally accepted. Both of them concern the diffraction from a half-filled surface. The interference approach says that the decrease in intensity is related to the different path lengths from the RHEED source to the screen for the different terraces on the surface. The channeling approach relates the drop in intensity to the increased probability for being scattered in many different directions at step edges.

During the formation of quantum dots, a transition between a 2D (layer-by-layer growth) and 3D surface structure occurs, which causes a dramatic change in the RHEED pattern. The "streaky" pattern from the 2D growth will be replaced by a "spotty" pattern related to the 3D growth. This transition can be understood starting from figure 2.6, in which the difference between diffraction by a 2D single crystalline structure and a lens-shaped quantum dot is outlined.
In Fig. 2.6 (a), an ideal 2D surface is illustrated in the X-Y plane, as assumed in the theoretical framework which is described above. The perfect 2D surface serves as an ideal diffraction grating in the X-Y plane. Since the incoming beam hits the sample under a grazing angle, it has a large component of momentum in the Y-direction, while the Z-component is really small. Therefore, the beam does not penetrate the sample much in the Z-direction, which is why there is no additional diffraction due to the periodicity in the Z-direction.

Upon formation of quantum dots, 3D structures arise on top of the 2D surface as illustrated in Fig. 2.6 (b). These structures act as additional line scatterers for the electron beam in the Z-direction, because in this case, the large momentum of the incoming beam in the X- or Y-direction makes it possible to penetrate deeper into the 3D structures on top of the 2D surface. These additional line scatterers will cause additional diffraction, so the final picture on the RHEED screen will be a superposition of 2 different patterns.

The spotty pattern is generated as a consequence of an ensemble of quantum dots, since the electron beam is illuminating a large area of the sample surface. The intensity depends on the number of dots and their sizes, but the related patterns are always similar. As discussed before, the distance between the streaks is dictated by the lattice constants in the X-Y plane. The additional scattering pattern due to the 3D structures is caused by a grating with a slightly larger lattice constant (strain
relaxation in Z-direction). The “spotty” pattern will show up on top of the “streaky” pattern, because the area in between the 3D structures is still a nice 2D surface which acts as a perfect 2D diffraction grating. The distance between the spots on the 1-streaks is related to the lattice spacing in the Z-direction, while the spacing of the streaks is related to the lattice spacing in the X-Y plane. Upon substrate rotation, the spots will brighten up and fade away on fixed positions (depending on the substrate orientation).

At the surface of a semiconductor, the bulk configuration is abruptly distorted, resulting in dangling bonds. These dangling bonds are involved in the surface passivation process, in which they will bind in such a fashion that the surface energy is minimized. Depending on the growth conditions, these reconstructions will differ in structure and energies. The reconstruction pattern depends on the growth temperature and the provided Arsenic flow. The transitions between the different surface reconstruction patterns happen in well-defined temperature ranges, which make them excellent calibration points for the temperature in MBE growth.

For this project two reconstruction patterns are used as temperature calibration points. The first one is the removal of the oxide and the subsequent appearance of the 2x4 reconstruction during the deoxidation of the substrate. The 2x4 surface reconstruction structure is illustrated in figure 2.7. The 2x4 reconstruction is a reconstruction which shows up at high temperatures.

![Figure 2.7: The structure of the 2x4 surface reconstruction in GaAs (001), both in top view (a) and side view (b).](image)

It can be seen that the 2-fold reconstruction appears when viewing along [110], while the 4-fold reconstruction appears along [1 1 0].

When the temperature is reduced, the 2x4 reconstruction remains until the temperature reaches 485 to 470 °C [18], where the transition to the c(4x4) reconstruction takes place. Since the transition between the 2x4 and c(4x4) is an intrinsic property of GaAs, it is a good calibration point for the substrate temperature. Moreover, the transition temperature is only weakly dependent on the provided Arsenic flux. The structure of the Arsenic-rich c(4x4) reconstruction is illustrated in figure 2.8.
In practice, the transition can be seen very nice along <100>, where the transition goes from 2-fold to 4-fold reconstructed. Furthermore, along [110] the reconstruction remains 2-fold, while the reconstruction along [1\overline{1}0] makes the transition from 4-fold to 2-fold.

2.1.3. Growth of III-V semiconductors

Over the last decades, III-V semiconductors have attracted a lot of attention in research for a variety of applications. The power of these structure lies within the large amount of available materials which can be combined in order to tailor material properties in a very broad range. The key materials are gallium (Ga), aluminum (Al) and indium (In) for group III and arsenic (As), antimony (Sb), phosphor (P) and nitrogen (N) for group V. By combining these materials, in binary, ternary and quaternary structures, one can compose materials with a large variety in optical and electrical properties. The most important binary compounds and their bandgap energies are shown in figure 2.9. For the materials used in this project, the bandgap energies and the corresponding wavelengths are listed in table 2.1.
The most widely studied material system in III-V semiconductors is gallium arsenide (GaAs) which often serves as the substrate material for III-V compounds. In the remainder of this section, the growth process for III-V semiconductors will be outlined starting from the GaAs material system.

During growth the GaAs substrate is heated to the desired temperature while being exposed to a constant As-flow, in order to prevent desorption of arsenic atoms out of the surface. When the temperature has stabilized the growth can be initiated by providing a flux of gallium atoms, which determines the growth rate of the GaAs. The growth rate in III-V compounds based on arsenic and antimony is determined by the flux of group III materials, which can be varied in a quite broad range. In section 3.1, the sample fabrication process will be outlined in detail, starting from substrate preparation up to indium arsenide quantum dot growth within a gallium arsenide matrix.

### 2.1.4. Self-Assembled Quantum Dot Growth

When a lattice mismatched material is deposited on top of a different material, there will be stress present at the interface. The amount of strain energy is largely dependent on the lattice mismatch between the two materials, and the thickness of the deposited layer. The strain can be relaxed by several different mechanisms. If a large amount of material is deposited, the strain will relax by defect-formation. For materials with a very large lattice mismatch, an entirely different process will take place. The formation of 3D-structures will be initiated after deposition of a certain amount of the strained material. This process was described by Stranski and Krastanov [3], after whom this mechanism was named self-assembled quantum dot formation in Stranski-Krastanov mode.
In Stranski-Krastanov growth, a material with a larger lattice constant is deposited on top of a material with a smaller lattice constant. 2 stages can be distinguished in this growth mode, as described in figure 2.10. Initially, a strained layer will be formed, which is called the Wetting Layer (b). The strained film will continue to grow until a critical thickness is reached. If the deposition is continued at that point, the stress will relax by formation of 3D islands, so-called quantum dots (c).

The critical thickness depends on the lattice mismatch between the 2 materials. The larger the difference in lattice constant, the smaller the critical thickness becomes. The shape of these dots can differ depending on materials, growth conditions and capping material and temperature. The most typical structures are shaped like a lens or a (truncated) pyramid, as depicted in figure 2.11.

For indium arsenide deposited on top of gallium arsenide, the lattice mismatch is 7.2%. The first 1.7 monolayers, the indium arsenide grows as a strained film, after which the strain is relaxed by formation of lens-shaped quantum dots [4]. Upon coverage with gallium arsenide, the structure of the dot will change, depending on the growth temperature and growth interrupt before capping. During this capping process, indium will intermix with gallium, changing the morphology of the dots and the wetting layer. High temperature capping (typically at the growth temperature of the dots) gives rise to intermixing of indium and gallium, which results in a broad smeared out wetting layer and small quantum dots. Low temperature capping on the other hand will limit intermixing which results in a thin wetting layer with larger dots, shaped as truncated pyramids [5].

2.2. Electronic structure of InAs/GaAs quantum dots

Semiconductor quantum dots are zero-dimensional structures, which can confine charge carriers in all 3 spatial directions. Therefore they can be seen as the realization of the textbook example of a particle in a box. Quantum dots are often called artificial atoms, because the discrete energy levels of electrons and holes in these structures resemble nicely the atomic binding energies for electrons.
The bound states of electrons and holes in a quantum dot can be calculated for the different types of dot shapes, ranging from lens-shaped to pyramids or truncated pyramids. However, as a starting point, it is instructive to look at the example of a 3D infinitely deep quantum well, the so-called particle in a box. The expression for the energy of the bound states is given by equation 2.4.

\[
E = E_{0}^{\text{InAs}} + \frac{\hbar^{2} \pi^{2}}{2m_{0}} \left( \frac{1}{m_{e}} + \frac{1}{m_{h}} \right) \left( \frac{n_{x}^{2}}{a^{2}} + \frac{n_{y}^{2}}{b^{2}} + \frac{n_{z}^{2}}{c^{2}} \right)
\]

(2.4)

Where \( E_{0}^{\text{InAs}} \) is the bandgap energy of InAs, \( m_{e} \) and \( m_{h} \) are the effective masses for electrons and holes, and \( a, b \) and \( c \) represent the size of the box in x-, y- and z-direction. The quantum numbers \( n_{x}, n_{y}, \) and \( n_{z} \) determine the confinement energy of the charge carriers, with \( n_{x} = 1, n_{y} = 1 \) and \( n_{z} = 1 \) representing the lowest energy state. For a typical quantum dot, the x- and y-size are substantially larger than the z-size, which means that confinement is strong in the z-direction and much weaker in the x- and y-direction. Note that the quantum numbers \( n_{x}, n_{y}, \) and \( n_{z} \) are assumed to be identical, since these transitions have the largest possibilities. There are several other allowed transitions (depending on the overlap of the electron- and hole-wavefunctions) but with much smaller transition probabilities.

For the real case, it is important to realize that the potential well is not infinitely deep, which causes the number of bound states to be limited, and which also causes large deviations for the higher excited states. For the lowest energy state the approximation is quite accurate. To obtain more accurate results, often a harmonic potential well is used in literature.

The electronic structure of a quantum dot can be probed in PL experiments, in which recombination of electrons and holes shows up as exciton lines. An exciton is an electron-hole pair, which consists of one electron from the conduction band, attracted by the coulomb interaction to a hole in the valence band.

### 2.2.1. The neutral exciton \( X^{0} \)

The simplest example of an exciton is the neutral exciton \( X^{0} \), which consists of one bound electron-hole pair. The electrons carry spin +1/2 (up) or -1/2 (down), while the heavy holes carry spin +3/2 (up) or -3/2 (down). Light holes do not take part in the exciton formation process, because the energy of heavy holes is far more favorable for this (due to the parabolic dispersion relation and differences in effective masses). The initial spin states of the charge carriers determine which transitions are allowed, and which of these are optically active. The total spin should be conserved, while a photon can only carry a spin +1 or -1, corresponding to circularly polarization \( \sigma^{+} \) (right-handed) or \( \sigma^{-} \) (left-handed). The different possible configurations for a single neutral exciton \( X^{0} \) are illustrated in figure 2.12.
Figure 2.12: Energy diagrams for the neutral exciton $X^0$, the two transitions on the left are optically active (bright states) and obey the conservation of spin, the two transitions on the right are not optically active (dark states), which means that due to the conservation of spin, no optical transition is allowed.

For the $X^0$ state, both the electron (solid circles) and hole (open circles) are in an $s$ orbital state, and their spin is represented by an arrow. The $m$ quantum number represents the projection of the total exciton spin along the $z$-axis. The bright and dark states are energetically separated as a consequence of the electron-hole exchange interaction, which is illustrated schematically in figure 2.13. This e-h-exchange interaction originates in the quantum mechanics of an identical particle system; which implies that two identical particles can not be distinguished from each other. The e-h-exchange interaction acts between the spins of electrons and holes, which are aligned parallel for dark states, and anti-parallel for bright states.

Figure 2.13: Schematic overview of PL energies for the neutral exciton $X^0$, showing the splitting due to e-h-exchange interaction and splitting of bright (dashed lines) and dark (solid lines) states due to anisotropy.

The magnitude of the e-h-exchange interaction can be deduced from the effective spin Hamiltonian, which is given in equation 2.5 [6].

$$\hat{H}_{\text{ex}}^{\text{eh}} = 2\Delta_{\text{eh}} J_z S_z + \Delta_1 (J_z S_z - J_y S_y) + \Delta_2 (J_z S_z + J_y S_y)$$  \hspace{1cm} (2.5)

In this expression, $S_z (J_z)$ is the $z$-component of the total electron spin $S$ (hole pseudo spin $J$). The pseudo spin for the holes is defined as $J_z = +1/2, -1/2$ corresponding to hole spin -3/2 and +3/2 respectively [6]. Note that by convention the sign of the pseudo spin is exactly the opposite of the hole spin.
The first term in equation 2.5 accounts for the isotropic e-h-exchange interaction and splits $X^0$ into two states, the bright states and the dark states. The second and third term account for the shape-anisotropy of the dots, which is a minor effect compared to the e-h-exchange. The anisotropy causes a splitting of both the bright and dark states into doublets, as illustrated in figure 2.13. The two bright states couple to photons with orthogonal linear polarization.

The magnitude of the e-h-exchange interaction follows from the Schrödinger equation (2.6) with the effective spin Hamiltonian given in equation 2.5.

$$\hat{H}_{eh}^x \psi = E \psi$$  \hspace{1cm} (2.6)

Filling out the different spin states for the $X^0$ exciton, as outlined in figure 2.12, a splitting energy of $\hat{H}_{eh}^x = -1/2 \Delta_{eh}$ is obtained for $m = +/- 1$ and $\hat{H}_{eh}^x = 1/2 \Delta_{eh}$ for $m = +/- 2$. This yields an energy splitting $\Delta E = \Delta_{eh}$ as illustrated in figure 2.12. In this calculation, the second and third term of equation 2.5 were neglected, since $\Delta_{eh} >> \Delta_1, \Delta_2$. Typical e-h-exchange energies for InAs quantum dots within GaAs are $\Delta_{eh} \approx 0.6 \text{meV}$, while the anisotropy splitting is of the order of $30 \text{µeV}$ [6].

Next to the neutral exciton $X^0$, several other exciton states can show up in PL-spectra by confining more carriers into one quantum dot. This can be achieved by using gates and applying a certain bias voltage, or alternatively by adding dopant atoms in or close to the quantum dot structure. In the case of an acceptor, an additional hole can be confined in the quantum dot.

In the remainder of this section, a few additional exciton states are discussed, focusing on neutral and positively charged exciton complexes (since manganese doping provides additional holes in our structures).

### 2.2.2. The positively charged exciton $X^+$

When an additional hole is provided for the neutral exciton $X^0$, it occupies an s-state (as illustrated in figure 2.14), resulting in a positively charged exciton $X^+$.
Both of the initial $X^+$ states are bright states, since the holes in the s-states have opposite spins due to the Pauli Exclusion Principle. When filling out the spin states for the initial $X^+$ states in equation 2.5, it follows that there is no e-h-exchange, so the positively charged exciton shows up as a single line in PL spectra. As a consequence of conservation of spin, the $m = -1/2$ exciton emits circular left handed polarized light, whereas the $m = +1/2$ exciton emits circular right handed polarized light.

2.2.3. The neutral biexciton $2X^0$
A neutral biexciton $2X^0$ consists of 2 electrons and 2 holes confined in 2 s-states for which the energy diagram is given in figure 2.15.

![Energy diagram of the neutral biexciton (2X0)](image)

2 different optical transitions are allowed for this configuration. The electron and hole on the left (right) can recombine, emitting a right (left) handed circular polarized photon and leaving a neutral exciton with $m = -1$ ($m = +1$). As a consequence of the coulomb interaction, the recombination energy of the $2X^0$ exciton is different from the neutral exciton line, which shows up after emission of the first photon.

2.3. Manganese in III-V semiconductors

2.3.1. Electronic structure of Mn in III-V lattice
In order to understand the interaction of manganese with the III-V semiconductor host material, one has to consider the electronic configurations of the different atoms that are involved. The electronic configurations for gallium, arsenic, indium and manganese in their ground state are schematically illustrated in figure 2.17.

![Electronic configuration of selected elements in their ground state.](image)

The group III elements gallium and indium show a similar electronic configuration, with 3 valence electrons in 4s and 4p and 5s and 5p orbital states respectively. Arsenic
as a group V element has 5 valence electrons in 4s and 4p orbital states. Manganese as a group VIIB element has 7 valence electrons, of which 2 are located in 4s orbital states, and 5 are located in 3d orbital states. These 5 d-electrons are responsible for the large magnetic moment of manganese, $S = \frac{5}{2}$.

Depending on its location within the host material, manganese can have several different electronic configurations. Manganese can be incorporated into the Zincblende structure in a tetrahedral configuration on a gallium site, where it acts as an acceptor or it can be an interstitial impurity, acting as a double donor. For manganese on a gallium site (Mn$_{Ga}$) or on an indium site (Mn$_{In}$), a few different electronic configurations are allowed. Two of these configurations will be described in detail.

The first configuration is the neutral acceptor state $A^0$. For this situation, the 3$d^5$ electrons form a negatively charged core, which can bind weakly to a valence-band hole, and in that way forming a Mn$^{2+}$3$d^5$+hole complex. The electronic configuration for this situation is outlined in figure 2.18, referring to this model as Mn1. The Mn 3d orbitals are well localized and far from the valence band top. The weakly bound hole occupies a hydrogen-like Bohr orbit $1S_{3/2}$ in its ground state, while the Mn 3d electrons remain in the same configuration as for the standalone Mn-atom. These 5 electrons occupy an isotropic $^1A_2$ pure spin state, and they do not participate in the bonding in the crystal lattice, so they are independent of the valence band. The valence band hole spin is four-fold degenerate and may be splitted by the exchange interaction between the 3$d^5$ $S = \frac{5}{2}$ core spin and the hole spin $J_h = \frac{3}{2}$.

In the second configuration, the 5 d-orbital states split into a doublet and a triplet when the atom is entered into the tetrahedral symmetry of the semiconductor lattice. For a small splitting energy between these two levels, the electrons will be divided over the different d-orbitals to maximize the net orbital spin, while obeying the Pauli Exclusion Principle.

![Figure 2.18: Electronic configuration of selected elements in the III-V lattice. Mn1 and Mn2 represent the electronic configuration for substitutional manganese on a Ga or In lattice spot.](image)
The two electronic configurations described above coexist in literature and are both used for explaining certain phenomena. Experimental arguments for the validity of both of the theories have been reported, so the subject is still matter for discussion.

In the ground state, manganese shows up as a deep acceptor 113 meV above the valence band of GaAs. Next to the ground state, several shallow excited states are observed which can be accounted for by effective-mass theory in terms of a hydrogen-like impurity [7].

2.3.2. Manganese in GaAs in Photoluminescence (PL)

In the previous paragraph, the electronic structure of manganese within the GaAs matrix was outlined. Manganese acts as a deep acceptor which is positioned 113 meV above the valence band. Therefore, it is possible to detect its presence in low temperature PL spectra. The substitutional manganese on a gallium spot shows up around 100 meV below the GaAs substrate peak, as illustrated in figure 2.19 [17]. Furthermore, phonon replicas show up in the spectrum below the peak of the substitutional manganese. From the energies of the Mn\textsubscript{Ga} peak, it can be identified that the manganese incorporates in the lattice and is not built in as an interstitial impurity.

![Figure 2.19: Manganese signature in PL [17.]](image)

2.3.3. Mn-doped InAs/GaAs Quantum Dots in Photoluminescence (PL)

Photoluminescence measurements on single quantum dots provide accurate information about the recombination processes taking place in that particular dot. The PL signal contains information on the local electronic structure of the quantum dot. Addressing single quantum dots can be achieved in a confocal microscope setup, as outlined in paragraph 3.3.3.

Based on the previous paragraphs, the interaction between the exciton states for InAs quantum dots (see 2.2) and the manganese wavefunction in the III-V lattice (see 2.3.1), a theoretical framework is developed. The model is derived starting from theoretical work which has been performed on manganese-doped II-VI quantum dots.
As outlined in 2.3.1, manganese acts as an acceptor within the III-V lattice. Therefore, it provides an additional hole to the quantum dot if it is positioned within or in the vicinity of a quantum dot. Therefore, for this project the focus is on neutral excitons and positively charged excitons. For the different exciton complexes described in 2.2, the interaction with a Mn-atom inside the quantum dot is described below.

The influence of the manganese is twofold. On the one hand, it provides the quantum dot with an additional hole, which is accounted for by focusing on positively charged excitons. On the other hand, it has a large magnetic moment due to the localized 3d⁵-electrons which do not take part in the binding, but result in a total magnetic moment \( S = \frac{5}{2} \).

The first theoretical framework for manganese-doped dots was considering a spherical quantum dot doped with a single manganese impurity [8]. This model was altered [9] to serve for describing manganese-doped cadmium telluride dots within a zinc telluride matrix [10-13]. These dots are lens shaped, resulting in a strong confinement in the z-direction and weak confinement in the x- and y-directions, similar to the InAs quantum dots which are studied in this project. Therefore their work will serve as the starting point for the theoretical description of the interaction of a manganese dopant within an InAs quantum dot.

In quantum dots doped with a Mn²⁺ ion, the eigenstates resulting from the exchange coupling between the exciton and the magnetic ion can be deduced by combining the magnetic moments of the exciton (both the electron and hole spins) and the Mn²⁺ spin. In flat, self-assembled quantum dots, the degeneracy between the hole spin projections (heavy- and light hole splitting) is lifted by biaxial strains in the plane of the quantum dot. Therefore, the system can be described using a heavy-hole exciton, in interaction with the 6 spin projections of the Mn²⁺ ion. (Note that in paragraph 2.2, the exciton complexes were also considered to be heavy-hole excitons.) For such a system, the spin interaction part of the Hamiltonian is given by equation 2.7. This model represents the special case of the manganese in the center of the dot, which provides insight in the physics behind the problem.

\[
H_{\text{int}} = -I_e (s \cdot S) - I_h (j \cdot S) - I_{e-h} (s \cdot j) \tag{2.7}
\]

Where \( I_e \) (\( I_h \)) is the Mn-electron (Mn-hole) exchange integral, \( I_{e-h} \) the electron-hole exchange integral and \( s, j \) and \( S \) the magnetic moment of the electron, heavy hole and manganese respectively.

Furthermore the influence of an external magnetic field can also be included in the calculations, which gives rise to Zeeman splitting which can be accounted for by a Zeeman Hamiltonian (equation 2.8).

\[
H_Z = \mu_\beta (g_{\text{Ms}} S \cdot B + g_e s \cdot B - g_h j \cdot B) \tag{2.8}
\]

The initial states of the transitions are obtained from the diagonalization of the spin and Zeeman Hamiltonians (equations 2.7 and 2.8) for the heavy-hole excitons and the Mn²⁺ spin components \( | \pm 1/2 \rangle_e, | \pm 3/2 \rangle_h, | S_z \rangle_{\text{Mn}} \), where \( S_z = \pm 5/2, \pm 3/2 \) and \( \pm 1/2 \).

Depending on the type of exciton under investigation, the final state involves Mn²⁺ states \( | S_z \rangle_{\text{Mn}} \) which have conserved their spin component and optionally electron states \( | \pm 1/2 \rangle_e \) and/or hole states \( | \pm 3/2 \rangle_h \).
The diagonalization of the Hamiltonian has been carried out for a manganese atom in the center of a spherical dot [8] and for a manganese atom inside a box-shape (with square base and a height much smaller than the dimensions of the base) [9]. The results from these calculations are discussed below, providing insight in the expected PL-spectra.

For all of the excitons, the presence of one manganese atom in an InAs quantum dot can be described by 3 exchange interactions, as indicated in equation 2.7. Depending on the type of exciton, these interactions have different contributions to the PL-emission.

For the neutral exciton $X^0$, two bright states are observed with $m = \pm 1$, as shown in figure 2.12. Both the hole and the electron interact with the manganese spin. These interactions can be described using 2 separate Hamiltonians (similar to equation 2.7), which also take into account the position of the manganese atom inside the dot. The exchange interaction of manganese with the electron and hole are given by equations 2.9 and 2.10 respectively, while the eh-exchange interaction can be neglected.

\[ H_e = H_0 - I_e \left| \Phi(\bar{x}_{\text{Mn}}) \right|^2 \bar{s} \cdot \bar{S} \]  
(2.9)

\[ H_h = H_0 + I_h \left| \Phi(\bar{x}_{\text{Mn}}) \right|^2 \bar{j} \cdot \bar{S} \]  
(2.10)

Since the exchange interaction between manganese and the hole is much stronger than the exchange interaction between the manganese and the electron, the exchange integral $I_e$ is assumed to be 0 in the first approximation. In that way, the only splitting of the exciton lines is induced by the exchange interaction between the manganese atom and the two bright exciton states $\chi^0_{+1}$ and $\chi^0_{-1}$ where $\pm 1$ denote the $m$ quantum number (projection of the total exciton spin along the z-direction). Since the manganese carries a total spin $S = 5/2$, there are six allowed spin states $S = \pm 5/2, \pm 3/2$ and $\pm 1/2$. The coupling of the exciton wavefunction with the manganese splits up the exciton line in 6 separate energy levels, which are both 2-fold degenerate for circularly left- and right-hand polarized photons (as determined by the $m$-quantum number). For the neutral exciton $\chi^0$ all allowed states are illustrated in figure 2.20.
Figure 2.20: Allowed energy states for the neutral exciton $\chi^0$. The neutral exciton is splitted into bright and dark states by the eh-exchange interaction, while the bright states are splitted in 6 energy levels which are 2-fold degenerate for left- and right-handed circular polarized photons.

In this spectrum, the largest splittings correspond to $S = \pm 5/2$, while the smallest ones correspond to the $S = \pm 1/2$. The splitting energies are related to the difference in magnitude of the m-quantum number and the z-component of the manganese spin. The 2 highest energy states are obtained when $m$ and $S$ are aligned parallel, whereas the lowest are obtained in the anti-parallel state. This also implies that by measuring both the photon energy and polarization, the exact spin state of the manganese atom can be deduced.

The positively charged exciton $\chi^+$ is more complicated than the neutral exciton $\chi^0$. This exciton can be described similar to the $\chi$ as performed by Leger et. al [1]. The positively charged exciton consists of two holes and one electron coupled to the manganese atom. In order to understand the spectrum, the different possible initial and final spin states have to be considered. In the initial state, the effect of the two spin-paired holes on the manganese is strictly zero, while the interaction with the electron determines the splitting of the initial states. The final states consist of a hole coupled to the manganese. Therefore, the initial states can be described by their total spin $J$ (allowed values 2 and 3) and its z-component, while the final states are described by the z-component of the manganese spin $S_z$ and the hole spin $j_z$. For the initial states, the spin Hamiltonian is given by the ferromagnetic Heisenberg model (equation 2.11) while for the final states an Ising Hamiltonian (equation 2.12) applies.

\[
H_{e-Mn} = -I_e \vec{S} \cdot \vec{\mathbf{s}} \tag{2.11}
\]

\[
H_{h-Mn} = I_h \left[ J_z \mathbf{J} + \frac{\mathcal{E}}{2} ( J_x S_x + J_y S_y ) \right] \tag{2.12}
\]
The final term in equation 2.12 is related to spin-flip interaction between the manganese spin and the hole spin, which is in first instance neglected, but will be briefly discussed later on. The allowed transitions and their probabilities are dictated by the different possible initial states \( |i\rangle = \left( \left| \uparrow \right\rangle \times |J_z\rangle \right) \) and final states \( |f\rangle = |S_z, j_z\rangle \). The weight of the optical transitions between these states is proportional to \( \left| \sum_s P(s,J_z) c_s d_{J_z} |i\rangle \right|^2 \), where \( c_s \) and \( d_{J_z} \) are the operators that annihilate a conduction band electron with spin \( s \) and a valence band hole with angular momentum \( j_z \), respectively. \( P(s,J_z) \) is given by the polarization selection rule.

The polarization of the emitted photons can be both right- and left-handed, depending on the spin state of the electron. For a given initial spin state \( |i\rangle \) and a final spin state \( |f\rangle \), the intensity of the optical transition is given by the overlap \( \langle S_z, s | J_z, j_z \rangle \), which is a Clebsch-Gordan coefficient. These Clebsch-Gordan coefficients are defined in quantum mechanics in order to describe the interaction between 3 spin states.

For the 2 non-degenerate initial states with \( J = 2 \) and \( J = 3 \), there are 6 different final states as a consequence of the interaction between the manganese and the hole in the final states. In that way, 12 separate peaks for each polarization would be expected. However, due to spin selection rules, 1 of these transitions is forbidden, since the z-component \( J_z \) cannot exceed the value of the total spin \( J \). (Initial states with \( J = 2 \) and \( J = 3 \) exist for all possible manganese spin states \( S \), except for \( S = \pm 5/2 \), where the only allowed spin state has a total spin \( J = 3 \).) All of the allowed transitions are illustrated in figure 2.21.

Figure 2.21: Allowed energy states for the positively charged exciton \( \chi^+ \). The spectrum is splitted into 11 different lines for both polarizations.

The experimental results for these excitons in II-IV quantum dots [1] show that the real situation is slightly more complicated. This is because the spin-flip interaction
term in equation 2.12 was so far neglected. The spin-flip interaction results in bonding and anti-bonding combinations of \( |S_z = -1/2, \uparrow \rangle \) and \( |S_z = +1/2, \downarrow \rangle \). As a consequence, the central part of the spectrum is significantly different from the theoretical spectrum given in figure 2.20. It is observed that the central lines are linearly polarized due to the spin-flip interaction.

For the neutral biexciton \( 2X^0 \), which shows up at high excitation energies, the coupling between the exciton and manganese can be described in the same framework as the neutral exciton \( X^0 \). Only one initial state exists, with both s-shells for electrons and holes filled with one spin up and one spin down. Therefore two different bright states can be observed, with left- or right-handed polarization. The emission energy of the double exciton is shifted to lower energies as compared to the single exciton, as a consequence of the coulomb interaction between the confined charge carriers. After annihilation of the first electron-hole pair, a single neutral exciton is left which emits a second photon with the opposite polarization as compared to the first photon.

By considering the initial and final spin states for the neutral biexciton, the expected spectrum can be deduced. In the initial state two holes and two electrons are present in the s-states, having opposite spins. This implies that for both electrons and holes, the net effect of the interaction with the manganese is zero. In the final state, an electron and hole are left with opposite spins, resulting in a total spin along the z-axis \( m = \pm 1 \). This means that the final state is similar to the initial state of \( X^0 \), whereas the initial state is similar to the final state for the \( X^0 \) exciton. Therefore, a similar spectrum to the one illustrated in figure 2.20 is also expected for the biexciton. However, the energies are shifted to lower energies as a consequence of the coulomb interaction between the 2 excitons. The intensity is lower as well due to the short lifetime of bright excitons and the need for high excitation energies.

For all of the exciton complexes described above, the influence of an external magnetic field can also be included in the calculations. This is done by diagonalization of the two Hamiltonians given by equation 2.7 and 2.8. The major effect of applying magnetic fields is a shift of the spectra for left- and right-handed polarized emission spectra, as shown by Léger et. al. [11]. Furthermore, anticrossings in the PL-spectra are observed for a particular value of the applied magnetic field, as a consequence of intermixing of the dark and bright exciton states. It is experimentally observed that within InAs quantum dots in a GaAs matrix, the g-factors are largely dependent on the quantum dot properties and significantly different from the bulk values for InAs [21]. Therefore, a more convenient way of describing the Zeeman-splitting for a particular dot is by using a quantum dot g-factor, as given by equation 2.13.

\[
\Delta E_{\text{Zeeman}} = g_{\text{dot}} \mu_B B \tag{2.13}
\]

Typical splitting energies for InAs/GaAs QDs are of the order of 1 meV for magnetic fields around 10T [21]. The splitting effect for the neutral exciton is illustrated in figure 2.21. A similar approach can be used for all other exciton complexes, which behave similarly.
Due to the application of a magnetic field, the intensity of the different peaks is also changed. The highest (lowest) spin state of manganese shows an increased (decreased) intensity as a consequence of the presence of the magnetic field. Similar effects are observed for other excitons, however, due to intermixing of spin states, depending on the geometry of the dot and the position of the manganese atom, linearly polarized emission spectra are also observed for certain dots, which are significantly different from the spectra without magnetic field.
3. Experimental methods and setups

3.1. Sample fabrication

3.1.1. Wafer preparation

In order to obtain optimal growth conditions, careful substrate preparation is required. The first cleaning steps are performed in wetbenches in cleanroom environment, while further preparation is performed in high vacuum in the sample transfer system, shortly before loading the sample into the MBE growth chamber.

In the first cleaning step, organic substances are removed from the wafer surface by a solution of 96% of Sulfuric Acid (H$_2$SO$_4$). Subsequently, the sample is rinsed under deionized (DI) water flow for 10 minutes, removing all of the sulfuric acid and organic adsorbands. In the second cleaning step, a flattening etch step of the gallium arsenide substrate is performed. The etch solution consists of a 100:10:2 mixture of DI-water, 29% Ammonium Hydroxide (NH$_3$OH) and 30% Hydrogen Peroxide (H$_2$O$_2$). The sample is etched for 2 minutes and afterwards kept under DI-water flow for 10 minutes, removing all of the etched material and the remnants of the etch solution. As a final step, the substrate is blown dry using Argon. During the exposure to the cleanroom environment, the top layer of the substrate gets covered with a thin oxide layer.

AFM measurements of the wafer surface before and after each of the cleaning steps confirm that both cleaning steps increase the RMS roughness of the substrate. The effect of the first cleaning step on the roughness is minor, no dramatic changes to the topography of the surface are observed. The etch step removes the larger structures on the substrate, reducing the peak-to-peak heights, but also doubling the RMS roughness of the substrate. AFM scans of the different steps are shown in figure 3.1, while the statistical properties related to the substrate roughness are listed in table 3.1.

![AFM scans](image)

**Table 3.1: Statistical properties for figure 3.a AFM scans**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Maximum Height (nm)</th>
<th>RMS roughness (nm)</th>
<th>Grain density (grains/µm$^2$)</th>
<th>Average grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before cleaning</td>
<td>9.44</td>
<td>0.097</td>
<td>0.68</td>
<td>29.0</td>
</tr>
<tr>
<td>After H$_2$SO$_4$ Cleaning</td>
<td>14.32</td>
<td>0.140</td>
<td>0.04</td>
<td>53.0</td>
</tr>
<tr>
<td>After flattening etch</td>
<td>2.49</td>
<td>0.223</td>
<td>0.00</td>
<td>0.0</td>
</tr>
</tbody>
</table>

As a next step, the sample is mounted onto a block for loading it into the high vacuum
transfer system. Indium-free blocks with a PBN diffuser are used, yielding thermo-couple read-outs which are closer to the actual sample temperature. Before loading the sample into the growth chamber, it will be outgassed in the transfer by mounting it on an oven and heating it for about half an hour, until it reaches a substrate temperature between 300 and 400 degrees. During this step, most of the substances covering the oxide layer will be removed, while the oxide layer itself will remain intact, ensuring that the substrate structure will be preserved.

3.1.2. Growth procedure

After the sample preparation procedure, the sample is brought into the MBE chamber.

The first step which is performed is the deoxidation of the substrate. The block is heated under a constant Arsenic flow in order to preserve good structural quality of the surface. At a certain point, the RHEED pattern becomes clearer, which indicates the onset of the deoxidation process. The theoretical deoxidation temperature for a GaAs substrate is 585ºC, so this point serves as a first temperature calibration. However, it should be noted that the accuracy of this calibration is limited to a range of 20 to 30 ºC. In first instance, a 1x1 pattern appears which makes the transition to a 2x4 pattern rather quick. The appearance of the 2x4 is an indication that the deoxidation process has successfully completed.

After the deoxidation, a high temperature GaAs buffer is grown, during which the RHEED pattern remains 2x4. This buffer layer ensures a good starting point for the rest of the growth procedure.

The following calibration step is performed immediately after the deposition of the high temperature (HT) GaAs buffer. In this step, the substrate rotation is stopped in order to determine the orientation of the sample. The positions of the [110] (2-fold reconstruction) and the [1T0] (4-fold reconstruction) are located. Then the sample is rotated into the position exactly in between these 2 positions, displaying the RHEED pattern along the <100> direction. This pattern shows a 2-fold reconstruction. Subsequently, the substrate is cooled down slowly while a constant Arsenic flow is maintained. The surface reconstruction will at a certain point make the transition from the 2x4 (showing 2-fold reconstruction along <100>) to c4x4 (showing 4-fold reconstruction along <100>), which happens at the characteristic temperature of 485 ºC [18]. Since this transition is an intrinsic property of the GaAs, this calibration is much more accurate than the deoxidation, providing a temperature calibration which is as accurate as 5ºC.

In the following steps, the actual sample structure is grown, which differs in quite a lot of the properties. In the remainder of this paragraph, the outline of the different procedures for growing the InAs quantum dots will be discussed.

Before depositing InAs, the sample is brought to the growth temperature for the quantum dots, which is in the range of 400 to 500ºC. Subsequently, a second buffer layer of 50 to 100 nm of medium temperature (MT) GaAs is deposited.

The indium shutter is opened for the deposition of InAs. The indium is deposited at a low flux with a beam equivalent pressure (BEP) of about 5.0 \(10^{-9}\) torr. This results in a growth rate of 0.01 ML/s for InAs, in case of 100% sticking of indium. At the top of
the growth window (substrate temperatures close to 500°C), the sticking coefficient of indium is already largely reduced, resulting in growth rates up to one third smaller than in the case for 100% sticking. The layer thickness of the deposited layer is monitored by looking at the transition from a streaky to a spotty RHEED pattern, which happens exactly at 1.7 ML of deposited InAs.

Next to the substrate temperature, several different parameters were varied, all of which are shortly described below:

- **Substrate rotation:** The rotation of the substrate during growth provides the uniformity of the deposited layers, because the different effusion cells are facing the substrate under different angles, and the beams from the effusion cells are not uniform. Therefore, growth without substrate rotation provides a non-uniform layer, which causes a gradient in both dot sizes and dot densities.

- **Direct manganese doping:** Despite the fact that a substantial background of manganese is already present in the growth chamber (see 4.2.1), in some samples, active doping of the dots with manganese is performed. The manganese flux was provided during the deposition of InAs but before the onset of quantum dot formation.

- **Manganese delta-layer doping:** In some samples, the manganese doping is introduced by deposition of a manganese delta-layer before deposition of the InAs quantum dots.

- **Manganese delta-layers without substrate rotation:** In these samples, both a gradient in Mn-concentration and the amount of deposited InAs is created. First a manganese delta-layer is deposited before deposition of InAs, after which the substrate was rotated for 90° for deposition of the InAs quantum dots. In that way, as a consequence of the different cell positions for manganese and indium, the two gradients are oriented more or less perpendicular with respect to each other.

After deposition of the first quantum dot layer, a GaAs capping layer of 100 nm is grown at the dot growth temperature.

Subsequently, a second layer of quantum dots is grown under the same conditions as the first dot layer, except for the doping, which is not applied in the second layer. This second dot layer is used for AFM characterization of the dot densities, sizes and distributions. During the deposition of this second dot layer, the onset of dot-formation is monitored through the RHEED, in order to verify the similarity of the growth conditions with the first dot layer.

Immediately after the deposition of the second dot layer, the substrate is cooled down and as the temperature reaches 400 °C, the flux of Arsenic is stopped. The sample is now completely finished and is taken out of the MBE chamber. The final sample structure is illustrated in figure 3.2.
Figure 3.2: Typical sample structure for an InAs/GaAs quantum dot sample. The orange layers represent the InAs Quantum dots and the purple layer represents the (optional) manganese delta-layer.

3.2. Flux calibrations

3.2.1. Rutherford Back-Scattering Spectrometry (RBS)
Rutherford Backscattering Spectrometry (RBS) is an analytical technique, which provides quantitative information on the composition of thin films. In RBS experiments, the sample under investigation is bombarded with high-energy (2 to 4 MeV) Helium-nuclei (Alpha particles) which will be scattered by the nuclei of the atoms in the sample. In RBS experiments, the energy of the particles scattered under angles close to 180 degrees is recorded. From the energy of the backscattered Helium-nuclei, the chemical composition of the sample can be deduced, since the energy of the scattered particle depends on the ratio of masses between the atoms in the sample and the He-nucleus. Therefore, RBS provides quantitative information of the sample composition, and allows depth profiling of the sample composition.

3.2.2. Secondary Ion Mass Spectroscopy (SIMS)
Secondary Ion Mass Spectrometry is an analysis method which provides qualitative information about the composition of the sample under investigation. The sample is bombarded with a primary beam of ions (Cs⁺, O⁻, Ga⁺), which causes atoms to be ionized and removed from the sample. These secondary ions are analyzed using a mass spectrometer, providing information about the sample composition.

In SIMS, qualitative information about the relative composition of the sample is obtained. Quantitative information can be obtained by comparing the measurement results with standards from which the composition is known. Depending on the experimental setup and the used parameters, detection limits for the different atoms within different host materials are in the range from $10^{12}$ to $10^{16}$ atoms per cubic centimeter.

3.3. Sample Characterization

3.3.1. Atomic Force Microscopy (AFM)
Atomic Force Microscopy (AFM) is a scanning probe technique which is used to
monitor the topography and surface structure of a sample. Two basic modes in AFM are most commonly used: Contact mode AFM (static mode) and Tapping mode or AC-mode AFM (dynamic mode).

In both modes, imaging is performed by scanning the sample surface with a silicon AFM tip, which is mounted on a cantilever spring. As the tip moves across the sample, it will be deflected as a consequence of the interaction with the sample surface. This deflection is monitored by shining with a laser on the backside of the tip, and recording the reflected signal using a photodiode. The schematic overview of the operational principle of an AFM is outlined in figure 3.3.

![Figure 3.3: Operational principle of AFM](image)

The interaction between the tip and the sample consists of several different types of forces, including mechanical contact force, Van der Waals forces, dipole-dipole interaction, capillary forces, chemical bonding, electrostatic forces, magnetic forces etc.

During tapping mode AFM, the tip is brought close to the surface of the sample, while oscillating close to its resonance frequency. Due to the interaction between the sample and the tip, the amplitude and phase of the oscillation will be changed, which provides information about the sample structure. The sample or the scanning unit is mounted onto a piezo stage which allows it to move in X, Y and Z direction. While scanning, an IP-controller is used in order to maintain a constant distance between the sample surface and the tip. By recording the changes in Z-position as a function of X and Y, the topography of the sample can be imaged.

AFM generates topographic images in a broad size range from 100 nm to 100 µm with resolutions up to the sub-nanometer regime in all spatial directions.

### 3.3.2. Photoluminescence Spectroscopy (PL spectroscopy)

Photoluminescence is a contact-less optical method which provides information on the electronic structure of a sample. A beam of monochromatic laser light is directed onto the sample. Photons will interact with the sample, providing energy to the electrons, which can be excited into a higher energy level, in case the photon energy exceeds the bandgap energy in a direct semiconductor. In that way the electron is excited into the conduction band, leaving behind a hole in the valence band. This process is called photo-excitation. The charge carriers generated in this fashion have a
limited lifetime, and will at a certain point recombine.

The recombination process can be both radiative and non-radiative, depending on the nature of the process. In direct semiconductors, the recombination process will be radiative, whereas in indirect semiconductors, the process will be non-radiative. However, this does not mean that all recombination processes for direct semiconductors will be radiative. The presence of defects in the crystal structure can also induce non-radiative recombination within direct semiconductors. This also indicates that the luminescence intensity provides information about the structural quality of the sample.

The energy of the emitted photons is determined by the energy state of the electrons and holes, which depends on bulk material properties such as the bandgap, and local material properties like defects and impurities (donors and acceptors). In room temperature PL the bulk effects will show up, whereas at low temperature, the fine structure due to impurities, (charged) excitons (bound electron-hole-pairs), phonon interactions and defects will become apparent.

A typical setup for PL consists of a laser for photo-excitation, some optical components for guiding and focusing the beam, a cryostat and a monochromator in combination with a linear CCD array or a simple photodetector. The basic setup is depicted in figure 3.4.

![Figure 3.4: Schematic setup for photoluminescence spectroscopy](image)

In a regular PL setup, the laser spot of the excitation laser is pretty large, up to several millimeters. This implies that the photoluminescence from a regular quantum dot sample, with dot densities ranging between $10^8$ and $10^{10}$ quantum dots per square centimeter, will be showing luminescence of a large ensemble of dots.

### 3.3.3. Micro-PL in Confocal microscope setup

As outlined in the previous paragraph, in regular PL the signal provides information on a large ensemble of quantum dots. In order to understand the underlying physics behind these recombination processes, it is necessary to look at PL from single dots. Experimentally this can be achieved by applying metal masks with pinholes, mesa-etching or in a confocal microscope setup. The latter is used in this project, and will be described in this paragraph.

In a diffraction limited confocal microscope, out-of-focus rejection is obtained by two strategies, which are outlined in figure 3.5, which shows the operational principle of a confocal microscope. First one spot on the sample is illuminated by a focused beam, so the illumination intensity drops rapidly outside of the plane of focus. Secondly, a blocking pinhole at the collector side is used to eliminate the degrading out-of-focus information.
Figure 3.5: Schematic overview of a confocal microscope setup [14]

From the schematic overview it can be seen that a confocal microscope setup provides the highest possible resolution attainable from conventional optics. Only the light from the exact focus of the objective is imaged, which implies that in optimized optical conditions, the performance of the setup is limited by diffraction. If one quantum dot is considered to be a point source, the spot size can be estimated using the Sparrow’s criterion [15], which estimates the full width at half maximum (FWHM) of the central peak of an Airy function to be $\Delta x$, as given in equation 3.1.

$$\Delta x \approx \frac{0.52 \lambda}{N_{\text{obj}} n_{\text{med}}}$$

Substituting the free wavelength $\lambda = 632.8 \, \text{nm}$, the numerical aperture of the objective $N_{\text{obj}} = 0.65$ and the refractive index of the surroundings $n_{\text{med}} = 1$, a spot size of $506 \, \text{nm}$ is obtained. This spot size can even be reduced by applying a Solid Immersion Lens (SIL), which is a tiny lens of high refractive index, which is pasted on top of the sample. The SIL offers two advantages: the collection efficiency is increased by a factor $n_{\text{sil}}^2$ for $n_{\text{sil}} < n_{\text{sample}}$ and the spot size is reduced by a factor $n_{\text{sil}}$ as can be seen from equation 3.1. Our solid immersion lenses have $n_{\text{sil}} = 1.82$, which results in a spot size of $278 \, \text{nm}$.

A more detailed overview of the confocal microscope setup is given in figure 3.6. It consists of 5 major parts: the optical head, the cryostat with magnet, the excitation unit, the microscopic stick with piezo stage and the detector CCD unit. Both the excitation laser and the detector are connected to the optical head through a single mode optical fiber. The optical head is mounted on top of the microscope tube, which is positioned inside the helium-cooled superconducting magnet. The pinhole for the collected PL light is provided by a single mode optical fiber with a mean field diameter of $5.6 \, \mu\text{m}$. 
Figure 3.6: Detailed schematic overview of the confocal microscope setup [16].

All parts of the setup will briefly be discussed, in order to provide sufficient information to understand the experimental results obtained in this setup. For a more detailed overview of the setup, the interested reader is referred to [16].

The optical head consists of several optical components for coupling in the excitation light, coupling out the PL light to the monochromator and for performing the alignment of the setup. A schematic overview and a picture of the optical head is given in figure 3.7 [16].
The excitation light is coupled in from arm I, where it is collimated by lens LI, after which it passes a beam splitter which directs 50% of the laser light into the cryostat. The PL light emerging from the cryostat is split by a second beam splitter, which directs half of it onto a CCD camera in arm II where it is focused by lens LII while the other half is transmitted and focused by lens LIII onto the pinhole of the single-mode optical fiber, which couples it into the monochromator unit. The CCD camera in arm II is used for alignment purposes, as will be explained later.

The overview of the cryostat can be seen in figure 3.8. It consists of two large reservoirs which are filled with liquid helium, and which are separated from one and other by a vacuum. The large outer reservoir contains large superconducting coils, which allow applying magnetic fields up to 11T. The smaller inner reservoir contains the microscopic stick which is positioned in such a fashion that the sample and piezo stage are exactly in the center of the superconducting coils, providing a uniform field during the measurements.

The microscopic stick consists of a 2 meter long stainless steel tube with a diameter of 50.8 mm. The top of the tube contains a vacuum sealed anti-reflection coated optical window, while the objective forms the bottom of the tube. During the measurements, the tube is evacuated and filled with a few mbar of helium exchange gas, in order to prevent formation of air and ice crystals on the sample and the optical components. The size of the objective is 4 mm, while the incoming beam is 3.6 mm wide, which exploits the high NA in the optimum conditions, resulting in the highest possible resolution (see equation 3.1).

The sample is mounted on the X, Y, Z piezo stage, which allows accurate controlling of the sample position in all spatial directions. The three piezo elements are all mounted on top of each other. The positioning of the sample is done by applying voltage pulses to the piezo elements, ranging from 0 to 20 volts. At 4.2K, the step size
corresponding to a 1V pulse is 4 to 5 nm, which implies that the positioning of the sample is controlled very accurately. Furthermore, the piezo elements serve as indicators for the sample temperature, since their capacity is reduced by a factor of 5 when cooling down from room temperature to 4.2K.

The excitation light is generated with a 632.8 nm laser diode, which is coupled to the optical head through a 630 nm single-mode fiber. The excitation power can be controlled by using neutral density (ND) filters.

The PL light is collected through a single-mode optical fiber. The core diameter of this fiber is 5.6 µm, so it serves as the pinhole for the collected PL light. In front of the collection fiber, a high-pass filter is inserted which filters out the laser light, while the collected PL light is focused onto the fiber by lens LIII. The light from the fiber is focused on the slit of the triple monochromator unit, as illustrated in figure 3.8.

The triple monochromator unit is equipped with a linear InGaAs photodetector array. For our experiments, only the third step was used, which is a monochromator unit of 75 cm with a grating of 750 lines/cm, which results in a resolution of 75 µeV.

In the confocal microscope setup, the alignment procedure is of utmost importance. Therefore, all of the optical components have accurate x, y and z positioning. The entire optical head can be moved in the x and y directions, with respect to the microscopic stick, which is necessary for maintaining a straight optical path throughout the microscope body.

Four major steps are taken during the alignment procedure.

1. The excitation and collection arms are aligned separately by collimating the beams coming from these arms. Afterwards, both of these spots are focused on the same position on the wall at approximately 5 m. Furthermore, the laser spot needs to be adjusted to approximately 3.6 mm so it can fully illuminate the objective. Once both of the arms have been aligned, separate movement of the arms is prohibited.

2. The optical head is mounted on top of the microscopic stick and only the tilt stage of the optical head and the x, y, z piezos of the sample holder are being used. The tilt stage is used to adjust the position of the laser beam until it is centered on the objective in order to obtain a clear focusing of the beam. The
x, y, z piezos are used in order to focus the beam onto the sample. A first rough approach is done by eye, after which a second step can be done using the piezos, in order to position the beam exactly on the top of the SIL. When the spot is in focus on the sample or the SIL, a refraction pattern appears on the camera. After this step, the tube is brought into the cryostat, and the contact gas is inserted, after which the cooling down is initiated. The temperature is monitored by measuring the capacitance of the piezos.

3. When the piezos reach liquid helium temperature, the next alignment step is performed. Due to the cooling down and little vibrations, the alignment of the optical head will be off and has to be corrected using the tilt stage, until the focus has been relocated. A strong ND filter is placed after the laser, while a small laser spot is visible on the camera, due to reflection from the SIL or the sample. By using the tilt stage and the x, y, and z positioners on the excitation arm, the spot has to be made round and clear. Subsequently, the Z-position of the sample stage is adjusted in order to verify the focusing. For a perfect alignment, the spot maintains its shape and position.

4. In the final step, the PL is focused onto the collection fiber. This is done by adjusting the x, y, z positioners of the collection arm, while looking for the maximum intensity at the laser wavelength. After that, the monochromator gratings are repositioned to focus onto the expected PL wavelength for this sample, where the signal is optimized once more using the positioners on collection arm. After the optimization with the collection arm, a high-pass filter is placed in front of the collection fiber. The focus is now still on the top of the SIL or sample, so the Z-piezo of the sample stage should be adjusted in order to find the PL signal. If no PL is found in that way, the ND filter should be removed and more intense excitation should be tried. Most probably, the matrix material or the wetting layer or quantum dots will show up, which can be used for optimizing the alignment. The ND filters are put back into place and the excitation intensity is brought down again, in order to perform the final optimization steps for the measurement.

3.3.4. Cross Sectional Scanning Tunneling Microscopy (X-STM)

Scanning Tunneling Microscopy (STM) is a scanning probe imaging technique which allows imaging of the electronic structure of semiconductor materials with atomic resolution. The conducting STM-tip is brought in proximity of the conducting sample (~ 1 nm), and a voltage is applied between the sample and the tip. As a consequence, a tunneling current will flow between sample and tip, which is directly related to the local electronic structure of the sample under investigation.

In Cross-sectional STM (X-STM), the sample is first cleaved in order to be able to study the internal sample structure. For the GaAs (001) substrates, the cleavage plane is the 110-plane. The schematic overview of an STM experiment for the GaAs material system is illustrated in figure 3.9.
Figure 3.9: Schematic overview of an STM experiment for a GaAs sample doped with an acceptor [16].

The picture above provides good insight in the operational principle of STM. By applying different bias voltages, the local electronic structure of a semiconductor can be imaged. In that way, it is possible to probe the wavefunction of carriers confined in quantum dots or bound to single impurities. The electronic structure of manganese in GaAs has been extensively studied over the last years, so for detailed information, the reader is referred to [16].

### 3.3.5. Hall Effect Measurements

The Hall Effect is commonly used in semiconductor science for determining the carrier concentration, conduction type and carrier mobility of samples. The principle of this method is illustrated in figure 3.10.

In a Hall measurement, a current $I$ is sent through a piece of semiconductor material, while a magnetic field $B$ is applied perpendicular to the sample, as illustrated in figure 3.10. As a consequence of the Lorentz force, the charge carriers which take part in the conduction will be deflected towards the left or right, depending on their charge and the orientation of the applied magnetic field. This results in a potential difference in the direction perpendicular to the current, the so-called Hall-voltage.

In practice, usually square samples are used in the Van der Pauw geometry, as illustrated in figure 3.10 (b). Van de Pauw pointed out that the electrical properties of a piece of semiconductor material can be determined for samples of an arbitrary shape [19].
By sending the current and sensing the voltage in different directions, a lot of useful information can be extracted. The Hall voltage is given by:

$$V_H = \frac{IB}{qn_s}$$  \hspace{1cm} (3.2)

where $q$ is the elementary charge of an electron/hole and $n_s$ is the sheet density of charge carriers. This value is measured for both positive and negative fields and for currents in both horizontal and vertical directions. The different voltages are denoted as $V_{AB,P/N}$ where A and B are the numbers of the contacts through which the hall voltage is measured, and P and N indicate if the field is positive or negative. The following measurement points are taken:

$$V_{13} = V_{13,P} - V_{13,N}$$  \hspace{1cm} (3.3)
$$V_{24} = V_{24,P} - V_{24,N}$$  \hspace{1cm} (3.4)
$$V_{31} = V_{31,P} - V_{31,N}$$  \hspace{1cm} (3.5)
$$V_{42} = V_{42,P} - V_{42,N}$$  \hspace{1cm} (3.6)

From which the overall voltage is determined through:

$$V_H = \frac{V_{13} + V_{24} + V_{31} + V_{42}}{8}$$  \hspace{1cm} (3.7)

The sign of this voltage indicates the conduction type (p for positive values and n for negative values). From equation 3.2 the sheet carrier concentration can be deduced. Furthermore the resistivity of the sample is given by:

$$\rho = \frac{1}{qn_m \mu_m}$$  \hspace{1cm} (3.8)

where $\mu_m$ and $n_m$ are the mobility and the carrier concentration of the majority charge carriers. The sheet resistance follows directly from 3.8 since it is defined as the resistivity divided by the sample thickness, while $n_S$ is the doping level multiplied by the thickness.

$$R_S = \frac{1}{qn_S \mu_m}$$  \hspace{1cm} (3.9)

Since the sample can have an arbitrary shape, a correction factor for the symmetry properties of the samples is introduced, which depends on the ratio between the voltages introduced in 3.3-3.6. The correction factor provides information on the accuracy of the Hall voltage as defined by 3.7.
4. Results and discussion

4.1. InAs quantum dot growth optimization

4.1.1. Sample requirements

Before the actual doping of the quantum dots with manganese was initiated, the growth conditions for the quantum dots were optimized. A few important parameters had to be optimized, in order to be able to have suitable samples for performing single-dot PL measurements in a confocal microscope setup.

First of all, the QD size should be tailored in such a way that the luminescence is within the right wavelength regime. For this project, the focus is on luminescence at 1300 nm, which is often used for optical communication purposes. Secondly, the density of the quantum dots should be sufficiently low to be able to address single dots. The minimum spot sizes for the confocal microscope are around 500 nm without and 300 nm with Solid Immersion Lens. Within this spot size, only a limited number of dots, in the order of 10 or less are desired. This corresponds to densities between $10^8$ and $10^9$ QDs per square centimeter.

Different growth conditions were studied in order to obtain the optimum growth window which matches the desires outlined above.

4.1.2. Indium flux calibration

For the deposition of quantum dots with the desired properties, an accurate calibration of the indium flux is required. The indium cell was calibrated using Rutherford Backscattering Spectroscopy (RBS). Two films of indium were deposited at different growth rates, without substrate heating, in order to obtain the maximum possible sticking coefficient. The film thickness in both samples was aimed to be 25 nm. The results of the RBS experiment and the associated growth parameters are given in table 4.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Intentional growth rate InAs (ML/s)</th>
<th>Beam Equivalent Pressure (Torr.)</th>
<th>RBS Results (atoms/cm²)</th>
<th>Growth Time (s)</th>
<th>Actual growth rate (ML/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1887</td>
<td>0.10</td>
<td>$5.0 \times 10^{-8}$</td>
<td>$9.98 \times 10^{16}$</td>
<td>1760</td>
<td>0.1040</td>
</tr>
<tr>
<td>M1889</td>
<td>0.01</td>
<td>$5.0 \times 10^{-7}$</td>
<td>$8.87 \times 10^{16}$</td>
<td>17625</td>
<td>0.0092</td>
</tr>
</tbody>
</table>

By calibrating the indium cell using the ion gauge (Beam Equivalent Pressure, BEP), the intentional flux can easily be calibrated using these results. It should however be noted that these values are only accurate when the sticking coefficient is close to 1. At elevated growth temperatures, the indium sticking is largely reduced. An accurate estimate of the film thickness is made by looking at the transition in the RHEED pattern between 2D and 3D growth, which happens exactly at 1.7 ML of deposited InAs.

4.1.3. RHEED Pattern analysis

In this paragraph, an overview of the typical RHEED patterns which are used in this project is given. All patterns will be shown along [110], <100> and [110] directions.
At high temperatures, the GaAs 2x4 reconstruction appears both during growth and growth interrupts. The surface structure for this reconstruction is illustrated in figure 2.7, and it yields a 2-fold pattern along [110] (a) and <100> (b) and a 4-fold pattern along [1 1 0] (c), which is shown in the RHEED patterns in figure 4.1.

When cooling down, the surface reconstruction makes the transition from 2x4 to c(4x4), as soon as the temperature goes below 485ºC. In order to determine the thermocouple read-out at the transition temperature accurately, the sample rotation is stopped and the RHEED pattern along <100> is monitored. This pattern makes the transition from 2-fold reconstruction to 4-fold reconstruction. Furthermore, the 4-fold reconstruction along [1 1 0] changes to a 2-fold reconstruction, while the 2-fold reconstruction along [1 1 0] remains 2-fold, as can be observed from figure 4.2. The corresponding surface pattern is shown in figure 2.8. During deposition of GaAs at temperatures below 485ºC, the reconstruction is still 2x4.

During the deposition of InAs, the streaky 2x4 or c(4x4) makes the transition to a spotty pattern after 1.7 ML of InAs. These spots appear on the 1-fold streaks along all the lattice directions considered before. The spotty pattern is illustrated in figure 4.3.
4.1.4. Growth parameters

In this paragraph an overview of the different growth parameters for InAs quantum dots is given. Several parameters can influence the dot formation process. The most important ones are the substrate temperature, indium flux and the amount of deposited material. All of the investigated parameters are discussed in the next paragraphs. For all of these experiments, the indium flux was kept constant at a nominal growth rate of 0.01 ML/s (assuming 100% sticking of indium), as calibrated through RBS. This particular growth rate was chosen because at low growth rates, the obtained quantum dot densities are small [24].

The substrate temperature is very critical in the quantum dot formation process. The substrate temperature determines the mobility of the deposited indium atoms. With increasing temperature, the mobility of the deposited indium is increased. During this project, quantum dots were deposited at temperatures ranging from 380ºC to 500ºC. The increased mobility at higher temperatures results in lower quantum dot densities and larger dots as compared to dots grown at lower temperatures. This is because atoms can move around longer and incorporate in the dots which are already present, instead of forming new dots on the position where they hit the substrate. In figure 4.4, AFM scans of quantum dots deposited at different temperatures are shown.
Some clear distinctions between the sample structures at 400°C and 480°C can be observed. In the first scan, the underlying wetting layer is rough, while in the second scan, atomic steps can be observed. Furthermore it can be seen that the nucleation of quantum dots happens at step edges. More accurate information can be obtained from the photoluminescence spectra of the different samples, since these provide the information about the buried layer, which is the optically active one and therefore the one which is of interest for this project.

The PL spectra used in this project were measured at room temperature (RT, 293K) and at liquid helium temperature (5K). First a few typical spectra are shown for these different conditions, after which an overview of all the measurements is presented.

At room temperature, the photoluminescence spectra all look very similar. The GaAs substrate is observed at 1.42 eV (873 nm). The wetting layer forms a thin quantum well of InAs within the GaAs matrix, with a thickness close to 2 ML. Therefore it is observed as a separate peak around 1.35 eV (918 nm), close to the GaAs peak. Furthermore a clear peak due to the InAs quantum dots is always present at lower energies. The corresponding wavelength and energy provide information about the sizes of the quantum dots. The width of the peak yields information about the size dispersion of the quantum dot ensemble. However, it is important to realize that the number of dots which cause the luminescence is dependent both on the spot size which is used for excitation, and the density of quantum dots in the sample. Two typical spectra at room temperature are shown in figures 4.5 and 4.6. It is important to realize that the intensity of the different peaks and the ratios between their intensities largely depend on the detector type. Therefore Fig 4.5 shows a typical spectrum with a germanium detector and Fig 4.6 shows a typical spectrum with an InGaAs detector.

![Figure 4.5: Typical room temperature PL spectrum for an InAs/GaAs QD sample measured with a germanium detector. Sample M1885.](image)

The spectrum in figure 4.5 shows a broad smeared out dot peak at 1.15 eV, while a large substrate peak appears at 1.42 eV and a small wetting layer peak at 1.35 eV. The large confinement energy of the quantum dots indicates their small size, and the large
peak width indicates large size dispersion for this sample. This is a consequence of low growth temperature of 400°C, resulting in high densities of quantum dots with a large size-dispersion.

![Image](image.png)

**Figure 4.6:** Typical room temperature PL spectrum for an InAs/GaAs QD sample measured with an InGaAs detector. Sample M1930.

The spectrum in figure 4.6 is remarkably different from the spectrum shown in figure 4.5. The luminescence of the dots is observed at much lower energies, indicating weaker confinement as a consequence of larger dot sizes. The growth temperature for this sample was 480°C. The quantum dot peak is several orders of magnitude larger than those from the GaAs and the wetting layer (WL), which are still visible when zooming in on the high energy side of the spectrum.

The reason for these large differences in the proportions of the different peaks is the different sensitivity for the detectors at different wavelengths. The spectral regime in which the InGaAs detector can be used ranges from 800 nm to 1600 nm. The detector response is nearly flat in the middle of this regime and drops off rapidly at the edges. This explains why the signal from the GaAs and the WL are largely suppressed as compared to the dot peak.

Next to the room temperature measurements, many measurements were carried out at 5K. In that way, thermal broadening of the photoluminescence signal is prevented, which allows to look to the fine structure of the sample in more detail. Moreover, these measurements are a crucial verification step for the sample quality, because the measurements in the confocal microscope have to be carried out at 5K as well. A typical PL spectrum at 5K is given in figure 4.7.
In figure 4.7, many more features appear in the PL spectra as compared to the RT measurements. Peak 2 is the quantum dot peak on which a shoulder is observed at 1.15 eV. Peak 1 is related to defect states, which can be either arsenic anti-sites or interstitial manganese atoms. The position of the peaks is shifted to higher energies (smaller wavelengths) as compared to RT measurements. The peaks indicated with number 3 are related to substitutional manganese on a gallium site (see 2.3.2) and phonon replicas of this particular peak. Peak 4 is the quantum well peak of the wetting layer and peak 5 is the GaAs peak. In figure 4.8, peaks 3 to 5 are shown once more, including all the related energies.
It can be seen that the peak energy of manganese on a gallium spot is about 100 meV from the GaAs peak, while the spacing of the phonon replicas of the substitutional manganese are also in perfect agreement with the results from [17]. The energy shifts of the WL and GaAs positions as compared to RT measurements also match the expected values.

The effect of the defect states was studied in more detail by performing PL and Hall measurements on thick films of manganese doped GaAs. The results of one of those measurements are given in figure 4.9.

Upon annealing of the sample, the PL spectrum has changed drastically. The broad background ranging from 0.77 eV to 1.25 eV has been largely suppressed as a consequence of the annealing step. This implies that many of the defect states responsible for this large background are removed by annealing the sample. This result is also confirmed by the Hall data. After annealing, the number of p-type charge carriers and their mobility is increased, while the sample resistance has dropped. Since both arsenic anti-sites and interstitial manganese act as double donors, the increase in p-type carrier concentration is within expectation. The small peak at 1.465 eV is characteristic for arsenic anti-sites [20], and has also decreased in magnitude after annealing. The presence of interstitial manganese could be the reason for the large smeared out background signal, since the location of interstitial manganese is not well defined, which could explain the smearing out of the PL signal.

Both interstitial manganese and arsenic anti-sites are defects which usually appear in low-temperature growth. The nature of the defects in our medium temperature growth
(400 to 500°C) could not yet be resolved unambiguously, but interstitial manganese and arsenic anti-sites are the most probable candidates.

Based on the RT PL measurements an overview of the quantum dot properties was composed. The growth rate was calibrated by monitoring the 2D to 3D transition in the RHEED pattern, which corresponds to a layer thickness of 1.7 ML. Based on that calibration, an estimate of the total layer thickness of the QD layer is obtained. In figure 4.10, an overview of the InAs growth rate and the indium sticking coefficient is given as function of the substrate temperature.

![Figure 4.10: InAs growth rate and indium sticking coefficient as calibrated through the 2D-3D transition in RHEED](image)

It can be seen that the RBS calibrated growth rate of 0.0092 ML/s is not reached during deposition of InAs quantum dots, not even at the lowest growth temperature of 380ºC, where the sticking coefficient is 85%. At the top of the growth window (500ºC) the sticking coefficient is already decreased to 40% of its initial value.

In figures 4.11 (a) and (b), the overview of the batch of samples for optimizing the quantum dot growth conditions is given. In both plots, the emission energy in RT PL is plotted as a function of the amount of deposited InAs (as calibrated through the RHEED transition from 2D to 3D) and the growth temperature.

![Figure 4.11: Overview of emission energies at RT for the batch of optimization samples. (a) Emission energy as function of the amount of deposited InAs. (b) Emission energy as function of the growth temperature.](image)

These results are in good agreement with similar experiments in literature [22, 23]. When larger amounts of InAs are deposited, larger dots will be formed, resulting in weaker confinement and therefore smaller emission energies. For lower growth temperatures, the mobility of the deposited indium atoms is largely reduced, resulting
in formation of many small dots, with strong confinement and therefore larger emission energies. Note that the different points for the same thickness in figure 4.11 (a) correspond to different growth temperatures whereas the different point for the same temperature in (b) correspond to different thicknesses of deposited InAs.

To conclude this section, the growth was optimized towards low quantum dot densities \(10^8 - 10^9\) QDs/cm\(^2\) with emission energies around 0.95 eV (1300 nm). The growth temperature for obtaining these properties is in the range of 470 to 480ºC, with a growth rate around 0.004 ML/s. The quantum dot layers are deposited in 10 to 20 minutes, which results in 2 to 2.5 ML of InAs (depending on the growth temperature). An AFM scan of such a quantum dot sample is given in figure 4.12. These growth parameters are exploited in the next paragraph in order to further optimize the conditions by growing without substrate rotation.

![AFM scans of an optimized QD sample.](image)

In optimized growth conditions, the quantum dot density is about \(10^9\) QDs/cm\(^2\) (10 QDs/\(\mu m^2\)), with a base length around 50 nm and a height of 10 to 15 nm. One such dot typically contains about \(10^6\) atoms. This also implies that the required manganese density for this kind of dots should be at least 4.5 \(10^{16}\) in order to have at least 1 manganese atom within every volume unit of the size of 1 QD.

### 4.1.5. Growth without substrate rotation

Several samples were grown without substrate rotation, both with and without active manganese doping. The sample position for these growth cycles was determined through the RHEED pattern. The sample was rotated to a 2- or 4-fold reconstruction streak, based on the positioning data obtained during the c(4x4) calibration step. In samples with active manganese doping, the doping was performed by deposition of a manganese delta-layer while the RHEED pattern was along [110] and before deposition of InAs. In that way a gradient in the manganese concentration is expected. After deposition of the delta layer, the substrate was rotated 90º, showing the RHEED pattern along [1 1 0]. In that way, the gradient in quantum dot sizes and densities will be more or less perpendicular to the gradient in manganese concentration. The amount of manganese is controlled by changing the cell temperature for the deposition of the delta layer. The manganese calibration is discussed in 4.2.2.

The distribution of the quantum dots and their sizes and densities is performed through AFM measurements and room temperature PL. These measurements give a
good indication of the effect of growing without substrate rotation. It is expected that the sticking coefficient for manganese at the growth temperature of the quantum dots will be close to unity, so therefore a similar gradient in the manganese concentration is expected.

Since these measurements for determining the dot distributions are quite time-consuming, they were only carried out in detail for sample M1959, while for the other ones only a few reference points were measured to confirm the similarity with sample M1959.

In AFM measurements, a large dispersion in the quantum dot properties was observed. The density of the dots was very low, ranging from less than 10 QDs/µm² up to 20 QDs/µm² and sizes from 40 to 130 nm. An overview of the AFM results is given in figure 4.13. It can clearly be observed that some unexpected values for the different parameters were measured. The dot densities and sizes are plotted in figure 4.13 (b) and (c), while an estimate of the volume of deposited material is given in (d). This estimate is calculated by multiplying the dot density with the average dot size for a given position. It should be noted that these numbers only give a qualitative impression of the actual amount of deposited InAs. The dispersion in these results is quite large, so for more qualitative results, the PL measurements are considered.

![AFM results](image)

Figure 4.13: Overview of AFM results as a function of sample position. (a) Different crystal directions for GaAs (001) wafers. (b) Dot densities. (c) Dot sizes. (d) Relative volume of deposited InAs inside the QDs. The colors correspond to the lattice directions as indicated in panel (a).

The PL results appear to be more consistent and reliable. For the different lattice directions, an overview is provided in figure 4.15. It was observed that 2 distinct
modes of dots were formed, one emitting close to 1 eV (1300 nm) and another emitting around 800 meV (1525 nm). One of those spectra is shown in figure 4.14.

![RT PL spectrum for sample M1959, clearly showing 2 modes of coexisting QD sizes.](image)

In figure 4.14, 2 broad quantum dot peaks are observed. Due to the decreasing sensitivity of the detector beyond 1600 nm, the left-hand edge of the peak around 800 meV is very steep. At the points where the two modes coexist, the wavelength corresponding to the dominant mode is plotted in figure 4.15.

![Emission wavelength as function of sample position for a sample grown without substrate rotation.](image)

Figure 4.15: Emission wavelength as function of sample position for a sample grown without substrate rotation. (Colors correspond to the lattice directions as illustrated in figure 4.13(a)).

### 4.2. Manganese doping of InAs quantum dots

#### 4.2.1. Manganese background calibration

In order to obtain quantum dots which contain only one single manganese atom, it is required to have detailed information on the manganese content of our samples.
Therefore, the first step towards manganese-doped InAs dots is to determine the background concentration for the different growth conditions. The background doping level of manganese is investigated using the Hall Effect. Since manganese is a deep impurity with a binding energy of 113 meV, only a small fraction will be ionized at room temperature.

The discrepancy between the measured free carrier concentration and the actual manganese concentration is estimated starting from results obtained in X-STM. In this particular sample, with active doping aimed at $10^{18}/\text{cm}^3$, the manganese concentration was estimated by counting individual manganese atoms. The obtained concentration is $3.0 \times 10^{18}$ manganese atoms per cubic centimeter. The room temperature sheet concentration from Hall Measurements is $1.77 \times 10^{17}$ manganese atoms per cubic centimeter. This implies that the real manganese concentration can be estimated to be over one order of magnitude larger than the sheet concentration obtained from Hall Measurements.

Several samples with different growth parameters are investigated through Hall measurements. An overview of these parameters and the measured manganese concentration is given in Table 4.2. The conduction is all samples is p-type, due to the manganese background. In these samples no intentional manganese doping was performed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Growth Temperature (°C)</th>
<th>Growth Rate (nm/min)</th>
<th>Sheet resistance (kΩ)</th>
<th>Carrier mobility (cm²/Vs)</th>
<th>Sheet Carrier concentration (cm⁻³)</th>
<th>Estimated manganese concentration (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1965</td>
<td>480</td>
<td>2</td>
<td>28.61</td>
<td>143</td>
<td>$6.91 \times 10^{15}$</td>
<td>$1.11 \times 10^{17}$</td>
</tr>
<tr>
<td>M1966</td>
<td>480</td>
<td>10</td>
<td>4.42</td>
<td>351</td>
<td>$1.67 \times 10^{16}$</td>
<td>$2.67 \times 10^{17}$</td>
</tr>
<tr>
<td>M1973</td>
<td>560</td>
<td>10</td>
<td>5.62</td>
<td>368</td>
<td>$1.25 \times 10^{16}$</td>
<td>$2.00 \times 10^{17}$</td>
</tr>
</tbody>
</table>

It can be seen that for all 3 samples the estimated manganese concentration is in the low $10^{17}$-range. The origin of the manganese contamination could not be derived from these experiments. The two possible sources of contamination are the effusion cells and the block on which the sample is mounted. The low carrier concentration for M1965 is rather unexpected (assuming that the flux of incident manganese on the block is constant), but could be explained by additional defect formation (e.g. formation of arsenic anti-sites) due to the low growth rate. These defects can compensate for manganese doping and in that way reduce the measured concentration of holes. The lower background concentration for M1973 on the other hand is within expectation, since high growth temperatures reduce the formation of defects. The carrier concentration in M1966 is of most interest for this project, since the growth conditions for this sample are similar to these used for growing quantum dot samples.

The manganese background was also estimated using cross-sectional STM on one of our quantum dot samples.

In the first measurement, over 2 micron of wetting layer was imaged, but due to the low dot density, no quantum dots were observed. Figure 4.16 shows the details of the wetting layer at negative sample bias.
Figure 4.16: X-STM images of wetting layer at negative sample bias. The indium atoms show up as bright structures. (a) 35 nm x 20 nm; V = -3 V; I = 0.042 nA; (b) 25 nm x 20 nm; V = -3 V; I = 0.042 nA; Growth direction is from right to left.

For estimating the manganese background concentration, a total area of 50 nm x 1 µm was scanned in X-STM with positive bias. The total number of manganese atoms observed in this area was 2. The typical bow-tie manganese signature can be observed for manganese located up to several atomic layers underneath the (110)-surface, which corresponds to a detection depth close to 1 nm [17]. In that way, the measured concentration corresponds to \( \sim 4 \times 10^{16} / \text{cm}^3 \), which is slightly smaller than the estimated values from Hall experiments. Note that due to the small number of manganese atoms, this result is only a rough estimate value, which confirms the results from our Hall experiments. The bow-tie shape of the manganese acceptor is illustrated in figure 4.17. As reported earlier [17], no perfect atomic resolution is required in order to observe the manganese wave-function.

Figure 4.17: Bow-tie shape in X-STM of manganese in GaAs lattice. 10 nm x 10 nm; V = +1.4 V; I = 0.037 nA.
4.2.2. Manganese flux calibration

From the previous paragraph, it is already clear that the required manganese fluxes for doping InAs quantum dots are very small. Therefore it is impossible to calibrate the flux through the ion gauge read-out, since the fluxes in the desired pressure regime are too small to be measured. Therefore, an estimate is made by extrapolation from higher fluxes used for GaMnAs growth cycles. For this extrapolation, the vapor pressure data for manganese are related to the BEP measured on the ion gauge, for one of the manganese calibration samples which was studied through RBS. The flux calibration fits are given in figure 4.14. The temperature is plotted on a linear scale, while the beam equivalent pressures (BEP) and the corresponding atomic fluxes are plotted on a logarithmic scale. The corresponding fit is a second order polynomial.

![Manganese Flux Calibration](image)

**Figure 4.18: Manganese flux calibration by extrapolation of BEP.**

The different lines in the plot are the vapor pressure (black), BEP (red) and the atomic flux (green). The starting point is the manganese cell temperature, which is set at 830°C for the calibration sample. The corresponding BEP is $3.0 \times 10^{-9}$ torr, and the vapor pressure is $1.8 \times 10^{-3}$ torr. By fitting the vapor pressure to the literature values, the scaling factors for the atomic flux and BEP are obtained, resulting in the relationships plotted in figure 4.18.

Based on the extrapolation of the BEP, a calibration sample was grown with different intentional manganese doping levels. The structure of this sample is outlined in figure 4.19. The orange layers represent a 1ML InAs spacer. The growth temperature for this sample is 480°C, similar to the quantum dot growth temperature.
The composition of this sample is analyzed using SIMS. The results of this measurement are given in figure 4.20.

The sputter direction in SIMS is from left to right, which explains the sharp edges for the different layers on the left-hand side, and the tails for the different elements on the right-hand side of each peak. The different layers are labeled by numbers in order to clarify the different features shown in the measurement. The substrate (1) shows a constant number of counts for manganese and indium. The reason for still measuring these 2 elements is probably redeposition of sputtered material (or the detection limit for SIMS). The large manganese peak (2) is due to the deoxidation of the wafer. At
that point, the wafer is exposed to the chamber for 30 minutes. It is clear that the manganese background causes substantial contamination of the substrate. After finishing the deoxidation, a 100 nm high temperature GaAs buffer (3) is grown at a growth rate of 10 nm/min. In this region, a large variation in the manganese concentration is observed. After the high temperature buffer the c(4x4) calibration is performed, which causes an additional manganese peak (4) due to a growth interrupt of about 20 minutes. After the calibration step, a first InAs marker of 1 ML is deposited, which results in the first indium peak (4). Subsequently, the first medium temperature undoped GaAs layer (5) of 40 nm is deposited, after which the next InAs marker (6) is deposited. Now 4 layers of GaAs with intentional doping follow. For these layers the doping is introduced during the deposition of the first 40 nm, which is followed by 40 nm of undoped GaAs, at a growth rate of 1 nm/min and a growth temperature of 480ºC. The different layers are separated using a 1 ML InAs spacer (8, 10, 12 and 14). The intentional doping level for the subsequent layers was $3.0 \times 10^{15}/\text{cm}^3$ (7), $3.0 \times 10^{16}/\text{cm}^3$ (9), $3.0 \times 10^{17}/\text{cm}^3$ (11) and $3.0 \times 10^{18}/\text{cm}^3$ (13). The manganese concentration seems to increase gradually with increasing intentional doping concentration, but it is not clearly observable where it becomes larger than the background doping level. From the Hall measurements, it is expected that in layer 13 the manganese concentration should exceed the background level, which is not clearly visible in the measurement. To finish up the structure, a final GaAs buffer (15) is grown at a growth rate of 10 nm/min. This implies that the gallium cell temperature had to be increased, which causes a short growth interrupt, which can partially explain the higher manganese concentration in this final buffer layer. Another possibility is migration of manganese by “surfing” on top of the growing GaAs.

Furthermore the Hall effect was also used to calibrate the manganese flux. In order to have the best possible sample structure, high temperature GaAs was grown in thick films of 2.4 µm at a growth rate of 10 nm/min. An overview of these results is given in table 4.3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Growth Temperature (ºC)</th>
<th>Manganese cell temperature (ºC)</th>
<th>Sheet resistance (kΩ)</th>
<th>Carrier mobility (cm²/Vs)</th>
<th>Sheet Carrier concentration (cm⁻³)</th>
<th>Estimated manganese concentration (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1972</td>
<td>560 BG</td>
<td>7.31</td>
<td>340</td>
<td>1.04 $\times 10^{16}$</td>
<td>1.66 $\times 10^{17}$</td>
<td></td>
</tr>
<tr>
<td>M1980</td>
<td>560 530</td>
<td>5.31</td>
<td>371</td>
<td>1.32 $\times 10^{16}$</td>
<td>2.11 $\times 10^{17}$</td>
<td></td>
</tr>
<tr>
<td>M1981</td>
<td>560 560</td>
<td>2.18</td>
<td>321</td>
<td>3.72 $\times 10^{18}$</td>
<td>5.59 $\times 10^{17}$</td>
<td></td>
</tr>
</tbody>
</table>

From these data it can be seen that the manganese cell temperature has to be above 500ºC in order to exceed the background doping level. The numbers for M1980 and M1981 are within the expected range. According to the extrapolation data, the concentration for M1981 should be 3 times larger as compared to M1980. However, due to the high background concentration of manganese, the concentration in M1981 is slightly less than 3 times the value obtained for M1980.

### 4.2.3. Direct doping of InAs quantum dots

The most straightforward fashion of doping InAs quantum dots is direct doping. This is done by providing a manganese flux during the deposition of InAs for a period of 1 minute. The flux calibration is performed through extrapolation of the BEP. In samples with direct doping, the manganese flux is provided before the onset of
quantum dot formation. Different cell temperatures are used, resulting in different manganese concentrations. An overview of the samples with direct doping and their growth properties are listed in table 4.4.

Table 4.4: Sample properties for quantum dots with direct doping.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Manganese cell temperature (ºC)</th>
<th>Intentional number of Mn/dot</th>
<th>Onset of QD formation (s)</th>
<th>Starting time of Mn-doping (s)</th>
<th>Growth Interrupt (s)</th>
<th>#ML of InAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1941</td>
<td>430</td>
<td>1.0</td>
<td>320</td>
<td>180</td>
<td>360</td>
<td>1.91</td>
</tr>
<tr>
<td>M1951</td>
<td>435</td>
<td>1.4</td>
<td>480</td>
<td>180</td>
<td>600</td>
<td>2.13</td>
</tr>
<tr>
<td>M1952</td>
<td>450</td>
<td>3.3</td>
<td>690</td>
<td>180</td>
<td>840</td>
<td>2.07</td>
</tr>
<tr>
<td>M1953</td>
<td>462</td>
<td>6.6</td>
<td>840</td>
<td>300</td>
<td>1200</td>
<td>2.43</td>
</tr>
<tr>
<td>M1942</td>
<td>480</td>
<td>17.9</td>
<td>330</td>
<td>180</td>
<td>360</td>
<td>1.85</td>
</tr>
<tr>
<td>M1943</td>
<td>530</td>
<td>232.1</td>
<td>350</td>
<td>180</td>
<td>360</td>
<td>1.75</td>
</tr>
</tbody>
</table>

In these estimates, the background concentration has not been accounted for. The successful implementation of manganese is verified in single dot PL measurements, which are discussed in 4.2.5. PL experiments have been carried out for the different samples both at RT and at 5K. In room temperature PL all samples show dot peaks around 1250 nm, while at 5K all samples, except M1942 and M1943 show a clear dot peak. This might be caused by the presence of an overdose of manganese. Therefore these two samples are not suitable for PL measurements in the confocal microscope setup. Note that the large dispersion in the onset times for the quantum dot formation are a consequence of having slightly different growth temperatures, located near to the top of the growth window for InAs quantum dots.

4.2.4. Indirect doping of InAs quantum dots

Next to the direct doping approaches, also indirect doping methods are used. For this project, the doping was applied by depositing a delta-layer of manganese before deposition of InAs. This method is used in samples without substrate rotation. As outlined before, the sample orientation for depositing InAs is orthogonal to the position for depositing the manganese delta layer. In that way, both a gradient in dot sizes and densities and in manganese concentration is expected, with perpendicular orientation with respect to each other. In these samples, different manganese cell temperatures are used, while the deposition time is always 1 minute. An overview of the samples is and their growth properties is given in table 4.5. The growth temperature for all these samples is between 460 and 480ºC, which explains the variety in the onset times for quantum dot formation. The manganese cell temperature of 0ºC corresponds to a closed manganese cell shutter, so no active doping.

Table 4.5: Sample properties for samples with indirect manganese doping.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Manganese cell temperature (ºC)</th>
<th>Onset of QD formation (s)</th>
<th>Growth Interrupt (s)</th>
<th>#ML of InAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1959</td>
<td>460</td>
<td>510</td>
<td>600</td>
<td>2.00</td>
</tr>
<tr>
<td>M1960</td>
<td>430</td>
<td>420</td>
<td>600</td>
<td>2.43</td>
</tr>
<tr>
<td>M1961</td>
<td>0</td>
<td>600</td>
<td>705</td>
<td>2.00</td>
</tr>
<tr>
<td>M1971</td>
<td>0</td>
<td>450</td>
<td>600</td>
<td>2.27</td>
</tr>
<tr>
<td>M1976</td>
<td>0</td>
<td>480</td>
<td>600</td>
<td>2.13</td>
</tr>
</tbody>
</table>
All samples were measured in PL at RT and 5K and all samples yield dot peaks around 1300 nm and 1500 nm (at RT), depending on the location on the wafer. This implies that all of the samples are good candidates for doing single dot measurements, since the dot densities are confirmed to be low in AFM measurements.

4.2.5. Micro-PL in confocal microscope setup

Three of our samples were investigated in the confocal microscope setup, in order to see PL from single quantum dots. Samples M1941, M1959 and M1960 did show luminescence from the wetting layer and the GaAs substrate, but no PL from quantum dots could be observed in the initial attempts. Therefore it was concluded that the luminescence of the quantum dots was probably too weak. The weak luminescence of the quantum dots is attributed to defects, which can be either interstitial manganese or arsenic anti-sites, as discussed in 4.1.4.

It was shown that these defects can largely be reduced by annealing of the samples. Therefore, sample M1941 was used for extensive annealing tests. This particular sample showed the best properties for these measurements since it was grown with substrate rotation, and therefore has a quite uniform density of quantum dots, with well-defined densities and sizes, suitable for single-dot measurements. An overview of the different macro-PL spectra after annealing at different temperatures is given in figure 4.21.

![Figure 4.21: PL spectra for sample M1941 at 5K before and after annealing for 30 minutes at different temperatures.](image)

It is observed that upon annealing at 380°C, the PL signal from the dots is increased by a factor of 20 as compared to the sample after growth. Furthermore the quantum dot luminescence peak is shifted to higher energies as a consequence of intermixing of indium and gallium. The sample annealed at 380 degree was used for measurements in the confocal microscope setup. The increased luminescence from the dots allowed observing quantum dot PL in this setup as well. In figure 4.22, the
emission lines from the free exciton (FX) at 1.513 eV (819 nm) and the exciton bound to a donor (XD) at 1.495 eV (830 nm) are shown.

![Graph of PL spectrum](image)

*Figure 4.22: PL spectrum of GaAs in confocal microscope setup.*

In order to find the PL signal related to the quantum dots, small steps towards longer wavelengths are made, while adjusting the Z-position of the sample in order to optimize the focus for the right wavelength regime. In that way, the wetting layer is found around 1.440 eV (860 nm), as illustrated in figure 4.23.

![Graph of PL spectrum of wetting layer](image)

*Figure 4.23: PL spectrum of the wetting layer in confocal microscope setup. Integration time is 60 seconds.*

As pointed out in the macro PL-measurements, the luminescence peak of the quantum dots is not only shifted to lower wavelengths, but it is also broadened after annealing. This broadening allows moving step by step from the GaAs peak to the quantum dot peak, while optimizing the focus for every step in between. In figure 4.24, two of the intermediate steps are shown.
The top of the quantum dot peak was observed around 1.092 eV (1135 nm) for the macro-PL measurements, which was also observed in the confocal microscope setup, as illustrated in figure 4.25. The shape matches the macro-PL measurement very well.

In this position, it was attempted to see single-dot lines by lowering the excitation power of the laser and subsequently reducing the width of the entrance slit to the monochromator, in order to attain the highest possible resolution. By reducing the laser power, the spectrum remains similar, but with much lower intensity, as shown in figure 4.26.
It can be seen that the intensity of the luminescence has decreased and therefore longer integration times were used after narrowing down the entrance slit of the monochromator. When using the longest possible integration time for our setup, some single dot lines could be observed, as illustrated in figure 4.27.

Figure 4.26: Top of the quantum dot peak with lower laser power (0.50 mW).

Figure 4.27: PL spectra of single quantum dots for 2 neighboring sample spots. Excitation power 0.50 mW, slit width 50 µm, integration time 5 minutes.
Single dot lines are observed in both spectra, although the intensity of the luminescence is really low. The peaks at 1.095 eV (1132 nm), 1.112 eV (1115 nm) and 1.121 eV (1106 nm) show up in both spectra, while each of them shows different dot lines as well due to the slight change in position of a few tens of nanometers. This confirms that the observed peaks are actual dot lines.

Due to the low intensity of the luminescence of the quantum dots, only a limited number of measurements were carried out. For future work, the luminescence of the quantum dots in macro-PL should be much stronger in order to obtain single-dot measurements within an acceptable time-frame and sufficiently high resolution.

The growth conditions should be optimized in order to obtain fewer defects. Since the nature of the defect states could not be determined unambiguously, solutions for both possible defect types should be considered. The effect of formation of Arsenic anti-sites could be reduced by growing samples with lower arsenic fluxes. For interstitial manganese, the story is more complicated. It is a common defect in low temperature growth (e.g. GaMnAs growth), but it is not expected in high temperature growth, where the solubility of manganese is up to the $10^{18}$ Mn/cm$^3$. Therefore, the behavior of manganese in the medium temperature regime for GaAs growth should be studied in more detail.
5. Conclusions and outlook

During this project, InAs/GaAs quantum dots were grown by Molecular Beam Epitaxy (MBE). The growth was optimized in order to introduce manganese doping aiming at exactly one manganese atom inside each quantum dot. The samples were characterized by AFM and photoluminescence (PL) in order to measure the quantum dot dimensions and their densities. In that way, the growth conditions were optimized in order to obtain quantum dots with base lengths of 50 nm, heights of 10 to 15 nm and a dot density of $10^9$ QDs/cm$^2$. The growth temperature for obtaining these parameters is between 470 and 480ºC (as calibrated through RHEED transitions). The beam equivalent pressure for indium is $5.0 \times 10^{-9}$ Torr, which yields a growth rate close to $0.005$ ML/s. The total amount of deposited InAs is in between 2.0 and 2.5 ML.

For the introduction of manganese doping, an accurate calibration of the required manganese fluxes was desired. Since a typical quantum dot for our experiments consists of about $10^6$ atoms, the desired concentration of manganese was determined to be around $5.0 \times 10^{16}$/cm$^3$. In order to realize such low concentrations, the required manganese flux is very low, below the detection range of the ion gauge used for flux calibrations. The small fluxes were calibrated using the Hall effect and Cross-sectional STM (X-STM). It was observed that the background doping level due to manganese-contamination of our MBE chamber is in the regime of high $10^{16}$ to low $10^{17}$/cm$^3$. This concentration is close to the required value for having one manganese atom inside each dot, but in order to increase the probability of having manganese-doped dots, some active direct and indirect doping paths were explored.

From macro-PL measurements, it was observed that the intensity of the luminescence from the quantum dots was rather weak. This is attributed to the presence of defects within the samples, which can be either interstitial manganese atoms or arsenic anti-sites (arsenic atoms on a gallium lattice spot). Many of these defects were removed by annealing, resulting in an increase of the quantum dot luminescence with over one order of magnitude. After the annealing treatment, the dot luminescence was strong enough to observe single quantum dot lines in the confocal microscope setup, although it required very long integration times. Due to these long integration times, only a limited number of quantum dots could be measured, in which no interaction between the manganese spin and the excitons was observed yet.

In possible future work, the key point for obtaining manganese doped InAs/GaAs QDs is to optimize the luminescence of the quantum dots. Therefore, the nature of the defect states which reduce the luminescence intensity should be investigated further. A reduction in the number of arsenic anti-sites might be obtained by growing the samples with lower arsenic fluxes. The nature of interstitial manganese is a more complex problem. It is common in low temperature grown GaAs:Mn and not expected in High temperature GaAs:Mn. For the medium temperature regime, the exact reason for the presence of interstitial manganese should be further investigated.

As soon as the intensity of the luminescence of the QDs has been optimized, all different direct and indirect doping methods can be investigated systematically and in more detail. Furthermore, the influence of different capping temperatures could be considered as a key element in incorporating exactly one manganese inside a single QD.
6. References

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- The first neighboring cubical neighbors: Koen “I will get 1000% next week” Cox, Koen Vervaeke, Willem Van De Graaf, Maarten “You know Wim, that student of yours, playing with those-dot-like things…” Van Kampen, Chengxun Liu and Jan “Mr. Flex” Mol.
- My second neighboring cubical neighbors: Xavier “Why use a small bottle if we have big ones?” Janssens, Reinier “Maar enfin” Van Heertum and Pieter “Where are my shoes” Neutens.
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