Atomic scale study of intrinsic and Mn doped quantum dots in III-V semiconductors

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Atomic Scale Study of Intrinsic and Mn Doped Quantum Dots in III-V Semiconductors

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Murat Bozkurt

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CHAPTER 0.

6 Incorporation and Spectroscopy of Mn in and near InAs/GaAs Quantum Dots

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Chapter 1

Introduction

In this chapter, first a brief overview of the history of semiconductor transistors in electronic and memory applications will be given and the main obstacles in the search for more powerful chips will be explained. In this quest, research on novel applications of semiconductors plays an important role. In particular, the field of doped semiconductors and semiconductor nanostructures will be explained in some detail. Cross Sectional Scanning Tunneling Microscopy (X-STM) is a powerful technique to investigate these kind of materials and the benefits of this technique will be explained in this chapter. Finally, the scope of this thesis will be described and related to the aforementioned subjects.

1.1 History

Although the working principle of a transistor was already known since the 1920's, the first transistors made of semiconductor materials (Si & Ge) were only produced after WW II. Shortly after that, Integrated Circuits or IC's were developed. In the course of years, the individual transistors were getting smaller and smaller while the complexity of an IC, in terms of number of transistors per chip, was increasing. In 1965, this trend was formulated by Gordon E. Moore [1]: for an IC having the optimal ratio of yield and price per transistor, the number of transistors per IC has to double about every 2 years. This speed of development has been more or less sustained up to now. This is illustrated in figure 1.1 where the number of transistors per chip and RAM unit are displayed. Beside a more efficient design of integrated circuits, the improvement of lithography techniques has been one of the main driving forces behind the continuation of this trend. Anno 2010, the industry is at the level of 45 nm and 32 nm nodes, i.e. the half-period of the features on a RAM or IC, and it is expected that a switch to 22 nm node will be made around 2012 [2]. The actual size of features on a single transistor can be much smaller than the node number and at some point, quantum mechanics has to be taken into account when the functioning of a transistor at this scale is considered. The limits of downscaling transistors is also determined by quantum mechanics. Heisenberg's uncertainty relations form the basis for the limit of downscaling:

$$\Delta x \Delta p = h$$  \hspace{1cm} (1.1)
Figure 1.1: Increase of the number of transistors per processor and RAM IC during the course of years. The green line depicts the data used by Moore and the purple line represents his projection for the future. Image is taken from [3].

\[
\Delta E \Delta t = h \tag{1.2}
\]

where \( x \) is the spatial position, \( p \) is the momentum, \( E \) is the energy of a particle and \( t \) is the typical timescale in which events take place. The smallest energy \( E_{\text{bit}} \) to process a bit is defined by the Shannon-von Neumann-Landauer expression [4]:

\[
E_{\text{bit}} = k_B T \ln(2) \tag{1.3}
\]

where \( k_B \) is Boltzmann’s constant and \( T \) is the temperature of operation. For 300 K, \( E_{\text{bit}}=17 \) meV with which also a minimum momentum is associated. From equations 1.1 and 1.2 a minimum spatial scale of 1.5 nm and a minimum timescale of 0.04 \( ps \) can be derived. An IC built with transistors with these parameters would use about \( 4 \times 10^6 \) Watt/cm\(^2\) (effective chip area) if tunneling effects are taken into account [4]. In comparison, the power density at the surface of the sun is 6000 Watt/cm\(^2\) [4]. Clearly, as the size of the transistors goes down, the heat generation of an IC becomes an obstacle which is impossible to go around at some point and new physical mechanisms for future transistor principles have to be investigated for more powerful ICs.

One such an idea is to use the spin of charge carriers as an additional degree of freedom for data storage and/or data processing. The addition of magnetism to such a system also opens the way for use of photons which can be used to manipulate or read out spin. The most commonly used semiconductor, Si, has an indirect bandgap and is not suited to emit light. In contrast, III-V semiconductors such as GaAs and InAs have direct bandgaps. III-V semiconductors doped with magnetic atoms and nanostructures made out of them offer the opportunity to build new devices which can utilize the combined electronic, spintronic and photonic properties. These novel devices could become the building blocks for future chips and memories which consume much less energy and allow further increase of the calculation power by utilising these new degrees of freedom.
1.2 Mn Doped III-V Semiconductors

Semiconductors which exhibit ferromagnetic properties would open the door for a new generation of devices which can use spin properties of charge carriers beside their electric properties. Diluted Magnetic Semiconductors (DMSs) are semiconductors to which magnetism is added by doping them with transition metals. The most common transition metal used for this purpose is Mn. It has an electron configuration of $3d^54s^2$ and the half filled $d$-shell provides the Mn atoms with a total magnetic moment of $\mu = g\mu_B\sqrt{3}/2$ where $\mu_B$ is the Bohr magneton and $g$ is the $g$-factor. The investigation of III-V DMSs started with Mn doping of InAs [5] but the achieved $T_C$ in this material system was only 7.5 K. For possible applications in devices, it is important that magnetization in these materials can be maintained well above room temperature. Research on magnetism in GaAs gained momentum with the demonstration of ferromagnetism in GaMnAs where a $T_C$ of 60 K was measured [6]. The physical mechanism responsible for ferromagnetism in GaMnAs had already been suggested long before [7]: electrons in the half filled 3$d$-shell of the Mn atoms have an antiferromagnetic interaction with the holes introduced by the Mn. The ferromagnetic interaction of the holes with each other results in hole mediated ferromagnetism in GaMnAs. In the course of years, more insight has been gained in increasing the $T_C$ of GaMnAs by increasing the amount of substitutional Mn. In the thermodynamical equilibrium, only 0.1% Mn can be incorporated into GaAs and to obtain higher $T_C$’s, Molecular Beam Epitaxy at Low Temperatures (LT-MBE typically around 200°C nowadays) has been used to incorporate more than 15% of Mn in GaAs [8]. One of the problems that occurs with LT-MBE is that the quality of the grown crystal is not as good as it should be. At these temperatures, one of the defects that start to occur is the appearance of Mn at interstitial sites. Interstitial Mn acts as a double donor contrary to substitutional Mn which acts as an acceptor in III-V semiconductors. For this reason, ferromagnetism in GaMnAs, which is mediated by holes, will be suppressed by the presence of interstitial Mn [9, 10, 11]. A common method used to remove interstitial Mn atoms is to anneal the samples for an extended period after the growth because these Mn atoms are much more mobile in comparison with the substitutional Mn atoms. In the recent years, a $T_C$ of around 180 K has been achieved with these post growth annealing techniques [12, 13]. The process of increasing the $T_C$ with this technique is illustrated in figure 1.2. If the trend of increasing $T_C$ can be maintained up to RT, then Mn doped GaAs can be used as building block for future spintronic devices.

1.3 Semiconductor Nanostructures

One of the most important properties of semiconductor materials is the bandgap: i.e. the energy difference between the conduction band, highest unoccupied state of electrons, and the valence band, lowest occupied state of electrons. The formation of bands in a semiconductor is a consequence of the periodicity of the atomic potentials in a semiconductor crystal. The most common crystal structure for III-V semiconductors is the Zinc Blende structure. Discrete states of single atoms start to hybridize and form bands when the atoms are placed in a crystal. In figure 1.3, the bandgap of different III-V semiconductors is plotted.
against their lattice constant. Apart from the fact that III-V semiconductors have a direct bandgap contrary to Si, this interesting wavelength range has been the driving force behind the development of III-V material based optical devices since the most interesting wavelength for telecommunication applications is the 1550 nm region where the absorption of light by fiberglass materials is minimal. The emission of light by semiconductors occurs when an electron, which is excited to the conduction band, recombines with an empty electron state (a hole) in the valence band with the emission of a photon. Before recombination, an electron and hole usually form an exciton to lower their potential energy. The energy of this effect is usually very small in comparison with the energy of the emitted photon. Simply using bulk semiconductors for applications in optical devices is not the optimal option since the recombination process of an electron and a hole might occur at a rate which is not effective enough because of the spatial freedom of electrons and holes. Also the emitted photon can have an energy which might deviate from the actual bandgap energy because of thermal fluctuations of both electrons and holes in the conduction and valence band respectively.

To obtain semiconductor devices which emit photons with a well defined energy at an effective rate, nanostructures made out of semiconductor materials can be used. In these nanostructures, quantization of electron and hole energy levels result in well defined photon energies. Furthermore, electrons and holes are confined spatially into the nanostructures resulting in a higher recombination rate due to spatial overlap of the electron and hole wavefunction. Figure

**Figure 1.2:** Increase of $T_c$ with post growth annealing technique for different Mn concentrations. The increase in Mn concentration also results in an increase in the concentration of holes which couple the different Mn atoms with each other. Image is taken from [14].
Figure 1.3: Bandgap of some III-V semiconductors at RT plotted against their lattice constants. Image is taken from [15].

1.4 illustrates how the quantization of a particle state by confinement in an increasing number of dimensions can result in well defined energetic states. The benefit of using nanostructures instead of bulk materials has shown itself in the evolution of lasers where the threshold current density has decreased in the course of years from $\pm 1000 \text{ Acm}^{-2}$ for bulk materials to less than $\pm 10 \text{ Acm}^{-2}$ for quantum dots [17]. Quantum dots have also found other applications like Light Emitting Diodes (LEDs) and Semiconductor Optical Amplifiers (SOAs).

One of the technological challenges that come with the application of semiconductor quantum dot technology is the actual growth of such structures. Molecular Beam Epitaxy (MBE) has emerged as one of the leading techniques for growing nanostructures. Parameters that play an important role during the growth of quantum dots are the lattice mismatch of the quantum dot material with respect to the matrix material, the surface free energy of the different materials and the formation energy of misfit dislocations [18]. The surface free energy can be considered as the increase in energy of a material with a free surface relative to the bulk situation. The process of quantum dot formation is a complex interplay of strain build up and strain relaxation via different mechanisms. When a thin layer of material A is grown on top of another material B, strain energy will build up in layer A for increasing layer thickness. This energy $E_{2D}$ of the 2D layer per square area is given by:

$$E_{2D} = M\epsilon_{ij}^2h$$  

where $M$ is the biaxial modulus of the layer, $\epsilon_{ij}$ is the strain in the plane of the growth front and $h$ is the height of the grown layer. At some critical height, the strain energy will be released by the formation of either quantum dots (elastic relaxation, also called the Stranski-Krastanov mode) or misfit dislocations.
Figure 1.4: Density of states as a function of energy for nanostructures with confinement in different dimensions. For bulk materials, the density of states is a continuous function. The optimal quantization of energy levels is obtained for confinement in three dimensions. This is the case for quantum dots. Image is taken from [16].

\[ h_{cr}^{2D\rightarrow QD} = \frac{\Delta \gamma}{M \varepsilon_{MD}^2 \alpha} \]  
\[ h_{cr}^{2D\rightarrow MD} = \frac{E_{MD}}{M \varepsilon_{MD}^2 d_o} \]

In these formula's, \( \Delta \gamma \) is the difference in surface free energy between the 2D situation and the elastically relaxed situation, \( \alpha \) is the fraction of the strain energy which is relieved when quantum dots are formed, \( E_{MD} \) is the formation energy of misfit dislocations per unit length in the plane of growth front and \( d_o \) the average distance between misfit dislocations for a fully relaxed layer. For the formation of quantum dots, it is important that \( h_{cr}^{2D\rightarrow QD} < h_{cr}^{2D\rightarrow MD} \). For the most common case of III-V nanostructures, InAs quantum dots in GaAs, the lattice mismatch between the two materials is 6.7% and the strain relaxation occurs elastically. For the case of CdTe quantum dots in ZnTe, which has a lattice mismatch of about 6% which is similar to InAs/GaAs, the formation of quantum dots is prohibited by the low \( E_{MD} \) which makes the formation of misfits easier. In this case, the formation of CdTe/ZnTe quantum dots is enhanced by lowering \( h_{cr}^{2D\rightarrow quantudot} \) by covering the surface with a material that lowers the free surface energy cost \( \Delta \gamma \) [19].

1.4 X-STM Characterization

Basic properties of semiconductor nanostructures that influence their optical characteristics such as size, shape and composition depend on many param-
Figures 1.5: A 1x1 \( \mu \text{m}^2 \) Atomic Force Microscope (AFM) image of InAs quantum dots on GaAs grown by Stranski-Krastanov method. The relaxation of the strain energy by the formation of droplets with minimal surface free energy has its analogon in nature where droplets, with minimal surface free energy, are formed on leaves. Images of the quantum dots and droplets are taken from [20] and [21] respectively.

Parameters that can be controlled during growth. These parameters include growth temperature, capping composition, flux ratio of different components and other parameters. Characterization of the quantum dots with different growth parameters can be done with many techniques which all have their particular benefits. The main characterization method of quantum dots has been optical characterization by photoluminescence (PL) measurements. This method can give accurate information about the emission energy of the quantum dots and the energetic ordering of different excitonic states. Structural characterization can be done with Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM) or Scanning Tunneling Microscopy (STM). With AFM, only quantum dots which are uncapped can be studied. However, it has been shown before [22] that capping can change the structural properties of quantum dots drastically and thus also their optical properties. For implementation in functional devices, it is necessary that the quantum dots are capped. Capped quantum dots can be analyzed with TEM or Cross Sectional STM (X-STM). TEM measurements can achieve atomic resolution but it is lost when strain is present like in the case of quantum dots. Because of the thickness of the TEM samples, which is in the range of 10-200 nm, the measured parameters are average values. The ideal way of characterizing quantum dots is thus by using X-STM. With this method, samples cut from a wafer are cleaved along the growth direction and the cleaved surface is scanned with an atomically sharp tip.

Figure 1.6 illustrates the imaging capabilities of X-STM with examples of single impurities, nanostructures and images of complex alloy interfaces. When operated in the constant current mode and depending on the applied bias to the sample, the X-STM can image either the electronic contrast in the sample or the topographic contrast caused by strain. Figure 1.6a shows single Mn acceptors in their neutral state in bulk GaAs at different depths below the surface. The electronic feature of the Mn appears as a bow tie and is only
visible at positive voltages applied to the sample. Figures 1.6b and c show images of nanostructures taken at somewhat higher voltages. At such voltages, the tunneling current mainly depends on the topographic profile of the cleaved surface. The amount of inward or outward relaxation depends on the composition of the nanostructure. In this way, the composition of a nanostructure can be calculated from the strain relaxation as measured with X-STM [23]. Thus X-STM is capable of providing information about the shape, size and composition of a nanostructure. Figure 1.6d shows an X-STM image of the interfaces of InP/InGaAs/AlAsSb/InP. The different atoms look as bright or dark features due to their different size and different bonding configurations. With images like this, X-STM is capable of providing useful information about the quality of a Quantum Well (QW) interface with a certain growth method.

Figure 1.6: a) A 14x14 nm image of single Mn acceptors in bulk GaAs imaged in their neutral state at a a low positive voltage applied to the sample. The growth direction is indicated by the white arrow. b) A 72x56 nm image of an InGaAs nanorod grown by repeated deposition of InAs/GaAs layers. The nanorod is grown by strain driven accumulation of InAs on top of the previously grown part of the nanorod. c) A 28x53 nm X-STM image of an InAs/InP quantum dot. It can be seen that the quantum dot has the shape of a truncated pyramid. d) A 20x29 nm image of interfaces of compound semiconductors. With images like this, the quality of the different interfaces can be judged at an atomic level.
1.5 Scope of This Thesis

In Chapter 2 of this thesis, experimental and theoretical descriptions of STM measurements are given. The tip and sample preparation method are explained in detail and the theory behind the tunneling process is summarized. In the sections after this, the use of X-STM on III-V semiconductors is explained with examples demonstrating sample preparation effects and voltage dependent appearance of the GaAs surface. The analysis of the outward relaxation caused by strained materials is explained which is crucial in the investigation of nanostructures. The limitations of using the STM in the topography mode are explained and Scanning Tunneling Spectroscopy, which is used to resolve the energy spectrum, is explained.

In Chapter 3, quantum dot characterization by X-STM is explained in detail. First, the theory behind the strain calculations is described. The software package Comsol Multiphysics is used to solve the differential equations numerically. The process of determining a quantum dot shape, size and composition by X-STM is illustrated with an example. Finally, the aforementioned properties of quantum dots as measured by X-STM are linked to optical properties of quantum dots by using the X-STM data as input for theoretical calculation of the multi exciton spectrum of a quantum dot.

In Chapter 4, the use of Sb during growth of III-V quantum dots to tune their emission wavelength is investigated by X-STM. Sb is used in two ways: as a GaAsSb capping layer of the quantum dots and by exposing the quantum dots to an Sb flux before being capped. InAs/GaAs and InAs/InP (311B) quantum dots are investigated. It will be shown that in all cases, the use of Sb during capping, either in the form of GaAsSb or in the form of an exposure to Sb flux, results in a reduced quantum dot decomposition. These quantum dots show a redshift in their emission wavelength. The capping of InAs/InP (311B) quantum dots by GaSb has resulted in a new type of quantum dots with an internal type II band alignment: the bottom part consists of pure InAs and the top part consists of pure GaSb.

In Chapter 5, a theoretical study of Mn doped InAs/GaAs quantum dots is performed. Quantum dots doped with a single magnetic impurity are potential building blocks for future spintronic devices. First a review of optical spectroscopy experiments on Mn doped quantum dots is given. To obtain information at atomic level about the behavior of the Mn acceptor wavefunction inside InAs/GaAs quantum dots, X-STM measurements are crucial. Simulations of the Mn acceptor wavefunction in and near quantum dots based on effective mass approximation are presented. The results indicate that the Mn impurity potential inside a quantum dot acts as a strong perturbation on the empty quantum dot states. Strong localization of the states at the Mn position is predicted. For Mn outside of a quantum dot, electronic coupling with the quantum dot states takes place which depends on the Mn-quantum dot distance and the energy level alignment.

In Chapter 6, an X-STM study of single Mn doped InAs/GaAs quantum dots is presented. Images taken in the topography mode show that the growth of Mn doped InAs/GaAs quantum dots is complicated because of segregation of Mn. The segregation of Mn in GaAs is investigated with separate samples and the results show that Mn atoms can end up at distances of up to >100 nm from
their intended location. Spectroscopy measurements are performed on quantum dots with a Mn acceptor inside. As predicted by calculations based on the effective mass approximation in Chapter 5, states localized around the Mn inside the quantum dot are observed. Mn acceptors near a quantum dot show coupling with the quantum dot states in good agreement with the theoretical understanding.
Chapter 2

Experimental Techniques and Theoretical Background

In this chapter, the experimental details of X-STM measurements will be explained. In particular, the correct preparation of tips and samples, which is essential for a successful X-STM measurement, will be described. After a description of the setup, the theory behind the tunneling process and the origin of contrast in the X-STM images will be explained. Finally both the constant current mode, which is used to get structural information from nanostructures, and the spectroscopy mode, which is used to resolve the energy spectrum of nanostructures and single impurities, will be discussed.

2.1 Tip and Sample Preparation

In order to obtain X-STM images with atomic resolution, the tip with which the images are made should have atomic quality at the apex. The tips are made from poly-crystalline Tungsten (W) wires of 0.25 mm in diameter. A 10 mm long piece of W wire is attached to an Omicron tip holder either by spotwelding or by clamping. The holders with the W wires are then cleaned several times in an ultrasonic bath with detergent containing water, distilled water and isopropanol. The tip holder is then placed in a construction where part of the W wire can be etched away in a 2.0 molar KOH solution using an electrolysis reaction. The setup for the tip etching can be seen in figure 2.1. The KOH solution is placed in a glass beaker with a glass plate in the middle which divides the top part of the fluid but not the bottom part where electrical contact is still present. In one half of the top part, the W wire is submerged in the KOH solution until about 1 mm of wire is still above the fluid level. On the other half of the top part, a Platinum-Iridium (90%,10%) counter electrode is placed in the KOH solution. An overview of the setup is displayed in figure 2.1a. The etching reaction starts with the application of +6.3 V to the W wire. Typical values for the current are approximately 38.0 mA for the first 8 minutes and a more or less linear decrease to approximately 14 mA during an additional 9 minutes. In the last few minutes of etching, the process is interrupted at least once to refresh the meniscus at the tip (see figure 2.1b). The process ends when the tip breaks.
Figure 2.1: a): overview of the setup for etching where the anode, cathode and glass plate in the middle of the beaker are indicated. b): sketch of the flow around the tip apex during the etching process. c): a Scanning Electron Microscope (SEM) image of the tip apex. SEM image is taken from [20].
EXPERIMENTAL TECHNIQUES AND THEORETICAL BACKGROUND

at its thinnest point. During the etching process, the following reactions take place at the anode (W wire) and cathode (Platinum-Iridium) [24]:

\[
\text{Cathode : } 6\text{H}_2\text{O}(l) + 6e^- = 3\text{H}_2(g) + 6\text{OH}^- \quad (2.1)
\]

\[
\text{Anode : } W(s) + 8\text{OH}^- = W\text{O}_2^{2-} + 4\text{H}_2\text{O}(l) + 6e^- \quad (2.2)
\]

The WO$_2^{2-}$ dissolves in the KOH solution and sinks down along the wire decreasing the reaction speed at the lower parts of the W wire. This stream of descending WO$_2^{2-}$ solution in the fluid causes a stream of fresh OH$^-$ towards the W wire at or just below the fluid surface. This causes an increase in reaction speed at that point of the W wire and therefore the wire finally breaks at the point where the reaction speed was highest. At the cathode, H$_2$ gas is formed which rises to the surface of the KOH solution. The glass plate in the middle prevents that these gas bubbles disturb the flow of fresh OH$^-$ towards the W wire. The moment at which the wire breaks is also influenced by the orientation of the W wire in the KOH solution. In the ideal case, the W wire hangs perfectly vertical in the KOH solution and the descending WO$_2^{2-}$ is perfectly aligned along the wire. This will avoid the premature breaking of the W wire which might result in blunt tips. This etching process results in tips with a typical shape as displayed in figure 2.1c. The etched tips are kept in iso-propanol until they are placed in the setup to prevent the thickening of an oxide layer at the outer part of the W tip.

The samples used for the X-STM experiments have dimensions of about 4x10 mm and they are cleaved from a wafer in such a way that the short side of the piece is always oriented along one of the <110> directions. This is the natural cleavage direction for most III/V semiconductors with Zinc-Blende structure.

The first step in the sample preparation is the deposition of electric contacts on the sample to enhance conductivity. To prevent the formation of a PIN junction, either P- or N-type contacts are used for samples doped accordingly. As N-type contacts, a stack of Ge/Ni/Au (20/10/150 nm) and as P-type contacts, a stack of Ni/Zn/Au (5/20/150 nm) are used. The contacts are put on the outer edges of the sample as can be seen in figure 2.2a.

After the deposition of contacts, a scratch of about 1 mm is put manually in the direction of the intended cleavage direction using a pen with a diamond tip. In the ideal situation, the scratch starts softly in the material and deepens as the edge gets closer. This is achieved by manually regulating the pressure during the scratching process. At the end of the scratch close to the edge, a piece of the sample is removed which results in a V-shaped groove. It is also important that the scratch is placed at 3.0 to 3.1 mm from the "bottom" part of the sample. Samples with this kind of scratches have been found to result in excellent cleavage quality.

After the scratching, the samples are thinned down by polishing away material from the substrate side. Typical thicknesses for unpolished samples are around 400 µm and after polishing they are thinned down to about 120 µm. The polishing is done by attaching the sample to a metal rod with beeswax and putting the metal rod on a rotating platform with Al$_2$O$_3$ powder and water. The weight of the rod (±220 gr) pushes the sample against the rotating platform during the polishing process. After the polishing, the metal rod with the sample on it is heated to about 220$^\circ$ C to melt the beeswax. The sample is pushed in
isopropanol where it stays for at least a day to dissolve the remaining beeswax. As a last step, the samples are clamped onto sample holders. As depicted in figure 2.2a, the samples are clamped between two bars with pieces of indium between the sample and the metal bars. After the first tightening of screws, the sample holder is placed on a heater and is heated to approximately 220°C. After the pieces of indium melt, the screws of the sample holder are tightened even further. After cooling down, the sample holders are placed in isopropanol for transport to the X-STM setup.

Figure 2.2: a): sample placed in the sample holder. The perimeter of the sample is indicated with white (dashed) lines. The gold colored top is the part where the contact layer has been deposited. The scratch is placed just above the clamping bars at approximately 3.0 to 3.1 mm from the bottom of the sample. b): overview of the Omicron STM-1, TS2 scanner with (1) being the sample stage, (2) the tip stage on a tripod scanner and (3) the current amplifier which is placed as close to the tip as possible to avoid noise introduced by wiring. The copper plates placed in a circular form on the outer side of the STM stage belong to the Eddy-current damping system.

The STM setup consists of three main compartments: the load-lock, the preparation chamber and the STM chamber. The load-lock is the first stop for transport of tips and samples from the outside world to the UHV system. It is being pumped by a V-70 Varian turbo pump which on its turn is prepumped by a BOC Edwards XDS10 scroll pump. Typical pressure in the load-lock is $1.6 \times 10^{-6}$ Torr. The same combination of V-70 and XDS10 pump is used for prepumping a larger V-120 Varian turbo pump which pumps the preparation chamber down to pressures of around $2.0 \times 10^{-9}$ Torr. The STM chamber is separately pumped by a combination of a Titanium Sublimation Pump (TSP) and an Ion Getter Pump (IGP). Pressures of down to $4 \times 10^{-11}$ Torr are achieved in the STM chamber.
EXPERIMENTAL TECHNIQUES AND THEORETICAL BACKGROUND

The prepared samples and tips are brought to the preparation chamber via the load lock. Both samples and tips are baked out at a temperature of approximately 220°C. The tips get an additional treatment of Ar-ion bombardment to remove the oxide layer from the surface of the tip. After these preparations, the tips and samples are transferred to the STM chamber. The samples are cleaved just before the measurement by giving a gentle push to the top right edge of the sample in figure 2.2a. It is very important that STM measurements are performed without any mechanical vibrations. During a measurement, the turbo pumps and the scroll pump are switched off to prevent any vibration of the setup. Only the IGP which has no moving parts stays on. Additional precautions are taken to isolate the system from vibrations. The entire setup is placed on an island which is isolated from the rest of the building. An active damping system is used to cancel low frequency vibrations of the setup. The STM stage is attached with springs to the UHV chamber. The last defense against vibrations is the use of an Eddy current damping system. As can be seen in figure 2.2b, the STM stage has copper plates on its outer sides. These copper plates hang in between magnets during a measurement.

2.2 Tunneling Theory

During an STM measurement, the tip and the sample are brought close to each other with typical distances of 4 Å. At such short distances, an electron wave function at the apex of the tip can start interacting with the surface states of the sample through the finite vacuum barrier. Depending on the applied voltage to the sample, electrons can tunnel to or from the tip through the barrier. The tunneling current is given to first order in Bardeen’s formalism by [25]:

\[
I = \frac{2\pi e}{\hbar} \sum_{\nu} \left[ f(E_{\nu}) \left( 1 - f(E_{\nu} + eV) \right) \right] |M_{\mu\nu}|^2 \delta(E_{\nu} - E_{\nu}).
\]  

(2.3)

In this formula, \( e \) is the electron charge, \( \mu \) and \( \nu \) are indices of the tip and sample states respectively, \( f(E) \) is the Fermi distribution function, \( V \) is the applied voltage between sample and tip, \( M_{\mu\nu} \) is the tunneling matrix element between tip state \( \psi_{\mu} \) and sample state \( \psi_{\nu} \) and \( \delta(E_{\mu} - E_{\nu}) \) implies that only elastic tunneling is taking place. As can be seen, the current is proportional to the occupation of electron states at the tip side \( f(E_{\mu}) \) and to the occupation of holes at the sample side \((1 - f(E_{\nu} + eV))\) for the case of a positive voltage \( V \) applied to the sample. The tunneling matrix elements \( M_{\mu\nu} \) are defined as [25]:

\[
M_{\mu\nu} = \frac{\hbar^2}{2m} \int d\mathbf{S} \cdot (\psi_{\mu}^* \nabla \psi_{\mu} - \psi_{\mu} \nabla \psi_{\mu}^*). 
\]  

(2.4)

where \( m \) is the electron mass and the integral is taken over any surface lying entirely within the vacuum barrier. For small voltages and low temperatures where the Fermi distribution can be considered as a step function, equation 2.3 can be rewritten as:

\[
I = \frac{2\pi e^2 V}{\hbar} \sum_{\mu\nu} |M_{\mu\nu}|^2 \delta(E_{\nu} - E_{F\text{Sample}})\delta(E_{\mu} - E_{F\text{Tip}}).
\]  

(2.5)
A further simplification can be obtained by assuming that the tip is a point like probe with an arbitrary localized wave function. The matrix element $M_{\mu \nu}$ is then proportional to the amplitude of the sample wave function at the position of the tip center $\mathbf{r}_0$:

$$I \propto \sum_{\nu} |\psi_{\nu}(\mathbf{r}_0)|^2 \delta(E_{\nu} - E_{F}^{\text{Sample}}).$$

(2.6)

The term on the right is just the local density of states (LDOS) of the sample at energy $E_{F}^{\text{Sample}}$. This expression is only valid for tunneling at small voltages where only states at the Fermi level are involved in the process. This is typically the case for metal to metal tunneling where voltages in the order of $mV$’s are applied. For semiconductors however, larger voltages in the order of $V$’s are applied and more states are involved in the tunneling process. The measured current is then no more proportional to the density of states of the sample. A more appropriate expression for the tunneling current is given by [26]:

$$I = \frac{4\pi e}{h} \int_{-\infty}^{+\infty} \left[ f(E_{F}^{\text{Sample}} - eV + \epsilon) - f(E_{F}^{\text{Tip}} + \epsilon) \right] \times$$

$$\rho_{S}(E_{F}^{\text{Sample}} - eV + \epsilon)\rho_{T}(E_{F}^{\text{Tip}} + \epsilon)|M|^2 d\epsilon.$$

(2.7)

The different energy levels are taken into calculation by the integral over $d\epsilon$ and $\rho_{S}$ and $\rho_{T}$ are the LDOS of the sample and tip respectively. This expression can be simplified if the Fermi distribution functions are again considered as step functions which is justified for low temperatures:

$$I = \frac{4\pi e}{h} \int_{0}^{eV} \rho_{S}(E_{F}^{\text{Sample}} - eV + \epsilon)\rho_{T}(E_{F}^{\text{Tip}} + \epsilon)|M|^2 d\epsilon.$$

(2.8)

For the case of a metallic tip which can be assumed to have a constant $\rho_{T}$, $\rho_{S}$ can be obtained by taking the derivative of $I(V)$:

$$\frac{dI}{dV} \propto \rho_{S}(E_{F}^{\text{Sample}} - eV)$$

(2.9)

Up to now we looked at the dependency of the tunneling current $I$ on the tip and sample LDOS but for a qualitative understanding it is also important to look at the explicit dependency of $I$ on the distance between tip and sample. Also the relative contribution of different sample states available for tunneling is important. This is especially the case for semiconductors where high voltages are applied for the tunneling process and a range of sample states contribute to the tunneling. The wave function of a sample state $\psi_{\nu}(z)$ in the classically forbidden vacuum barrier shows an exponential decay and this also holds for the probability density $\psi_{\nu}(z)\psi_{\nu}^{*}(z)$ [26]:

$$\psi_{\nu}(z) = \psi_{\nu}(0)e^{-\kappa z}$$

(2.10)

where the decay constant $\kappa$ is given by:

$$\kappa = \sqrt{\frac{2m\phi}{h}}$$

(2.11)

In the last expression, $m$ is the free electron mass and $\phi$ is the height of the potential barrier. During an STM measurement, the condition of the tip doesn’t
vary and variations in $I$ are caused by variations of the sample LDOS. The tunne-
ing process is further explained in figure 2.3. In figure a, the movement of
the tip over the surface is shown when the STM is operated in the so called
constant current mode. In this mode, the distance between the tip and sample
is kept constant during the scan by keeping the current constant via a feedback
loop. The vertical movement of the tip during the scan then reflects the surface
properties of the sample. In figure b, the tunneling process is illustrated for a
semiconductor sample. Tunneling at this bias is only possible for sample states
with energies from the top of the valence band (VB) to $E_{F}^{\text{Tip}}$. Notice the decay
of the tunneling current as a function of the effective barrier height $\phi$, which is
higher for states lying deeper in the valence band. The energy parameter $\epsilon$,
used in equation 2.7, ranges from 0 to $V B - E_{F}^{\text{Tip}}$. These are the states in the
sample that are available for the tunneling process.

---

**Figure 2.3:** a) A bias is applied between the tip and sample. The tunneling
current $I$ is kept constant during the scan via a feedback loop and the vertical
movement of the tip reflects the variation of the sample surface states. b) Tunneling of electrons from the filled valence band (VB) states of the sample to
the empty states in the tip through a barrier with width $d$ and height $\phi$ when a
negative bias $V$ is applied to the sample. The barrier height $\phi$ is different for
the different states in the valence band which results in the characteristic $e^{-\kappa/d}$
decay. Note that Tip Induced Band Bending (TIBB) is not taken into calculation
in the expression for characteristic decay.

An additional important effect is the Tip Induced Band Bending (TIBB) which is
also illustrated in figure 2.3b. When a voltage is applied between the sample
and tip, $E_{F}^{\text{Tip}}$ is shifted with respect to $E_{F}^{\text{Sample}}$ and both the conduction band
and the valence band are bent towards $E_{F}^{\text{Tip}}$. The magnitude of the TIBB and
its characteristic decay deeper into the sample scale with the doping concentra-
tion. A consequence of TIBB is that larger or smaller voltages may need
to be applied to address certain sample states for tunneling. In a sample with
regions doped with different types of dopants, this results in an apparent height
contrast between the two regions. TIBB is especially important for the study of
CHAPTER 2.

single impurities where it can be used to change the charge state of a single impurity [27].

2.3 General use of X-STM on Semiconductors

In this section, some physical effects relevant to X-STM measurements will be explained and illustrated with X-STM images. One of these effects is the buckling behavior of atoms at the cleaved surface. The semiconductors investigated in this thesis have the Zinc-Blende crystal structure. Natural cleavage planes for this kind of crystal structure are the (110) and the (1\text{1}10) planes. After cleavage, the atoms at the surface have dangling bonds and the positions of the atoms are energetically unstable. The surface atoms lower their energy by changing their relative positions: group III atoms move inwards and group V atoms move outwards as illustrated in figure 2.4a. In the new situation, the

![Diagram of buckling behavior](image)

**Figure 2.4:** a) side view of the cleavage plane with the cleaved surface being at the top. b) an 8x15 nm X-STM image of GaAs taken at two voltages with opposite polarity. In the bottom part, the Ga rows are imaged and in the top part, the As rows are imaged.

...group III atoms have an empty electron state (C3 state) which is energetically located at the minimum of the conduction band. The group V atoms have a filled electron state (A5 state) which is located at the top of the valence band. By applying a positive or a negative voltage to the sample during an X-STM measurement, empty states related to group III atoms or filled states related to group V atoms are imaged. This is illustrated in figure 2.4b where the top
half of the GaAs image is taken at a negative voltage and the bottom part at a positive voltage applied to the sample. This means that the atomic rows in the top part are As rows and in the bottom part, they are Ga rows. Apart from imaging different atoms (Ga or As), it is also possible that tunneling from other states than the aforementioned A5 or C3 states contribute to the tunneling process. Different states could result in different atomic corrugation in the X-STM images [28]. This is illustrated in figure 2.5 where Zn doped GaAs has been imaged at different voltages applied to the sample. It can be seen that the corrugation for the cases of +1.65 V and +2.00 V mainly points in the (001) direction. For all other cases, the corrugation is pointing in the (110) direction. It is also very interesting to see that in the +1.65 V image, the corrugation points in the (001) direction. For all other cases, the corrugation is pointing in the (110) direction.

Figure 2.5: 22x18 nm images of GaAs doped with Zn acceptors taken at different voltages. The atomic corrugation is different for +1.65 V and +2.00 V. These measurements have been performed at the London Center for Nanotechnology in a 6 Tesla B-field pointing out of the image planes.
rugation is visible in both directions on top of the Zn atoms. This is caused by a local change in tunneling conditions due to the presence of the Zn acceptor. Interestingly, the appearance of Zn acceptors is different at different voltages. The effect of the applied bias on the charge state of an impurity will be discussed in the course of this thesis.

Another effect that is visible on cleaved surfaces is the appearance of cleavage induced defects on the surface. In GaAs, these defects mainly consist of step edges. If the cleavage is worse, the density of these step edges increases with eventually a rough surface as a result. A type of cleavage related defect which is not so common for GaAs is illustrated in figures 2.6a and 2.6b. These are

![Figure 2.6: a) A 25x19 nm image of missing rows of probably As or GaAs pairs. The streaky pattern of the upper missing rows indicates that they are being created as the tip is passing by. b) The same area imaged approximately 15 minutes later.](image)

rows of atoms which have been pulled out of the material during the cleavage process. Logically, also rows of atoms which remain behind on the cleaved surface are observed but these rows are much less stable and the atoms in the rows tend diffuse over the surface. Missing rows of atoms after cleavage have been reported before for II-VI materials [29] probably because they occur much more often than in III-V materials. This is most probable related to the lower band strength in II-VI’s compared to III-V’s. The rows of missing atoms in figure 2.6b have been imaged approximately 15 minutes after figure 2.6a. It can be seen that the empty rows have changed position between the two images. It is very likely that the movement of the missing rows is induced by the tip. This can be seen in the top part of figure 2.6a. The missing rows which are visible there in the image have a streaky appearance which is typical for things that appear or disappear during the scan. In figure 2.6b, the missing rows don’t seem to shift anymore which indicates that they have ended in a stable situation. Not much is known about the nature of these missing rows. Since both images where taken at high negative voltages, they look like missing rows of As atoms but it could also be that they are missing rows of Ga-As pairs.
2.4 Topography Analysis in Constant Current Mode

X-STM measurements can provide information about the shape, size and composition of semiconductor nanostructures. While the shape and size determination from the X-STM images is straightforward, the composition of the nanostructures is determined indirectly by looking at the strain of the cleaved surface. The magnitude of the strain depends on the lattice mismatch between the nanostructure and the matrix material. This process is illustrated in figure 2.7 for the case of an InAs QW in GaAs. Logically, the amount of strain relaxation will depend on the amount of In in the QW. In this thesis, the composition of a nanostructure is determined in two steps. The first step concerns the measurement of the surface relaxation with X-STM. In the second step, this measured relaxation is compared with numerical calculation based on continuum elasticity theory until a good fit is found.

![Figure 2.7: Strain relaxation of an InAs QW in GaAs. The lattice constant is 6.05 Å for InAs and 5.65 Å for GaAs. Due to the compression of InAs by GaAs, the InAs QW has an outward relaxation at the cleaved surface.](image)

For a correct measurement of the surface relaxation, the X-STM is used in the constant current mode and any contrast observed at the surface should be only due to the relaxation and not due to the electronic contrast caused by the band offsets of the different materials. This suppression of the electronic contrast is usually achieved at high sample voltages and it depends on three effects which are illustrated in figure 2.8. Both the case of a positive and a negative voltage applied to the sample are depicted in figure 2.8.

The first effect that is responsible for the suppression of electronic contrast is related to the exponential decay of the tunneling current as a function of the energy level. The strongest contribution comes from the highest energy states because of the smallest effective barrier there. At high positive sample voltages, the tip Fermi level $E_{F}^{tip}$ is aligned with empty states deep in the conduction band and most of the tunneling takes place to these empty states. This results in a small sensitivity to tunneling to the bottom of the conduction band where the electronic contrast is present. At negative sample voltages however, most of the tunneling takes place from the top of the valence band to empty states in the tip. Also the electronic contrast is most present at the top of the valence band. From this point of view, suppression of electronic contrast is best
achieved if one applies a (high) positive sample voltage.

The second effect which influences the suppression of the electronic contrast concerns the ratio of the band offsets to the height of the effective potential barrier \( \frac{\Delta \phi}{\phi} \). The tunneling current \( I \) decays as \( e^{-2\kappa d} \) with \( \kappa \) defined in equation 2.11. So a small \( \Delta \phi \) would mean that the variations in \( I \) due to the band offsets will also be small and thus the electronic contrast will be small. The ratio \( \frac{\Delta \phi}{\phi} \) is smaller for the case of tunneling at negative voltages than for positive voltages applied to the sample if one assumes similar variations in conduction band and valence band. This is because the effective barrier height \( \phi \) is larger for electrons tunneling from the filled valence band states [30]. In both cases of positive and negative voltages applied to the sample, voltages with high absolute values result in a small \( \frac{\Delta \phi}{\phi} \).

The third effect is the actual size of the offsets in the conduction band and the valence band. For most common III-V semiconductors having In or Ga as group III element and As or P as group V element, the offset in the valence band is usually smaller than the offset in the conduction band [31]. This leads to a preference for large negative sample voltages for the measurement of the surface relaxation. The eventual influence of the electronic contrast will be determined by a combination of all these three effects.

After the surface relaxation of the nanostructure has been determined, it has to be related to an actual composition of the nanostructure. By using the shape and size of the embedded nanostructure, a model of the cleaved nanostructure is built in a software program. The strain relaxation is then calculated numerically with finite elements method using continuum elasticity theory [32, 23]. We used the software package Comcol Multiphysics for this. By changing the

\[ \text{Figure 2.8: a) Tunneling at a negative voltage applied to the sample. The ratio } \frac{\Delta \phi}{\phi} \text{ is relatively small in comparison with the positive voltage case which is illustrated in b. TIBB is neglected in this figure.} \]
composition of the simulated nanostructure and fitting the calculated outward relaxation to the experimental curve, a composition profile can be deduced.

2.5 Spectroscopic Analysis

Using the STM in the constant current mode has the disadvantage that many sample states are contributing to the tunneling current as can be seen in figure 2.8: all states between $E_{F,\text{tip}}$ and $E_{F,\text{Sample}}$ contribute to the tunneling current. The strongest contribution comes from the highest energy states because of the smaller effective barrier for these states. If one is interested in resolving the energy scale, the STM can be used in the Current Imaging Tunneling Spectroscopy (CITS) mode. In this mode, $I(V)$ curves are taken at every pixel of the image while the tip remains at the same distance from the surface. The tip Fermi level is then swept across the energy spectrum of the sample by changing the applied voltage. Every time, the tip addresses an additional energy level, an increase in the measured current $I(V)$ will be observed at the corresponding voltage $V$. In the $\frac{dI}{dV}$ curve, this level will show up as a peak. As was mentioned before, $\frac{dI}{dV}$ signals are proportional to the LDOS of the sample. CITS measurements are employed to study the LDOS and energetic position of single impurities. In this thesis, CITS measurements have been performed on Mn doped InAs/GaAs quantum dots to study the effect of the quantum dot on the Mn wavefunction.
Chapter 3

Nanostructure Characterization with X-STM

In this chapter, characterization of strained nanostructures with X-STM will be explained. First, a theoretical description will be given of strain and the differential equations which are solved when the relaxation of a strained nanostructure is calculated. The differential equations are based on the continuum elasticity theory and they are solved numerically using the software package Comsol Multiphysics for a quantum dot composition given as input. After this, the procedure of finding a quantum dot composition, of which the numerically obtained strain relaxation fits the experimentally obtained strain relaxation, is described with an example. At the end, the shape, size and composition of a quantum dot structure obtained from X-STM measurements and Comsol simulations are linked to quantum dot properties as seen by PL measurements and theoretical calculations. Both in sections 3.2 and 3.3, my contribution to the projects was analyzing the X-STM data and finding the best quantum dot models with Comsol Multiphysics.¹

3.1 Strain Calculations with Comsol Multiphysics

The deformation process of a cubic volume element due to forces acting on the surfaces of the volume element in different directions is depicted in figure 3.1 where $\sigma_{ij}$ is the force in direction $j$ per unit area acting on the plane perpendicular to direction $i$. For $i = j$, the stresses are in the axial directions and they are responsible for the scaling of the volume element if they are equal on all surfaces of the cube. The stresses for $i \neq j$ are called the shear stresses and they are responsible for the deformation of the volume element. The 9 independent terms $\sigma_{ij}$ form the so called stress tensor. In case of equilibrium, the sum of all forces acting on the volume element and their momenta is zero and the shear stresses fulfill the condition $\sigma_{ij} = \sigma_{ji}$. In this case, the stress tensor consists of 6 independent elements.

The application of stress to the volume element will result in scaling and deformation which is expressed with the strain tensor. The amount of scaling

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and deformation depends of course on the elasticity of a material. The strain tensor components are related to the displacement $u, v$ and $w$ of the volume element in the $x, y$ and $z$ directions respectively. These relations are given by the following equations for the limit of small displacements:

$$
\varepsilon_{xx} = \frac{\partial u}{\partial x}, \quad \varepsilon_{xy} = \frac{y_{yx}}{2} = \frac{1}{2} \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) \tag{3.1}
$$

$$
\varepsilon_{yy} = \frac{\partial v}{\partial y}, \quad \varepsilon_{yz} = \frac{y_{zy}}{2} = \frac{1}{2} \left( \frac{\partial v}{\partial z} + \frac{\partial w}{\partial y} \right) \tag{3.2}
$$

$$
\varepsilon_{zz} = \frac{\partial w}{\partial z}, \quad \varepsilon_{xz} = \frac{y_{zx}}{2} = \frac{1}{2} \left( \frac{\partial w}{\partial x} + \frac{\partial u}{\partial z} \right) \tag{3.3}
$$

where, $y_{ij}$ is defined as the engineering strain. Similar equilibrium conditions as in the case of the stress tensor result in 6 independent components of the strain tensor. The stress-strain relation can be expressed as:

$$
\sigma = D \varepsilon \tag{3.4}
$$

with $D$ being the 6x6 elasticity matrix (also called the stiffness matrix). The inverse of the elasticity matrix is called the flexibility or compliance matrix. The stress and strain tensors $\sigma$ and $\varepsilon$ are rewritten in 6x1 vectors:

$$
\sigma = \begin{pmatrix}
\sigma_{xx} \\
\sigma_{yy} \\
\sigma_{zz} \\
\sigma_{xy} \\
\sigma_{yz} \\
\sigma_{xz}
\end{pmatrix}, \quad \varepsilon = \begin{pmatrix}
\varepsilon_{xx} \\
\varepsilon_{yy} \\
\varepsilon_{zz} \\
\varepsilon_{xy} \\
\varepsilon_{yz} \\
\varepsilon_{xz}
\end{pmatrix} \tag{3.5}
$$

The 6x6 elasticity matrix $D$ depends on the properties of the material. A distinction can be made between isotropic, orthotropic and anisotropic materials.
An isotropic material has equal elastic properties in all directions which is not the case for an anisotropic material. An orthotropic material has equal elastic properties in two directions and different properties in the third direction. In this thesis, we use isotropic materials for the strain simulations. The use of isotropic materials in the strain simulations to determine nanostructure composition has been justified by other techniques: atom counting [33] and atom probe technique [34] for the case of InAs/GaAs nanostructures. For isotropic materials, the elasticity matrix is defined as follows:

\[
D = \frac{E}{(1 + \nu)(1 - 2\nu)} \begin{pmatrix}
1 - \nu & \nu & 0 & 0 & 0 \\
\nu & 1 - \nu & \nu & 0 & 0 \\
\nu & \nu & 1 - \nu & 0 & 0 \\
0 & 0 & 0 & \frac{1 - 2\nu}{2} & 0 \\
0 & 0 & 0 & 0 & \frac{1 - 2\nu}{2} \\
0 & 0 & 0 & 0 & 0 \\
\end{pmatrix}.
\] (3.6)

In the elasticity matrix, \(E\) is Young’s Modulus and \(\nu\) is the Poisson’s ratio of the material. The equilibrium equations, expressed here in stresses, are solved by Comsol Multiphysics numerically:

\[
-\frac{\partial \sigma_{xx}}{\partial x} - \frac{\partial \tau_{xy}}{\partial y} - \frac{\partial \tau_{xz}}{\partial z} = F_x \\
-\frac{\partial \tau_{xy}}{\partial x} - \frac{\partial \sigma_{yy}}{\partial y} - \frac{\partial \tau_{yz}}{\partial z} = F_y \\
-\frac{\partial \tau_{xz}}{\partial x} - \frac{\partial \tau_{yz}}{\partial y} - \frac{\partial \sigma_{zz}}{\partial z} = F_z.
\] (3.7, 3.8, 3.9)

The parameters \(F_i\) are the so called volume forces which are set at 0 in our simulations. Note that these equations can also be written in terms of displacement by using equations 3.4, 3.1, 3.2 and 3.3.

The procedure of simulating the relaxation of a nanostructure consists of several steps. The first step is the definition of the geometry of a cleaved quantum dot. This can be seen in figure 3.2. The quantum dot has a base of 26 nm and a height of 8 nm. The box around the quantum dot has the dimensions 30x60x60 nm\(^3\) which is large enough to minimize the effects of the boundary on the strain relaxation of the quantum dot.

The second step is the assignment of different physical properties to the quantum dot and the matrix material. Straining of the quantum dot material in Comsol can be achieved in two different ways. One way is to assign initial strain values to the quantum dot material and then solve the equilibrium equations. Another way is to assign different thermal expansion coefficient to the quantum dot material and the matrix and then let the temperature increase.

The third and last step is the definition of boundary conditions. The boundaries of the box around the quantum dot have periodic boundary conditions: they can only move in their own plane. The cleaved surface is an exception which is totally free to move in any direction. After all the settings are done, the equilibrium equations are solved numerically using the finite elements method at each point of the meshgrid which is also visible in figure 3.2.
3.2 Shape, Size and Composition Determination of a Quantum Dot

In this section, the procedure of determining the shape, size and composition of quantum dots by means of X-STM is illustrated with an example. The investigated sample structure contains InAs/GaAs quantum dots which are grown by deposition of 2.0 ML InAs in 15 cycles of 4 s deposition and 4 s interrupt [35]. The substrate temperature was kept at 510 °C during the growth of the InAs layer and for 30 s after the quantum dot formation. After that the temperature was lowered to 500 °C and 8 nm GaAs was deposited. During the quantum dot formation and the 8 nm GaAs (0.185 nm/s) overgrowth, the As flux was 6x10^-6 mbar beam equivalent pressure. A small FWHM of the PL peak indicated a narrow size, shape and composition distribution [35]. A number of quantum dots (13) were analyzed with X-STM, all cleaved at random positions. The measured height and base will depend on the cleavage position through the dot. We assume that the biggest quantum dot is cleaved through the middle which is justified if the quantum dot size and shape is considered to be uniform over the sample. We found that the biggest quantum dot had a base of 27.5±4.0 nm and a height of 8.1±0.4 nm. By taking into account the height versus base length dependence for dots cleaved at various (central and non-central) positions for different quantum dot shapes, we found that an ellipsoidal shape with a base length of 26 nm and a height of 8 nm results in the best agreement with the experimental results. This is illustrated in figure 3.3 where the experimental data is fitted with the height vs base profiles of several types of quantum dots. It is found that the best fit to the height vs base curve is given by using an ellip-
NANOSTRUCTURE CHARACTERIZATION WITH X-STM

Figure 3.3: Height vs base statistics of the quantum dots determined from X-STM images. The lines correspond to the profiles of different quantum dot models. Blue: lens shaped quantum dot with a height of 8 nm and baselength of 22 nm. Red: ellipsoidal quantum dot with a height of 8 nm and baselength of 26 nm. Black: a pyramidal quantum dot with a height of 8.7 nm and baselength of 29 nm.

tical quantum dot with a height and baselength of 8 nm and 26 nm respectively. Further information about the composition can be extracted from the outward relaxation curves which are the result of compressive strain inside the quantum dot. The outward relaxation is the change in topography of the cleaved surface due to the compressive strain in the quantum dot. The strain depends on the In-profile inside the quantum dot [23]. The outward relaxation has been measured through several sections of the quantum dot as indicated in figure 3.4a. Models with different size, shape and compositions were simulated using Comsol Multiphysics until a good match was found between the experimental and the calculated outward relaxations. Two different models were considered: a lens shape (spherical curvature) and an ellipsoid. Again, the ellipsoid resulted in the best fit. The In profile inside the quantum dot has been modeled with linear gradients occurring between 4 corner points of the cross-section through a dot: i.e bottom center, top center, bottom corner and top corner. The In profile of the ellipsoidal quantum dot with the best fitting outward relaxation is depicted in figure 3.4b which shows a quantum dot with 70% In at bottom center, 100% at top center and top corner and 25% at bottom corner. The calculation also includes a wetting layer which has been measured and modeled in a similar way and resulted in 7 MLs of In$_{0.73}$Ga$_{0.27}$As far away from the quantum dots. Figure 3.5a shows the experimental and calculated outward relaxations of the wetting layer and the quantum dot at different positions through the quantum dot. The small difference between X-STM and calculation of the wetting layer outward relaxation in figure 3.5a is probably the result of some In segregation during the growth which results in an exponential In concentration decay and which is not taken into calculation. The strong gradient in the In concentration in both lateral and vertical directions is very important information and can lead to strong exciton polarization or a reduction of the effective height of the dots for electron
and hole confinement. The consistency of the model with the experiment can be confirmed further by a comparison of the measured and calculated lattice constant profiles taken in the vertical direction through the center of the quantum dot. Figure 3.5b shows an excellent agreement between the calculated and the measured profiles confirming the quality of our analysis.

3.3 Linking X-STM Results to PL and Theory

The previous section described the procedure which results in an In profile of a quantum dot. It is however very important to link the structural data obtained from X-STM to quantum dot properties obtained with different methods. In this section, we link X-STM measurements with PL measurements done on quantum dots from the same sample. The link is provided by a theory step in which the PL multi-exciton lines can be calculated for a given X-STM quantum dot model. Alternatively, several X-STM quantum dot models can be calculated in the theory step for a given set of PL multi-exciton lines.

The investigated InAs/GaAs quantum dots were grown with MBE on 17 nm of GaAs. An n+ doped substrate was used. The quantum dots were capped with 10 nm GaAs and an additional 105 nm of AlAs/GaAs superlattice. One piece of the wafer was used for single dot spectroscopy. For this purpose, a charge tunable device was made by putting ohmic contacts on the backside of the sample and a 5 nm NiCr Schottky barrier on the front side. By applying a voltage across the sample, the charging state of the quantum dot can be influenced [36]. PL measurements have been performed at 4.2 K at different charging
states of the quantum dot. Charge carriers were created by excitation of the WL. In figure 3.6, the multi-exciton lines of two typical quantum dots (Dot A and Dot B) of such a charge tunable sample are shown. Both quantum dots show a neutral exciton line at 1.071 and 1.081 eV. The different exciton lines show a Stark shift but the ordering of the exciton lines and their energy differences are not influenced. The labeling of the different excitons is as follows: the neutral exciton $X^0$ has 1 electron and 1 hole, the negative trion $X^{-1}$ has two electrons and one hole, the double negative single exciton $X^{-2}$ has 3 electrons and 1 hole (causing the "triplet" $X^{-2}_T$ and the "singlet" $X^{-2}_S$ emissions) and the neutral biexciton $2X^0$ has 2 electrons and 2 holes. Despite small differences between individual quantum dots, a specific ordering of the multi-exciton lines has been found to be a fixed property of the quantum dots in this sample. This specific ordering of the multi-exciton lines has been decomposed in 3 hard rules (HR1, HR2 and HR3). HR1 is that the energies of $X^{-1}$, $XX^0$ and $X^{-2}$ are always redshifted with respect to the neutral exciton $X^0$ line. HR2 is that $XX^0$ always lies in between $X^0$ and $X^{-1}$. HR3 is that $X^{-2}_T$ is always redshifted relative to $X^{-1}$.

The theoretical calculations are based on the many-body pseudo potential theory [37, 38]. The shape, size and composition of a quantum dot is used as input for the calculations and the multi-exciton spectrum is calculated. X-STM measurements were done on a piece of the wafer adjacent to the piece on which PL measurements were done. The relaxation of the surface through the quantum dots was analyzed with Comsol Multiphysics in a similar way as explained in the previous section to obtain information about shape, size and composition. Because of the low density of the quantum dots, only 6 quantum dots were found of which the largest was analyzed.
In the following, two methods of linking the PL data to X-STM structural data are considered. In the first method, the PL multi-exciton lines are calculated with theory for a given set of X-STM quantum dot models. The calculated PL multi-exciton lines are then compared with the experimental ones. In the second method, the theory step determines a set of quantum dot structures which all fulfill the experimental hard rules regarding the ordering of the multi-exciton lines. The calculated outward relaxation of this set of quantum dot structures is then compared with the X-STM outward relaxation data.

**Method 1: X-STM is used as input for the theoretical model.**

The largest quantum dot which was found with X-STM has a height of 7 nm and a baselength of 24 nm. This quantum dot is depicted in figure 3.7. The quantum dot has been modeled with several shapes: truncated pyramids, truncated cone, ellipsoid and truncated cone with a wetting layer which gets thicker near the quantum dot (models 1-5 in figure 3.7). The In profiles within the models have been defined as being linear between 4 points in the quantum dot: bottom center ($T_{Base}$), top center ($T_{Topp}$), top corner ($T_{ToppR}$) and bottom corner ($T_{BaseR}$). The expression for the In concentration $C_{In}$ inside the quantum dot is:

$$C_{In} = T_0 + \sqrt{\left(\frac{2x}{b}\right)^2 + \left(\frac{2y}{b}\right)^2} \ast (T_R - T_0)$$  \hspace{1cm} (3.10)

$$T_0 = T_{Base} + (T_{Top} - T_{Base}) \ast \frac{Z}{h}$$  \hspace{1cm} (3.11)

$$T_R = T_{BaseR} + (T_{TopR} - T_{BaseR}) \ast \frac{Z}{h}$$  \hspace{1cm} (3.12)
Figure 3.7: An 37x73 nm X-STM picture of the largest quantum dot which has a height of 7 nm and a base length of 24 nm together with the 5 X-STM models that were extracted from the outward relaxation curve shown in figure 3.8. Models T1 and T2 are quantum dot models provided by theoretical calculations based on the spectroscopic data. The RMS values indicate the quality of the fit of the outward relaxation calculations with respect to the experimental outward relaxation curve.
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![Graph showing experimental outward relaxation curve and calculated outward relaxation curves for X-STM models 1-5 and model T2.](image)

**Figure 3.8:** Experimental outward relaxation curve as measured with X-STM and the calculated outward relaxation curves for X-STM models 1-5 and model T2.

with $x$ and $y$ being the coordinates in the bottom plane of the quantum dot, $z$ the height coordinate, $b$ the baselength of the quantum dot and $h$ the height. For each quantum dot shape, the optimum In distribution has been found with Comsol simulations. The comparison of the experimental outward relaxation with the calculated outward relaxation of the different models can be seen in figure 3.8. Only the outward relaxation through the center of the quantum dot is shown here. The quality of the fits is also indicated in figure 3.7 with the RMS values of the calculated outward relaxations with respect to the experimental outward relaxations of each model. It can be seen that each model is more or less equally likely. The following step is the calculation of the multi-exciton lines of these 5 X-STM models.

In figure 3.9, the multi-exciton lines of the X-STM models are given together with the experimental multi-exciton lines. It can be seen that the experimental single exciton line of 1.071-1.081 eV is reasonably reproduced with all of the X-STM quantum dot models. This is an indication that the overall estimate of shape, size and composition is provided by the X-STM models is close to the real values. However, if we go one step further and compare the ordering of the different multi-exciton lines, we see that none of the X-STM models is fulfilling all of the spectroscopic hard rules which were defined previously. The ordering of the multi-exciton lines is much more sensitive than the energy of the single exciton line to details of the In distribution inside the quantum dot. With this we conclude that the conventional approach of closing the loop between X-STM and Single Dot Spectroscopy by using the X-STM models as input for the theoretical calculations does not work.
Figure 3.9: Calculated ordering of the multi-exciton lines for X-STM models 1-5 and models T1 and T2 and the experimentally determined spectrum. The different excitonic complexes to which the lines belong are indicated in the top plot of X-STM model 5.
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Method 2: Spectroscopy is used as input for the theoretical model.

A second way of closing the loop between X-STM and spectroscopy is by using the spectroscopy data as input for the theoretical calculations and obtaining a set of quantum dots which fulfill the spectroscopic hard rules and which can be compared with the X-STM data. For 200-300 different quantum dot structures, the spectroscopic properties are calculated theoretically. With data reduction techniques, a link is made between the quantum dot structural properties and the ordering of the multi-exciton lines. It is found that the aforementioned hard rules are satisfied when the height, baselength and average In content are in a certain range. These parameters will be called $h_{\text{spectr}}$, $b_{\text{spectr}}$ and $C_{\text{In-Spectr}}$ since they are based on spectroscopic data. Other quantum dot properties like shape and composition profile are found not to influence the spectroscopic behavior. The set of quantum dot structures that satisfies the hard rules is illustrated in figure 3.10a for $C_{\text{In-Spectr}} \geq 80\%$. It can be seen that for a baselength of approximately 21-26 nm, several critical values for $h_{\text{spectr}}$ are found which divide the diagram in regions where the ordering of the excitonic lines is different. The ordering that corresponds with the experimental data belongs to region I in figure 3.10a. When increasing the height $h_{\text{spectr}}$, the ordering of the excitonic lines changes. X-STM models 1-4 belong to the region where all of the hard rules are violated. Only model 5 satisfies one of the hard rules: $X^0$ is redshifted with respect to $XX^0$.

The last step is to find a quantum dot model which satisfies both the X-STM criteria and the spectroscopic hard rules. The geometrical base and height of a quantum dot as measured with X-STM (24 nm and 7 nm respectively) are accurate and any model provided by the theoretical step should satisfy these conditions. On the other hand, the In content as determined by X-STM is calculated indirectly from the outward relaxation and is not so accurate as the geometrical parameters. Furthermore, for $C_{\text{In-Spectr}} = 85\% \pm 5\%$ and $b_{\text{spectr}} = 20 \pm 2$ nm, the limit of region I in figure 3.10a is given by $h_{\text{spectr}} = 2.5 \pm 0.38$ nm. The trick is thus to find a quantum dot which fulfills the geometrical restrictions set by the X-STM measurements (24 nm baselength and 7 nm height) and which simultaneously lies in region I in figure 3.10a. Such a quantum dot can be constructed by fixing the quantum dot shape to that of a truncated cone with 24 nm baselength and 7 nm height (which was the best X-STM model) and by varying the In content inside the quantum dot such that the quantum dot lies in region I in figure 3.10a. With this procedure, 2 quantum dot models, T1 and T2 are obtained. Their In profile can be seen in figure 3.6. These quantum dots are characterized by a gradient in the In profile in the growth direction which is much stronger than that of the X-STM models. This leads to an In rich top of the quantum dot where the actual confinement takes place. This is illustrated in figure 3.10c for the conduction band and the valence band. It can be seen that $h_{\text{spectr}}$ is defined by the In rich top of the quantum dot and that it is indeed much smaller than the geometrical height of the quantum dot as determined by X-STM. In figure 3.6, the outward relaxation of quantum dot T2 as calculated by Comsol is also plotted. It can be seen that there is a good match also between this model and the experimental outward relaxation. The difference between the In profiles of X-STM model 5 and model T2 is illustrated in figure 3.10b. For model 5, the In profile through the center and along the edge of the
Figure 3.10: a) A "phase diagram" which indicates the different regions in which the spectroscopic hard rules regarding the ordering of multi-exciton lines are still valid. The diagram is made for an average In content of $\bar{C}_{In - Spectr} \geq 80\%$. Only in region I where $h = \leq h_{Spectr}$, all of the hard rules are satisfied. b) The In profile of X-STM model 5 and model T2. Both models have similar outward relaxation curves but only model T2 satisfies all spectroscopic hard rules. Model T2 is distinguished from the X-STM models by a stronger gradient in the In content along the growth direction. c) The consequence of the strong In gradient for the confinement of electrons (left plot) and holes (right plot) is that the effective height of the quantum dot ($h_{Spectr}$) is smaller than the actual geometrical height ($h_{Geom}$) of the quantum dot.
quantum dot is plotted together with the In profile of quantum dot T2. Clearly, the In gradient of model T2 is much stronger than that of X-STM model 5 while the calculated outward relaxations for both models fit the experimental outward relaxation equally well. With this, we conclude that X-STM is very accurate in determining the geometric dimensions of a quantum dot and less accurate in determining the composition profile of a quantum dot. The accuracy of X-STM is good enough to predict the energetic position of a single exciton $X_0$ line but for more details like the ordering of the multi-exciton lines, also a more detailed description of the In profile inside the is needed. Theoretical calculations, based on experimental data from single dot spectroscopy, were able to complement the X-STM models with those details about the In profile inside a quantum dot. It is found that a beyond linear In profile inside the quantum dot is needed to explain the multi-exciton ordering.

3.4 Conclusion

In this chapter, we have shown how strain calculations of nanostructures based on continuum elasticity theory are performed. The calculations are done with the software package Comsol Multiphysics and the differential equations are solved with finite elements method. By comparing the experimental strain relaxation of a nanostructure, as measured with X-STM, with Comsol calculations, the composition of such a nanostructure can be determined. We have demonstrated this with an example quantum dot. The shape, size and composition of a quantum dot determined with X-STM is linked to experimental data from single dot spectroscopy with theoretical calculations. We have found that both techniques, X-STM on one side and theoretical calculations based on spectroscopic data on the other side, complement each other and that both techniques have their shortcomings individually in describing a quantum dots shape, size and composition. It must be noted that an earlier attempt was made to link structural data obtained with X-STM to PL properties [39] for the much simpler case of a quantum well. The conclusion of that work was that many quantum well models fitted equally well the measured outward relaxation measured with X-STM but a specific selection could only be made with additional PL data. This confirms the main conclusions of this chapter that X-STM and spectroscopy are two techniques that complement each other.
Chapter 4

Atomic Scale Characterization of Sb Capped III-V Quantum Dots

InAs/GaAs quantum dots are the most common type of quantum dots which are investigated for applications in optoelectronics devices. However, their emission wavelength of around 1200 nm is not interesting for applications in telecommunication devices which work at wavelengths of around 1550 nm. One of the methods to redshift the emission wavelength of InAs/GaAs quantum dots is growing larger quantum dots which can be achieved by deposition of more quantum dot material [40], by controlling the epitaxial growth conditions [41, 42] or by growing on high index surfaces [43, 44]. Another method of redshifting the emission wavelength of InAs/GaAs quantum dots is by embedding them in an InGaAs matrix [45, 46, 47, 48, 49]. An interesting material that also can be used for quantum dot tuning is Sb. By capping InAs/GaAs quantum dots with GaAsSb, the emission wavelength can be extended to longer wavelengths [50, 51, 52, 53, 54]. A GaAsSb capping layer can act as a strain reducing layer but Sb can also act as a surfactant which influences the quantum dot formation during the capping process. In this chapter, a review is given of X-STM studies on GaAsSb capping of InAs/GaAs quantum dots in section 4.1. I contributed to this section by the analysis of the X-STM data either by contributing to the discussions (section 4.1.1) or by determining composition profiles with Comsol Multiphysics (section 4.1.2). In section 4.2, the effect of exposure of InAs/GaAs quantum dots to an Sb flux before capping is treated. X-STM measurements (not presented in this thesis) were performed by me to support the analysis of these samples. At the end in section 4.3, a similar study of GaAsSb capping and exposure to an Sb flux before capping of InAs/InP (311B) quantum dots is treated. The X-STM measurements in this section were performed by me.1

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4.1 Review Use of Sb to Tune InAs/GaAs Quantum Dots

The work in this section of the thesis is published already [55, 56, 57] and serves as an introduction to the section where Sb soaking of InAs/GaAs has been used to tune the emission wavelength and to the section where similar investigation has been performed on InAs/InP (311B) quantum dots.

4.1.1 GaAsSb Capping of InAs/GaAs Quantum Dots

The influence of GaAsSb capping layers on InAs/GaAs quantum dots has been investigated in two sets of samples grown with solid source MBE on n⁺ Si doped (100) GaAs substrates [55]. In the first sample (sample A), 2.7 MLs of InAs were deposited at a growth temperature of 500 °C and capped with a 6 nm thick layer of GaAs₀.₇₅Sb₀.₂₅ which was grown at a lower temperature of 475 °C. The second sample (sample B) contained quantum dots grown in the same manner but the 6 nm thick GaAs₀.₇₅Sb₀.₂₅ layer was grown at an elevated growth temperature of 500 °C. On the sample surface, quantum dots were grown for AFM measurements. In figure 4.1, a quantum dot from sample A is shown in filled states imaging. The bright atomic features above the quantum dot correspond with the Sb atoms. It can be seen that the GaAsSb layer grows uniformly over the quantum dot contrary to what has been observed for quantum dots capped with GaAs. The reason for the diffusion of GaAs away from the quantum dot can not be explained in terms of chemical bond energies since the Ga-As bond is stronger than that of Ga-Sb (50.1 kcal/mol vs 45.9 kcal/mol). It is rather the lattice mismatch between the GaAs and InAs that drives the Ga adatoms away from the quantum dot [58, 59]. The strain driven migration of InGaAs is also utilized during the formation of columnar quantum dots [60]. The uniform thickness of the GaAsSb layer is thus probably the consequence of the smaller strain between GaAsSb layer and the InAs quantum dots.

Figure 4.1: X-STM image of an InAs quantum dot capped with GaAsSb taken at a bias voltage of -3.0 V applied to the sample. The dark area on the right is a cleavage induced defect. Image is taken from [55].
Another argument for the absence of GaAsSb transport away from the quantum dot is the surfactant effect of Sb atoms which can result in reduced mass transport. The quantum dot in figure 4.1 is a full pyramid with a diagonal baselength of 32 ± 2 nm. With a height of 9.5 ± 0.2 nm, it is much taller than typical quantum dots capped with GaAs [61, 62, 22]. This indicates that the GaAsSb layer also prevents the decomposition of the quantum dots during capping. We propose that the reduced quantum dot decomposition is due to a smaller lattice mismatch between the quantum dot and the capping layer. This is in agreement with previously reported results where a reduced lattice mismatch in the capping layer has resulted in reduced quantum dot decomposition [63, 64, 65]. However, it is also possible that the surfactant effect of Sb is also responsible for the reduced quantum dot decomposition.

The actual amount of Sb in the capping layer has been determined by counting the Sb atoms in the STM image and comparing the measured outward relaxation of the InAs/GaAsSb wetting layer with simulations based on continuum elasticity theory. The atom counting resulted in an Sb content of about 22% in the GaAsSb layer and the relaxation simulations resulted in an Sb content of 25% [55]. Both are in good agreement with the intended amount of 25% Sb in the GaAsSb layer. Also the In content inside the quantum dot has been determined in the same way. A quantum dot model with an almost full pyramidal shape has been used. The best fit to the experimental outward relaxation was found for a model with an increase in In content from 40% at the corner bottom to 80% at the center bottom and to 100% at the center top of the quantum dot. The presence of In poor corners in our mostly intact quantum dot indicates that they are not caused by quantum dot decomposition as has been reported elsewhere [66].

In order to have a direct comparison of InAs quantum dots capped with either GaAs or GaAsSb, sample B was studied. The quantum dots and the GaAs and GaAsSb capping layers are grown at the same temperature of 500 °C. This is 25 °C higher for the capping layers than in the case of sample A. In figure 4.2a, the GaAsSb capped quantum dot is visible as a full pyramid with a height of 8.3 ± 0.2 nm and in figure 4.2b, the GaAs capped quantum dot is visible as a truncated pyramid with a height of only 3.8 ± 0.2 nm. AFM measurements on similar quantum dots on the surface of this sample have resulted in an average quantum dot height of 8 ± 1 nm. This indicates that the GaAsSb capping has completely stopped quantum dot decomposition during capping which is significantly different from capping with GaAs. The baselength of the quantum dot capped with GaAsSb is 26 nm while the baselength of the quantum dot capped with GaAs is 20 nm. This indicates that quantum dot decomposition doesn’t result in material redistribution from the apex of the quantum dot to the baselength of the quantum dot as suggested in [66]. Instead, the In from the dissolved quantum dot apex goes to the wetting layer which is confirmed by the higher amount of counted In atoms in the wetting layer in the case of GaAs capping (1.8 MLs) than in the case of GaAsSb capping (0.8 MLs). The increased growth temperature of the GaAsSb layer from 475 °C in sample A to 500 °C in sample B has resulted in the migration of GaAsSb away from the quantum dot apex as can be seen in figure 4.2a. This migration was not observed for the lower growth temperature of 475 °C of the GaAsSb layer as can be seen in figure 4.1.
Another interesting physical phenomenon that is observed in these measurements is the segregation of In and Sb atoms in the growth direction. Segregation is the process whereby atoms belonging to a certain species move towards the surface during the growth. This process is determined by differences in the binding energy and atomic size. Intermixing and segregation of In and Ga have been investigated in the past for quantum wells [67, 68, 69, 70, 71, 72, 73] and quantum dots [74, 75, 76, 77, 78, 79, 80]. Similar investigations have been done for Sb and As intermixing and segregation for quantum wells [81] and for interface qualities of superlattices of GaAs/GaSb [82], InAs/GaSb [83, 84, 85] and InAs/GaInSb [86]. In this part of the review, we show the experimental segregation profiles of In and Sb atoms and conclude that only one out of several segregation models is able to describe the Sb segregation correctly. Furthermore, it is shown both experimentally and theoretically that the segregation processes of In and Sb are not related to each other [57].

The segregation profiles of In and Sb have been obtained from X-STM images of InAs wetting layers overgrown with GaAsSb similar to those of sample A with the only difference that the nominal Sb amount in the GaAsSb layer has been varied from 12% to 15% and 20%. In figure 4.3, two STM images of the InAs wetting layer capped with GaAsSb are presented taken at a positive and a neg-

Figure 4.2: X-STM images of quantum dots capped with GaAsSb in a) and with GaAs in b) taken at a bias of -3.0 V applied to the sample. The GaAsSb layer is grown at an elevated growth temperature of 500 °C which makes the migration of GaAsSb away from the quantum dot apex possible. Image is taken from [55].
ATOMIC SCALE CHARACTERIZATION OF SB CAPPED III-V QUANTUM DOTS

Figure 4.3: Two X-STM images of an InAs wetting layer capped with GaAsSb taken at different polarities. At a positive bias applied to the sample, group III elements are imaged directly enabling us to identify In atoms in the Ga-rows. At a negative bias applied to the sample, group V elements are imaged directly enabling us to identify Sb atoms in the As-rows.

ative bias applied to the sample. As explained, group III and group V elements are imaged directly in the case of a positive and a negative bias respectively. In this way, the segregation profiles of In and Sb atoms, which show up as bright features in the Ga and As rows respectively, have been obtained. In figure 4.4, the experimental segregation profiles for In and Sb atoms are shown together with two theoretical fits which will be explained later. Several models exist that describe the segregation process in alloy materials. One of them was presented by Muraki et al. [87] which describes the segregation process as a constant fraction of the investigated species being exchanged between the surface layer and the bulk during epitaxial growth. A typical value of the fraction of In moving to the next monolayer during the exchange process in GaAs is around 0.8. Another model is the so called kinetic model [88, 89] which was initially verified for the SiGe system and was later adapted for III-V systems [90]. This model is chemically more justified since it takes into account the energy involved in the segregation steps. This energy determines the probability of an atom to jump from the bulk material to the surface layer during the epitaxial growth. A variant of this model is the so called thermodynamic model [91] which is valid for high growth temperatures where there is an equilibrium between the migration of atoms in and out of surface layer. All of these models only allow the exchange of atoms between the surface layer and the bulk material. Godbey and Ancona considered the segregation in a three layer model in which exchange takes place between the two most upper layers of the bulk
CHAPTER 4.

and the surface layer \[92\]. This model could be more applicable for situations in which the growth front has mono-atomic steps. In this situation, buried layers can still exchange atoms with the surface layer via lateral diffusion of atoms to places on the growth front where the layer is not fully covered yet. This three layer model resulted in the best fit to the experimental segregation data. Especially the slow decay of the Sb segregation profile was best approached when this model was used.

The details of this model are as follows for the case of In segregation in GaAs. The three layers involved in the segregation process are indexed with \(s\), \(s-1\) and \(s-2\) being the surface layer and the 2 layers below it. The monolayer fractions of Ga in the different layers are denoted by \(X^s_{Ga}\), \(X^{s-1}_{Ga}\) and \(X^{s-2}_{Ga}\) and similar notations are used for In. The In fractions fulfill the following equations in the limit of infinite diffusion rate in the plane of the growth front:

\[
\begin{align*}
\frac{dX^s_{In}}{dt} &= \varphi_{In} + E_{s,s-1} & (4.1) \\
\frac{dX^{s-1}_{In}}{dt} &= E_{s-1,s} + E_{s-1,s-2} & (4.2) \\
\frac{dX^{s-2}_{In}}{dt} &= E_{s-2,s-1} & (4.3)
\end{align*}
\]

In these equations, \(E_{i,j}\) is the supply rate of In to layer \(i\) from layer \(j\) and \(\varphi_{In}=x/\tau\) is the In deposition rate with \(x\) the number of monolayers grown and \(\tau\) the growth time of 1 monolayer. Furthermore, the In fractions fulfill the conditions \(X^s_{In} + X^s_{Ga} = \frac{x}{\tau}\), \(X^{s-1}_{In} + X^{s-1}_{Ga} = 1\) and \(X^{s-2}_{In} + X^{s-2}_{Ga} = 1\) where \(r\) is the total growth time. The supply rate \(E_{i,j}\) can be expressed as:

\[
E_{i,j} = P_1 X^i_{Ga}.X^j_{In} - P_2 X^j_{In}.X^i_{Ga}
\]

In this equation, \(P_n\) is the probability for a certain exchange process and is given by:

\[
P_n = \nu_n e^{-\frac{E_n}{kT}}
\]

with \(\nu_n\) being the vibrational frequency for the exchange process and \(E_n\) the energy barrier between the initial and final state of the exchange step. As explained in \[92\], the energy \(E_n\) is a fitting parameter. As mentioned already, in figure 4.4, the experimental segregation curves of In and Sb seem to be independent from each other. To confirm this, the energies \(E_n\) are for In and Sb made dependent on the Sb and In concentrations respectively. In other words, from strain energy point of view, it might be energetically more favorable for an In atom to occupy a spot in a GaAsSb lattice than in a GaAs lattice. This has been taken into account by adding a strain dependent part to the energy barrier \(E_n\) in equation 4.5. Both models, with and without strain are plotted in figure 4.4 but the differences between the two are so small that they are indistinguishable. The reason behind this is probably the fact that in the three layer model, the strain corrections to the energy barrier \(E_n\) are in the order of tens meV’s while \(E_n\) is around 2 eV \[85\] for Sb segregation in the As sublattice. With this, we conclude both theoretically and experimentally that the segregation of In and Sb can be considered as two independent processes.
Figure 4.4: Experimental segregation curves of In (empty blocks) and Sb (filled circles) for different amounts of Sb. The solid line is the theoretical segregation profile according to the three layer model. The purple dashed line, which is almost equal to the solid line, is the modified three layer model for Sb in which In and Sb segregation are made dependent on each other via strain energy. The blue dashed line is the In segregation profile according to the three layer model. Image is taken from [57].
4.1.2 Influence of Sb Content

The previous section has shown that the effect of capping quantum dots with GaAsSb is that quantum dot decomposition during capping can be stopped and that a layer of GaAsSb can be formed on top of the quantum dots which can cause type-II band alignment between the quantum dot and the capping. Both the enhanced size and the type II alignment will result in a redshift of the PL emission wavelength. For a comparison of both effects, quantum dots with different amounts of Sb in the GaAsSb capping are investigated by means of PL, AFM and X-STM [56].

A series of 11 samples containing a single quantum dot layer were grown for PL studies. In all these samples, 2.7 ML of InAs was deposited at 450 °C and 0.04 ML/s on an intrinsic GaAs buffer layer. After InAs deposition, a 30 s growth interruption under arsenic flux was performed during which the temperature was raised to 470 °C. The quantum dots were subsequently capped with a nominally 4.5 nm thick GaAs$_{1-x}$Sb$_x$ layer grown at 470 °C followed by 10 MLs of GaAs grown at the same temperature. The Sb content was nominally changed from 0% to 25% by keeping a constant flux resulting in values of the Sb$_{4/3}$As$_{4/3}$ beam equivalent pressure ratio between 0 and 0.05. 200-250 nm of GaAs grown at 580 °C were finally deposited on top of the GaAsSb capping. Four of the GaAsSb-capped quantum dot layers with different Sb contents were reproduced in a single sample for X-STM measurements. The surface of all samples was covered with a layer of uncapped quantum dots for AFM measurements. The PL measurements were done at room temperature using a He-Ne laser for excitation. The PL was dispersed through a 1 m spectrometer and detected with a liquid nitrogen cooled Ge detector.

AFM measurements on uncapped quantum dots showed that all of the quantum dots have similar size before capping (7.5±0.5 nm height and 26±2 nm baselength) so any change in PL properties must be caused by the capping process. In figure 4.5a, the PL of samples with different Sb amounts is shown. It can be seen that a red shift in the emission wavelength is caused for increasing amount of Sb in the GaAsSb capping layer. Thus Sb can be used to tune the emission wavelength of InAs/GaAs quantum dots in the wavelength region of 1150 to 1500 nm. Figure 4.5b shows the FWHM of the ground state PL peak and the integrated intensity of the PL emission. It can be seen that for increasing amount of Sb in the capping layer, initially the PL quality both in terms of FWHM and integrated intensity improves up to a wavelength of approximately 1280 nm. Further increasing of the Sb amount reduces the PL quality. Use of Sb in the capping and the improvement of PL integrated intensity was observed before[93, 94]. The improvement was attributed to Sb incorporation inside the quantum dots. Also reduced strain and type-II band alignment have been proposed as possible mechanisms that influence the PL properties of quantum dots [50, 51, 52, 53, 54, 95, 96, 97, 98, 99]. It must be mentioned that in our case, type-II PL behavior has been observed only for sample II in figure 4.5b and for other samples with longer emission wavelength. X-STM measurements are done to determine the influence of the GaAsSb layer on the quantum dot properties for different amounts of Sb.

In figure 4.6, three X-STM images can be seen of quantum dots capped with GaAsSb with different amounts of Sb. The Sb amount has been determined by analyzing the outward relaxation of the InAs/GaAsSb wetting layer in a sim-
Figure 4.5: a) Evolution of the PL emission wavelength for increasing amount of Sb in the GaAsSb capping layer. b) the initial improvement of the PL quality for increasing amount of Sb in the capping layer is visible up to approximately 1280 nm. Sample II is the first sample to show type II behavior. Figure is taken from [56].
height and thus the emission wavelength of quantum dots by controlling the Sb amount in the capping. To further support the observed effect of Sb on the quantum dot height, AFM measurements are performed on quantum dots which are partly capped with 3 MLs of GaAs or 3 MLs of GaAsSb. This is illustrated in figure 4.8 where also an AFM measurement on uncapped quantum dots is shown. It can be seen that 3 MLs GaAs capping is already enough to initiate the In-Ga intermixing which is responsible for the quantum dot decomposition [101, 102, 22]. Figures 4.8a and 4.8b show the AFM measurements on uncapped quantum dots and GaAs capped quantum dots respectively and it can be seen that most of the GaAs capped quantum dots are not visible due to decomposition. The process of In-Ga intermixing is stopped when GaAsSb capping is used as can be seen in figure 4.8c. This is attributed to the surfactant effect of Sb which limits the In-Ga intermixing by reducing the surface diffusion of adatoms.

We now relate the Sb induced changes in the quantum dot shape to the PL properties for different amounts of Sb in the capping layer. For this, we again
Figure 4.7: The increase of the quantum dot height after capping for different amounts of Sb in the GaAsSb capping layer. The height is normalized to the uncapped quantum dot height as measured with AFM. Note that the quantum dot decomposition has stopped for an Sb amount of 22%. A linear fit through the first 3 points shows however that a complete stop of decomposition can be already achieved for a much lower Sb content of around 14%. Figure is taken from [56].

make the distinction between two regimes which is illustrated in figure 4.5b. The first regime is characterized by emission in the 1150-1280 nm region. In the first regime, a redshift of the emission wavelength and an improvement of the PL characteristics is observed for increasing amount of Sb in the capping layer. Figure 4.7 shows that the redshift is partially caused by the increased height of the quantum dots. The improvement of the PL characteristics is also the consequence of larger heights of the quantum dots. Taller quantum dots show an increase in PL intensity because of stronger carrier confinement [104]. Also the quantum dot energy levels become less sensitive to constant size fluctuations when the quantum dots are taller [105, 106]. This results in a smaller FWHM of the PL peak as was illustrated in figure 4.5b. The optimum of the PL quality is reached for an Sb amount of 11-12% in the capping layer. Within error bars, this coincides with the anticipated 14% Sb in figure 4.7.

In the second regime with wavelengths of 1280-1500 nm, the PL shows a further redshift of the emission wavelength and loss of PL quality for increasing amount of Sb in the capping layer. This is explained by the formation of Sb rich GaAsSb clusters in the GaAsSb capping layer [56]. These clusters form both on top of the quantum dots and in the wetting layer. The clusters on top of the quantum dots cause a redshift because of the type-II band alignment between quantum dots and the Sb rich clusters. Fluctuations in the size and Sb content of these clusters can cause a broadening of the PL peak. An example of an Sb rich GaAsSb cluster on top of a quantum dot is shown in figure 4.6c. Clusters of GaAsSb in the wetting layer degrade the PL further by capturing charge carriers which would otherwise recombine in the quantum dots. This results in reduction of the PL signal.
Figure 4.8: a) AFM image of InAs quantum dots on a GaAs substrate. The z-range in this image is 20 nm. b) AFM image of similar quantum dots partially capped with 3 MLs of GaAs. Strong quantum dot decomposition due to In-Ga intermixing can be seen with only a few very large quantum dots still visible in the image. The z-range of this image is 10 nm. c) Same quantum dots this time capped with 3 MLs of GaAsSb. It can be seen that the decomposition has been reduced drastically. The z-range of this image is 10 nm. d) the decrease in quantum dot decomposition as seen by AFM for different amounts of Sb in the partial capping layer. Figure is taken from [56].

4.2 Sb Soaking of InAs/GaAs Quantum Dots Before Capping

In the previous sections, Sb was used as a component of the capping layer to reduce the quantum dot decomposition process. The In-Ga intermixing, which occurs during the quantum dot decomposition process during the capping, was found to be minimized by the presence of Sb acting as a surfactant. In this section, we investigate the use of elemental Sb before the capping process on the quantum dot properties by means of AFM and PL measurements[107]. The samples were grown by MBE. Quantum dot nucleation was observed by RHEED after deposition of 1.65 MLs of InAs at a growth temperature of 510 °C. After nucleation, the growth temperature was decreased to 440 °C and the In deposition continued up to 2.20 MLs. After the quantum dot formation, the quantum dots were exposed to an Sb flux from a valved cracker Sb cell for 10 seconds at different beam equivalent pressures ranging from $2.0 \times 10^{-7}$ to $3.1 \times 10^{-6}$ mbar. After this step the quantum dots were capped with 20 nm
GaAs at a growth temperature of 460 °C and an additional capping layer of 85 nm GaAs was deposited at a growth temperature of 580 °C. Samples for AFM measurements were grown in the same manner but the growth was stopped after the Sb exposure. PL measurements were done on capped quantum dots with a 0.3 m focal length spectrometer and an InGaAs detector. A frequency-doubled Nd:YAG laser (λexc=532 nm) was used for excitation. In figure 4.9, AFM images of surface quantum dots with and without exposure to Sb flux are shown. It can be seen that the presence of Sb reduces the quantum dot density and increases the quantum dot size thus enhancing the quantum dot ripening process as reported elsewhere [108].

![Figure 4.9: a) AFM image of surface quantum dots with no exposure to an Sb flux. b) AFM image of similar quantum dots exposed to an Sb flux at a beam equivalent pressure of 8×10^{-7} mbar. It can be seen that Sb has increased the quantum dot ripening process. Figure is taken from [107].](image)

In figure 4.10, the height of capped and uncapped quantum dots is plotted as a function of the Sb beam equivalent pressure. The height of capped quantum dots has been measured with Transmission Electron Microscopy (TEM). For an increasing amount of Sb, both the capped and uncapped height of the quantum dots becomes larger as shown before. It must be mentioned that the AFM measurements underestimate the measured quantum dot height for high Sb beam equivalent pressures. This is caused by the remaining Sb on the surface which makes the quantum dots look less tall than they actually are. The effect of Sb on the quantum dots can also be seen in the PL. The emission wavelength shows a redshift as a function of the Sb beam equivalent pressure which is the consequence of taller quantum dots. Although it is possible that Sb incorporation in the quantum dots is also responsible for the redshift, no type-II band alignment has been observed in power dependent PL measurements. These
results show that also elemental Sb can be used before the capping process to reduce quantum dot decomposition. Furthermore, it has been shown that Sb enhances the ripening process of quantum dots in which larger quantum dots are formed at the expense of smaller quantum dots. In a first consideration, this might seem to be in contradiction with the earlier statement that Sb reduces the in plane mass transport. The process of quantum dot ripening consists of mass transport to and from large and small quantum dots in an ensemble [109, 108]. During the ripening process, large quantum dots exhibit an increased probability of absorbing atoms from the environment due to their size compared to smaller quantum dots. On top of this, larger quantum dots are also more stable and thus the outflow of atoms is also smaller than for the case of small quantum dots [109]. These effects determine the ripening process which eventually leads to an ensemble of quantum dots which have grown at the expense of smaller quantum dots. We suggest that the presence of Sb affects the attachment-detachment ripening process [110] by increasing the stability of larger quantum dots even more which results in a reduced mass flow out of the large quantum dots.

4.3 Effect of Sb on InAs/InP (311B) Quantum Dots

In the previous sections, it has been shown that the emission wavelength of InAs/GaAs can be extended to longer wavelengths by using Sb during the capping process either in the form of GaAsSb or in the form of elemental Sb. To obtain quantum dots emitting in the interesting wavelength range of 1550 nm, also alternative materials are used like InAs/InP quantum dots. Room temperature PL at around 1590 nm has been achieved for InAs/InP (311B) quantum dots [111]. The growth of InAs/InP quantum dots is challenging because of
As-P exchange which can take place during growth and capping of quantum dots. During the deposition of InAs on InP, As-P exchange can take place with the InP substrate leading to a larger amount of deposited InAs than intended. This can result in larger quantum dots with a redshift as result [112]. During capping, As-P exchange which is enhanced by the lattice mismatch between the quantum dot and the capping layer, can reduce the quantum dot size with a blueshift as result. The control of the As-P exchange could permit to set the emission wavelength of InAs/InP quantum dots [113].

It is also very interesting to investigate the possibility of tuning the emission wavelength of InAs/InP (311B) quantum dots by using Sb in the capping either in the form of GaAsSb or by soaking the quantum dots with Sb before capping in a similar way as in the previous sections. For the purpose of X-STM investigation, a sample with multiple InAs/InP quantum dot layers with 30 nm were grown on a (311B) InP substrate at a growth temperature of 450 °C [114]. The quantum dots in each layer were formed by depositing 2.1 (001) equivalent MLs of InAs. The quantum dots in layer 1 were capped with InP in the usual way. This layer will act as a reference layer hereafter. The quantum dots in layer 2 were exposed to an Sb flux with a beam equivalent pressure $2.7 \times 10^{-7}$ Torr before being capped with InP. The quantum dots in layers 3 and 4 were covered with a 1 nm and 2 nm thick layer of GaAs$_{0.51}$Sb$_{0.49}$ respectively. Similar quantum dots to those in layers 1-4 were grown in separate samples for PL measurements. Uncapped quantum dots were analyzed with AFM.

In figure 4.11, X-STM images of quantum dots from layer 1 and 2 are depicted. It can be seen that the quantum dots from layer 1 have a rather flat shape. This shape is the result of a pyramidal InAs quantum dot of which the apex has eroded during the capping process. The erosion is induced by the lattice

![Figure 4.11: X-STM images of quantum dots in layer 1 (bottom) with the InP capping and layer 2 (top) with the exposure to Sb flux before InP capping. The bright atoms in the top quantum dot layer are Sb atoms. Exposure to Sb before capping has resulted in taller quantum dots. Figure is taken from [114].](image)
mismatch between the InAs quantum dot and the InP capping layer [65]. The quantum dots in layer 2 are exposed to an Sb flux before capping and show a full pyramidal shape with no erosion of the quantum dot apex. This can be explained with the surfactant effect of Sb which limits the in plane diffusion of atoms [81, 115]. The driving force behind the quantum dot apex erosion, which is the lattice mismatch between the quantum dot and the capping layer, is still present during capping but the As atoms of the InAs quantum dot apex are not able to move away because of the presence of Sb. Some Sb atoms even diffuse into the quantum dot as can be seen in figure 4.11. The Sb atoms look like bright features in and outside of the quantum dot.

In figure 4.12, X-STM images of quantum dots from layer 3 and 4 are shown. In both layers, the InAs quantum dots preserve their pyramidal shape. Quantum dot shape conservation has been reported before for InAs/GaAs Qds capped with InGaAs and GaAsSb layers [65] and very recently also for InAs/InP quantum dots covered with GaAsSb [116]. In the first two cases, the capping layers acted as a strain reducing layer. In the present case however, the GaAsSb layer is lattice matched to InP so the strain between the quantum dot and the capping is the same for capping with InP and GaAsSb. This indicates that it is the surfactant effect of the Sb in the GaAsSb layer which prevents the quantum dots from decomposing. A second effect which can be seen in figure 4.12 is that the GaAsSb capping layer has a uniform thickness over the entire growth front. From strain point of view, one would expect that the GaAsSb, which is

![Figure 4.12](image-url)

**Figure 4.12:** InAs quantum dots capped with 1 nm GaAsSb (layer 3) in a) and with 2 nm GaAsSb (layer 4) in b). Due to the surfactant effect of Sb, the quantum dots are taller, the GaAsSb shows a uniform thickness over the growth front despite the nonuniform strain distribution and there are no alloy fluctuations in the GaAsSb layer. Figure is taken from [114].
lattice matched to InP, should grow mainly in between the quantum dots. We suggest that the conformal growth is an indication of reduced mass transport due to the surfactant effect of Sb. The third effect which is visible in figure 4.12 is that there are no alloy fluctuations in the GaAsSb layer despite the large miscibility gap of GaAsSb. This is again an indication of reduced mass transport due to the surfactant effect of Sb. It must be mentioned however that in section II of this review, alloy fluctuations in the GaAsSb layer were observed for high amount of Sb (see figure 4.6). The behavior of the GaAsSb layer depends critically on the growth conditions as was shown in section C.

In figure 4.13, the height statistics of quantum dots in the different layers as determined from X-STM images is plotted together with the height statistics of quantum dots on the surface as measured by AFM. It can be seen that the AFM measurements show a distribution around 3.3 nm. The conventionally capped quantum dots of layer 1 show a truncated height distribution with a maximum located at 2.4 nm. This indicates that the quantum dot apex decomposition results in an average height reduction of 0.9 nm. The distribution for layer 2, where exposure to Sb had taken place before capping with InP, shows a distribution centered around 3.5 nm which is very close to the 3.3 nm as determined with AFM. This indicates that exposure to Sb has completely stopped the quantum dot decomposition process during capping. The height statistics of the quantum dots in layer 3 and 4 is centered around 3.2 nm which again indicates that quantum dot decomposition is completely suppressed by the use of a GaAsSb layer.

**Figure 4.13:** Height statistics of capped and uncapped quantum dots as measured by X-STM and AFM respectively. The use of Sb during the capping process, either as pure Sb or in the form of GaAsSb, eliminates the quantum dot decomposition process completely. Figure is taken from [114].
Figure 4.14 shows PL measurements performed on quantum dots of layers 1, 2 and 4. It can be seen that the increase in quantum dot height of 2.4 to 3.5 nm (layer 1 to layer 2) results in a relatively small redshift of about 0.03 eV. Quantum dots from layer 4 show an even larger redshift in their PL while they have similar quantum dot sizes as the quantum dots in layer 2. This can be only explained by type II band alignment between the quantum dots and the GaAsSb layer. Power dependent PL measurements (see inset figure 4.14) indeed show that the PL peak position is dependent on the excitation power as is expected for samples with type II behavior.

A very strange behavior is observed for quantum dots in layer 5 where the 2.1 MLs (001) equivalent InAs was capped with 2 nm GaSb. As can be seen in figure 4.15a, the GaSb has accumulated on top of the InAs quantum dots. This is caused by the fact that the lattice constants of InAs and GaSb are nearly the same (6.05 Å vs 6.10 Å respectively). The stacking of GaSb on top of the InAs results in quantum dots with a flat InAs bottom part and a flat GaSb top part. The boundary between the two regions seems to be very sharp. Since there is a type II band alignment between GaSb and InAs, it is expected that these quantum dots exhibit a spatial separation of electrons and holes inside the quantum dot which might lead to long exciton lifetimes. The band offsets of the InP, InAs and GaSb with respect to each other are plotted in figure 4.15b. It is expected that these quantum dots emit light at long wavelengths (>2 μm) but it was not possible to do PL measurements with these samples.
4.4 Conclusions

We have shown how a layer of GaAsSb on top of InAs quantum dots on a GaAs substrate eliminates the quantum dot decomposition process. This has been attributed to the reduced strain between the quantum dot and capping layer and to the surfactant effect of Sb in the GaAsSb layer. For Sb amounts of up to 14% in the GaAsSb layer, the PL show a redshift and the PL properties initially improve both in terms of FWHM of the PL peak and the integrated intensity. This is attributed to an increased height of the quantum dots which results in better carrier confinement and smaller dependency of the energy levels to size fluctuations. Further increase of the Sb amount results in more redshift and degradation of PL properties. This is attributed to Sb rich regions of GaAsSb above the quantum dots and above the InAs wetting layer. The size and Sb content fluctuations of the Sb rich parts above the quantum dots result in broadening of the PL on top of the redshift caused by the type-II band alignment between the quantum dot and the GaAsSb layer. The Sb rich regions above the InAs wetting layer act as traps for charge carriers and reduce the PL integrated intensity. It is also shown both theoretically and experimentally that the segregation of In and Sb atoms in the group III and group V sublattices respectively are two independent processes. The surfactant effect of Sb has also been used by soaking InAs quantum dots with Sb before capping with GaAs. With this method, an increase in quantum dot height before and after capping has been achieved with a redshift of the emission wavelength as result. The possibility to tune the PL of quantum dots has also been investigated for InAs/InP (311B) quantum dots. AFM and X-STM measurements have shown that the use of Sb, either in the form of GaAsSb capping or as elemental Sb soaking before InP capping, results in elimination of the quantum dot decomposition process. This offers a new way of controlling the quantum dot height and thus the emission wavelength of InAs/InP quantum dots. Furthermore, capping
of InAs quantum dots with 2 nm GaSb has resulted in bilayered quantum dot structures with an InAs bottom part and a GaSb top part. These quantum dots are expected to exhibit an internal type II band alignment resulting in spatial separation of electrons and holes.
Chapter 5

Electronic Properties of Mn in and near a Quantum Dot

In this chapter, the behavior of the Mn acceptor wavefunction in and near quantum dots will be discussed theoretically. It is expected that the Mn acceptor wavefunction will be influenced by strain, spatial confinement in the quantum dot and coupling between quantum dot states and acceptor states. After an introductory discussion of Mn in bulk GaAs, a review is given of a number of optical experiments on II-VI and III-V quantum dots doped with a single Mn atom. The necessity of performing X-STM measurements on Mn acceptors in and around III-V quantum dots is explained. In the last section, we will present calculations of the wavefunction and energy levels of Mn in and near a quantum dot and finally draw some conclusions. The work in this chapter was carried out by me for this thesis.

5.1 Mn in Bulk GaAs

Mn atoms in bulk GaAs have been investigated in great detail in the past both theoretically and experimentally [117, 118, 119, 120, 121, 122]. It was found that the hole introduced by the Mn acceptor has a highly anisotropic shape [119, 120] which is caused by the cubic symmetry of the GaAs crystal. In figure 5.1a and b, X-STM topography images of a Mn acceptor are shown in its ionized and neutral state respectively. The neutral state of the Mn acceptor in the gap was analyzed in more detail in [122] by means of Scanning Tunneling spectroscopy (STS). At positive voltages of about 1.4 V, the dI/dV signal was composed of 3 different peaks which arise from the splitting of the 3-fold degenerate F=1 ground state of Mn. All of the three peaks showed a decreasing energy level with respect to the top of the valence band for an increasing distance to the cleaved surface of GaAs which was confirmed theoretically [123]. The observed bow tie shape was found to show additional symmetry breaking when the GaAs matrix is strained. The strain can be caused either by the relaxation of the cleaved surface [121] or by the presence of a strained quantum dot [120]. Calculations of the Mn state by a Tight Binding Model (TBM) were performed
In figure 5.1c and d, the TBM results are shown for the Mn acceptor in bulk GaAs. In figure 5.1c, these calculations predict a neutral state which consists of 3 separate levels which correspond with different total momenta \((F=1,2,3)\) of the Mn complex in the GaAs crystal [117]. At low temperatures, the hole bound to the Mn is captured in the highest \(F=1\) state. The resulting LDOS as calculated by TBM for this ground state is averaged over all spin directions \((F=1, F_z=\pm 1, 0)\) and is shown in figure 5.1d and it corresponds well with the experimental image in figure 5.1b. In X-STM where the neutral Mn state is studied, the hole is captured in the uppermost state \(F=1\), 3 fold degenerate state. The degeneracy is lifted near a surface which breaks the symmetry. Furthermore, a Mn resonance deep in the valence band is predicted by TBM modeling (figure 5.1c) which was experimentally observed by D. Kitchen et al. [124]. Also the effect of strain, either caused by the cleaved surface or a quantum dot, was calculated by TBM and the results correspond well with the experimental observations [120, 121].

Figure 5.1: a) Topography image of a Mn acceptor in its ionized state. The main contribution to the contrast comes from the Coulomb field of the ionized Mn. b) Topography image of a Mn acceptor in its neutral state. The contrast is due to the charge distribution of the hole bound to the Mn. c) The LDOS of a neutral Mn consists of 3 separate states \((F=1,2,3)\) close to each other and a Mn resonance deep in the VB. d) STM contrast of the Mn acceptor in its neutral state as calculated by Tight Binding Method. Images are adapted from [119] and [117].
5.2 Optical Spectroscopy of a Single Mn in a Quantum Dot

In the past decade, Mn doped quantum dots were mainly studied by optical techniques. The first major achievement in this field concerned the optical probing of a CdTe/ZnTe quantum dot doped with a single Mn atom [125, 126, 127]. Mn is an isoelectric impurity in II-VI semiconductors and the electrons in the half filled d-shell of the Mn atom have a net spin of 5/2. This spin can interact with charge carriers in the semiconductor nanostructure.

The results of the first optical experiments with single Mn doped CdTe/ZnTe quantum dots are summarized in figure 5.2. In the absence of a Mn atom and a magnetic field, the emission line of a neutral exciton in a quantum dot simply consist of two degenerate PL lines which correspond to bright excitons with a total spin \( \chi = 1 \) and with spin projections \( X_z = \pm 1 \). We do not consider

\[
\begin{align*}
J_z &= -1, J_z = +1 \\
M_{\text{Mn}} &= -5/2, +5/2 \\
J_{\text{z}} &= -3/2, +3/2 \\
J_{\text{z}} &= -1/2, +1/2 \\
J_{\text{z}} &= +1/2, -1/2 \\
J_{\text{z}} &= +3/2, -3/2 \\
J_{\text{z}} &= +5/2, -5/2 \\
\sigma^- &\rightarrow \sigma^+
\end{align*}
\]

\[
\begin{align*}
\text{s character electron} (s_z = \pm 1/2) \\
\text{p character hole} (J_{\text{z}} = \pm 3/2) \\
\text{Mn atom} (M_{\text{z}} = \pm 5/2, \pm 3/2, \pm 1/2)
\end{align*}
\]

Figure 5.2: Schematic overview of the interaction of a Mn impurity with the exciton in the quantum dot and the resulting PL spectra at 0 T and 11 T. Images are adapted from [128]
dark excitons which are described by $X_z = \pm 2$. The presence of a Mn atom in a quantum dot results in 6 different energy levels both for $X_z = +1$ and for $X_z = -1$. These effects can be seen in the PL spectra presented in figure 5.2. At 0 T, the 6 lines correspond to the 6 different orientations of the Mn spin with respect to the exciton spin. In a magnetic field the degeneracy of the $X_z = +1$ and $X_z = -1$ levels is lifted as can be seen in the PL spectra in figure 5.2.

Also III-V InAs/GaAs quantum dots doped with a single Mn have been optically investigated. This situation is more complicated as in II-VI quantum dots since the Mn acceptor introduces a hole which acts as an additional spin object interacting with the charge carriers constituting the exciton and the Mn spin. The experimental observation of a single Mn doped InAs/GaAs quantum dot was made by Kudelski et al. [129]. The PL signature of a single Mn in an InAs/GaAs quantum dot is given in figure 5.3a. In [129], the three lines, indicated in figure 5.3a with FM, O and AFM, are attributed to respectively ferromagnetic, orthogonal and anti-ferromagnetic alignment of the spin of the Mn-hole complex to the exciton spin. The additional splitting of the FM and the AFM lines are attributed to asymmetries in the quantum dot-Mn system like an asymmetric quantum dot shape or an off-center Mn position.

A more extensive theoretical study of the Mn in a III-V quantum dot was performed by Van Bree et al. [130]. In that work, two possible electron recombination schemes were considered for the emission of a photon in a Mn doped quantum dot. These were the so called band-to-band transitions and band-to-acceptor transitions. Both are illustrated in figure 5.3b. The Mn core electrons with spin 5/2 and the acceptor hole with spin 3/2 interact strongly and form a single spin object which interacts with the quantum dot exciton. This approach,

![Figure 5.3: Image a) shows the PL spectrum of a single Mn doped InAs/GaAs quantum dot [129]. Image b) shows the two possible recombination schemes which were considered in [130].](image-url)
which considers Mn to form a localized acceptor level in an InAs/GaAs quantum dot [131] is more commonly accepted than the theory which suggests that the Mn introduces a hole in the quantum dot very similar to the quantum dot hole ground state [132].

For a qualitative explanation of the PL spectrum presented in figure 5.3a, a two spin model [130] turned out to be sufficient: the first spin object is the Mn complex, consisting of the Mn d electrons with spin 5/2 and the hole bound to the Mn atom with spin 3/2, form an entity with spin $F=1,2,3$ and 4 where at low T only the ground state with $F=1$ has to be considered [117, 119]. The bright exciton is considered to be the other spin object with spin $X=\pm 1$, which consists out of an electron with spin 1/2 and a hole with spin 3/2. In [130], the ground state Hamiltonian $H_G$ for a quantum dot with a Mn acceptor is defined as follows:

$$H_G = -DF_z^2 + E(F_x^2 - F_y^2) + g_F \mu_B F_z B_z$$

(5.1)

where $F_i$ is the i'th component of the total Mn spin $F$, $D$ and $E$ are constants, $g_F$ is the Mn g-factor, $\mu_B$ is the Bohr-magneton and $B_z$ is the magnetic field applied in the z-direction. The D-term is a consequence of confinement in the z-direction and it splits the $F=1$ triplet in a singlet $F_z=0$ and a doublet $F_z= \pm 1$. The E-term takes into account the in plane asymmetry of a quantum dot and it splits the $F_x= \pm 1$ in two states in plane of the quantum dot. This term accounts for a broken symmetry between the x- and y-direction in the quantum dot plane which can be caused by an asymmetric quantum dot shape or an off center Mn position.

The excited state Hamiltonian $H_X$, which involves an additional exciton in the quantum dot is defined as follows:

$$H_X = H_G + JF_x X_z + g_X \mu_B X_z B_z$$

(5.2)

where $J$ is the coupling constant between the exciton and the Mn complex and $g_X$ is the exciton g-factor. Both the ground state and the excited state Hamiltonians are solved numerically and the obtained energy diagram is shown in figure 5.4. The energy splitting $\Delta$ indicated in figure 5.3a is a result of the $-DF_z^2$ term and the splitting $\delta$ is a result of the terms $E(F_x^2 - F_y^2)$ and $JF_x X_z$.

Although the PL spectrum of figure 5.3a is well understood with the theory explained in [130], there is still no definite answer to several questions concerning the behavior of the Mn acceptor inside an InAs/GaAs quantum dot. It is for example not clear how the Mn acceptor state behaves inside the quantum dot. One possibility is that the Mn acceptor wavefunction is strongly localized around the Mn itself [131]. A second possibility is that the Mn impurity potential acts as a perturbation on the quantum dot potential and that the Mn related state is actually a slightly perturbed quantum dot state [132]. Another issue is the dependence of the Mn acceptor wavefunction on the spatial position inside the quantum dot. Both a theoretical and an experimental analysis were performed by me and will be discussed in this chapter and chapter 6 and the controversy between [132] and [131] will be clarified.
Figure 5.4: Schematic representation of the splitting of the ground state and the excited state due to z-confinement (D-term) and in plane anisotropy (E-term). The E-term takes into account effects like an asymmetric quantum dot shape or an off center Mn position. X-STM is the ideal tool to investigate the behavior of Mn acceptor wavefunction inside a quantum dot. Image is taken from [130].

5.3 Effective Mass Approximation for Degenerate Bands

In Effective Mass Approximation (EMA), the general form of a Hamiltonian which describes a degenerate band is given by [133]:

$$\sum_{j'} [D^\alpha_\beta_{j'j} \rho_{\alpha j} \rho_{\beta j'}] F_{j'}(r) = E \cdot F_j(r)$$  \hspace{1cm} (5.3)

where the indices $\alpha$ and $\beta$ are summed over the directions $x$, $y$, $z$ and the summation over $j'$ is over the number of degenerate states. The operator $\rho_{\alpha j}$ is the momentum operator $\frac{\hbar}{i} \frac{\partial}{\partial \alpha_j}$. The solutions $F_j(r)$ are the coefficients in front of the periodic Bloch functions $\phi_j$ which make up the total solution $\psi$:

$$\psi = \sum_j F_j(r) \phi_j.$$  \hspace{1cm} (5.4)

The quantities $D^\alpha_\beta_{j'j}$ are a set of numbers which take into calculation the effective mass:

$$D^\alpha_\beta_{j'j} = \frac{1}{2m_0} \delta_{\alpha j'} \delta_{\beta j} + \frac{1}{m^2} \sum_{i'} \frac{\rho_{\alpha j}^i \rho_{\beta j'}^{i'}}{\epsilon_0 - \epsilon_i}.$$  \hspace{1cm} (5.5)

The summation over $i$ is over all states which do not belong to the degenerate set of states $j$, $\epsilon_0$ is the energy of the degenerate states, $\epsilon_i$ is the energy of state
ELECTRONIC PROPERTIES OF MN IN AND NEAR A QUANTUM DOT

i and the terms \( p_i^\alpha \) are just the momentum matrix elements between different bands.

In III-V semiconductors which have the Zinc-Blende crystal, the top of the valence band is 4 fold degenerate due to spin orbit interaction and consists of 2 heavy hole (\( J_z = \pm 3/2 \)) and 2 light hole (\( J_z = \pm 1/2 \)) bands. Consequently, acceptors like Mn in bulk GaAs or InAs can be modeled with the 4 band Luttinger Hamiltonian \( H_L \) which has the same symmetry as the Zinc-Blende crystal:

\[
H_L = (\nu_1 + \frac{5}{2}\nu_2)p^2 - 2\nu_2 \sum_i p_i^2 J_i^2 - 2\nu_3 \sum_{i>j} p_ip_j\{J_i,J_j\} \tag{5.6}
\]

with \( \{J_i,J_j\} \) being the symmetrized product:

\[
\{J_i,J_j\} = \frac{1}{2}(J_iJ_j + J_jJ_i). \tag{5.7}
\]

In these equations, \( \nu_1, \nu_2 \) and \( \nu_3 \) are the Luttinger parameters in cubic approximation which take into calculation the effective mass of a hole in different directions, \( p_i \)'s are the momentum operators and \( J_i \)'s are 4x4 matrix representations of the total angular momentum components in different directions. These matrices are defined as follows:

\[
J_x = \begin{pmatrix}
0 & \frac{i \sqrt{3}}{2} & 0 & 0 \\
-\frac{i \sqrt{3}}{2} & 0 & i & 0 \\
0 & -i & 0 & \frac{i \sqrt{3}}{2} \\
0 & 0 & -\frac{i \sqrt{3}}{2} & 0 \\
\end{pmatrix} \tag{5.8}
\]

\[
J_y = \begin{pmatrix}
\frac{\sqrt{3}}{2} & 0 & 1 & 0 \\
0 & 1 & 0 & \frac{\sqrt{3}}{2} \\
0 & \frac{\sqrt{3}}{2} & 0 & 1 \\
0 & 1 & \frac{\sqrt{3}}{2} & 0 \\
\end{pmatrix} \tag{5.9}
\]

\[
J_z = \begin{pmatrix}
\frac{3}{2} & 0 & 0 & 0 \\
0 & \frac{1}{2} & 0 & 0 \\
0 & 0 & \frac{1}{2} & 0 \\
0 & 0 & 0 & \frac{3}{2} \\
\end{pmatrix} \tag{5.10}
\]

Using these matrices in equation 5.6 results in a set of 4 coupled equations for \( F_j(r) \) in equation 5.4. The index \( j \) runs from 1 to 4 and indicates the heavy hole spin up, light hole spin up, light hole spin down and heavy hole spin down respectively.

Effects of strain are taken into calculation with the additional Bir-Pikus term \( H_{BP} \):

\[
H_{BP} = a \epsilon + b \sum_i l_i^z (\epsilon_{ii} - \frac{1}{3}\epsilon) + \frac{d}{\sqrt{3}} \sum_{i>j} \{J_i,J_j\}\epsilon_{ij}. \tag{5.11}
\]

In this equation, \( a, b \) and \( d \) are deformation potentials and \( \epsilon_{ij} \) are the strain tensor components with \( \epsilon = \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz} \) being the hydrostatic strain.

Finally, in order to calculate the Mn acceptor states, a potential based on the Yukawa model is used:

\[
V(r) = -V_0 e^{-r/\alpha} \frac{1}{r/\alpha}. \tag{5.12}
\]
CHAPTER 5.

Other possibilities are the so called zero-range potential and the Coulomb potential. The zero-range potential [134] gives good results for rapidly decreasing potentials at distances larger than the effective radius of the potential. However, the zero-range potential is an inconvenient object in numerical calculations. On the other hand, the Coulomb potential is more applicable for shallow impurities like Zn in GaAs (~25 meV). Use of the Yukawa potential results in the correct size of wavefunctions and energy levels for impurities like Mn in GaAs. The final set of equations to be solved are given by:

\[(H_L + H_{BP} + V)\mathbf{F}(r) = E\mathbf{F}(r)\]  

(5.13)

The vector \(\mathbf{F}(r)\) describes the envelope function and consists of 4 components. Each component is the envelope wavefunction of the state with a certain projection \(J_z\) of the total angular momentum \(J=3/2\) along a quantization axis (heavy and light holes, up and down):

\[
\mathbf{F}(r) = \begin{pmatrix} F_{hh\uparrow} \\ F_{lh\uparrow} \\ F_{hh\downarrow} \\ F_{lh\downarrow} \end{pmatrix}.
\]  

(5.14)

The solution \(\mathbf{F}(r)\) is obtained with the software Comsol Multiphysics by solving equation 5.13 numerically. An uncleaved InAs/GaAs quantum dot with a diameter of 10 nm and a height of 2.8 nm is defined which is shown in figure 5.5. The first step of the process is the calculation of the strain distribution with the method which was explained in Chapter 3. The strain tensor components are then used in the expression for the Bir-Pikus term.

The second step is the solution of equation 5.13. A potential step of 310 meV in the valence band between the quantum dot and the matrix material is introduced. The parameters \(\gamma_1, \gamma_2\) and \(\gamma_3\) in equation 5.6 and \(a, b\) and \(d\) in equation 5.11 are the same for the quantum dot and the matrix material. This practically means that the entire material consists of InAs with only a potential step at the position of the quantum dot interfaces. In this approach, the differences in effective masses and deformation potentials inside and outside the quantum dot are not taken into account. This will however not affect our general conclusions on the Mn states that we find. Conservation of flux is the boundary condition between the quantum dot and its environment. Furthermore, the Mn spin and the acceptor hole spin and their interactions are neglected. TBM calculations, where the Mn spin was taken into calculation, have shown that averaging over all spin orientations gives very similar results with EMA [119]. An overview of the parameters used in the EMA calculations is given in table 5.1.
The COMSOL geometry in which equation 5.13 is solved for $F(\mathbf{r})$. The quantum dot has a diameter of 10 nm and a height of 2.8 nm and the large box has sides of around 70 nm. The $x$ (red), $y$ (green) and $z$-axis (blue) are oriented along the (100), (010) and (001) directions respectively.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_1$</td>
<td>20.40 eV</td>
</tr>
<tr>
<td>$\gamma_2$</td>
<td>8.30 eV</td>
</tr>
<tr>
<td>$\gamma_3$</td>
<td>4.55 eV</td>
</tr>
<tr>
<td>$a$</td>
<td>-1.0 eV</td>
</tr>
<tr>
<td>$b$</td>
<td>-1.8 eV</td>
</tr>
<tr>
<td>$d$</td>
<td>-3.6 eV</td>
</tr>
</tbody>
</table>
5.4 Results Effective Mass Calculations

The Mn acceptor wavefunction is calculated in bulk InAs, in a quantum well (simulating the wetting layer) and in and near a quantum dot as depicted in figure 5.6. Each solution has two degenerate eigenvalues corresponding with the spin up and down states. For each solution the normalized probability density as defined in formula 5.15 will be plotted as an isosurface plot and in a cross section plot. The value of the probability density at the isosurface can change in order to have an optimum impression of the shape of the impurity state. The color at the isosurface is proportional to the distance to Mn center. The directions are indicated by the axis system in each plot. Positive x-axis (100) is red, positive y-axis (010) is green and positive z-axis (001) is blue. The cross section plane is always the (110) plane.

\[
\sum \frac{|F_i(r)|^2}{\int_V \sum |F_i(r)|^2 dr^3}
\]  
(5.15)

Mn in bulk InAs

As a start, Mn in bulk InAs has been simulated by putting the Yukawa potential in the middle of a sphere with a radius of approximately 36 nm. As expected, a four-fold degenerate ground state with eigenvalues \(\lambda_{1,2,3,4}\) has been found with a negligible splitting between the spin doublets of the heavy- and light hole levels (see figure 5.7). The total isosurface of the probability density has the form of a cube with sides which are slightly pushed in. The cubic symmetry is introduced in the Luttinger Hamiltonian by using the appropriate Luttinger parameters for InAs where \(\gamma_2 \neq \gamma_3\). The cubicity is found to be more pronounced in bulk GaAs than in bulk InAs because of the specific Luttinger parameters describing the dispersion. For bulk InAs in figure 5.7, the bow tie shape, which is normally observed at the (110) cleavage surface, can be recognized in the shape of the isosurface when one looks from the (110) direction.

The parameters \(V_0\) and \(\alpha\) in equation 5.12 for the Yukawa potential are taken to be 12 and 1 respectively in the dimensionless Comsol units. These units are

![Figure 5.6: Schematic drawing of the positions of the Mn acceptors in and near a quantum dot and wetting layer which were calculated in the Effective Mass Approximation.](image)
chosen to simplify the calculations in Comsol Multiphysics. The kinetic part of the Hamiltonian can be made dimensionless by choosing scaling factors $\beta$ for energy and $\eta$ for distance:

$$\frac{h^2}{2m} \frac{1}{\eta^2} \frac{\partial^2}{\partial x'^2} = \beta E'$$

(5.16)

In this expression, $x'$ and $E'$ are the new distance and energy units. The following choice for $\beta$ and $\eta$ can be made:

$$\eta^2 \beta = \frac{h^2}{2m}$$

(5.17)

In this case, the Hamiltonian becomes dimensionless:

$$\frac{\partial^2}{\partial x'^2} = E'$$

(5.18)

One possible set of such units, which fulfill equation 5.17, is the Rydberg energy and the Bohr radius. In our case, the eigenvalue of $E'=-0.36$ found in the Comsol simulations is set equal to the Mn binding energy of -26 meV. This fixes the energy scaling in our calculations and consequently, also the spatial scaling in our calculations is also fixed by equation 5.17. The constants with which Comsol units are converted to SI units are $\beta=0.0725$ eV for energy and $\eta=0.725$ nm for distance.

**Mn in quantum well**

An InAs quantum well of 1.5 nm thick is defined in Comsol with a bandoffset of 310 meV in the valence band. The zero level of energy is at the bottom
of the quantum well. We take the same Luttinger parameters for inside and outside the quantum well. A Mn impurity in a quantum well is simulated by the Yukawa potential. The off-center Mn positions in the quantum well will clarify the situation of a Mn in an InAs/GaAs wetting layer which has an asymmetric spatial confinement due to exponential distribution of In atoms in the wetting layer. In figure 5.8, a cross section plot of the normalized probability density of the ground state for each Mn position is depicted. It can be seen that the ground state is localized around the impurity potential for the Mn at the center of the quantum well. The ground state is a doublet in contrast to the Mn in bulk case where a 4-fold degenerate ground state was found. When the Mn is localized closer to the barrier, the ground state is less localized and eventually the empty quantum well state, which has an eigenvalue of 67 meV, becomes the ground state. For the Mn close to the quantum well interface, an asymmetry in the z-direction is observed in the ground state feature. It is expected that a similar symmetry breaking will be observed in an InAs/GaAs wetting layer where an exponential In distribution is present because of In segregation in the growth direction [33].

The effect of Mn on the energy level of the quantum well ground state is depicted in figure 5.9 where the ground state energy level is plotted as a function of Mn position. As expected, the Mn impurity potential lowers the ground state energy level as it moves through the quantum well.
Figure 5.8: Cross section plots for the normalized probability density for Mn at different positions in the quantum well. The position of the Mn is clear from the localization of the probability density. The interfaces of the quantum well are indicated by the dashed lines. The cross section plot with $\lambda_{1,2} = 67$ meV belongs to an empty quantum well where the localization in the xy-plane is caused by the finite size of the box. The vertical direction coincides with the (001) direction.
Figure 5.9: The ground state energy level of the quantum well as a function of the Mn position. The vertical dashed lines indicate the perimeters of the quantum well. The horizontal dashed line indicates the ground state energy level of the empty quantum well.
Empty quantum dot

An empty quantum dot has been simulated to serve as a reference for the results with Mn acceptors in and near a quantum dot (see figure 5.10). An ellipsoidal quantum dot with a baselength of 10 nm and height of 2.8 nm is chosen. This shape and size fit to the quantum dots as observed in our sample in the next chapter (see figure 6.5). The size of the quantum dots in this sample is relatively small because of the low growth temperature of 320 °C.

As explained in the previous section, the quantum dot is simulated by defining a step potential of 310 meV between the matrix and the quantum dot. The proper strain distribution of the relaxed quantum dot is included in our calculations. As expected, the quantum dot states are sequentially states with an s-, p- and d-character. Only the 4 doublets with the lowest eigenvalues are depicted in figure 5.10; the ground state (s-like), the two p-like states (with a small energy splitting) and one of the d-like states. The p-like state with an eigenvalue of 180 meV shows an admixture of an s-like state at the top of the quantum dot which is caused by the broken symmetry in the z-direction. The same effect is probably responsible for the admixture of an s-like state on the d-like state. The eigenvalues and the probability densities for the empty quantum dot will be compared with cases where a Yukawa potential representing a Mn impurity is situated in or near the quantum dot.

Mn in and near a quantum dot

Calculations have been performed for different Mn positions in and near a quantum dot as depicted in figure 5.6. The resulting eigenvalues are given in table 5.2. Only the doublets with the 4 lowest eigenvalues are mentioned in table 5.2. Some of the calculated states are mainly localized at the Mn position and some of the calculated states show a clear resemblance with the states in an empty quantum dot. In table 5.2, the doublets which belong to a state which are mainly localized at the Mn ion are printed in bold.

In figures 5.12 to 5.20, the isosurface plots and cross section plots of the normalized probability density are shown for 4 doublets with the lowest eigenvalues at each Mn position. For Mn positions 5 and 9, doublets with higher eigenvalues are depicted to clarify the coupling between quantum dot states and Mn states.

Some general trends of the interaction between the Mn impurity potential and the quantum dot states are clearly visible in figures 5.12 to 5.20. For Mn inside the quantum dot, the effect of the Mn must be considered as a (strong) perturbation of the quantum dot states by the Mn impurity potential. The quantum dot states are strongly modified by the presence of the Mn both in terms of their wavefunction and their energy level. No additional states in the quantum dot are introduced by the Mn. For Mn outside of the quantum dot, coupling between the Mn states and the quantum dot states takes place. The coupling changes both the energy level and the wavefunction of the quantum dot states. The influence of Mn on the quantum dot states can be roughly classified in three effects:
Figure 5.10: Isosurfaces and cross sections in the (110) plane of the normalized probability density for different quantum dot states.
Table 5.2: Calculated eigenvalues in meV for the case of Mn in and near a quantum dot. The eigenvalues printed in bold belong to states which are mainly localized at the Mn ion. Positions 1 to 5 are located along the central axis of the quantum dot and position 6 to 9 are located along the diagonal through the quantum dot.

<table>
<thead>
<tr>
<th></th>
<th>Empty QD</th>
<th>Pos 1</th>
<th>Pos 2</th>
<th>Pos 3</th>
<th>Pos 4</th>
<th>Pos 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{1,2}$</td>
<td>111</td>
<td>72</td>
<td>11</td>
<td>81</td>
<td>109</td>
<td>111</td>
</tr>
<tr>
<td>$\lambda_{3,4}$</td>
<td>180</td>
<td>160</td>
<td>140</td>
<td>135</td>
<td>150</td>
<td>178</td>
</tr>
<tr>
<td>$\lambda_{5,6}$</td>
<td>182</td>
<td>177</td>
<td>174</td>
<td>179</td>
<td>181</td>
<td>182</td>
</tr>
<tr>
<td>$\lambda_{7,8}$</td>
<td>241</td>
<td>194</td>
<td>181</td>
<td>199</td>
<td>240</td>
<td>240</td>
</tr>
</tbody>
</table>

Energy shift:
The first effect concerns the energy shift of the quantum dot states. The influence of the Mn impurity potential on the energy level of quantum dot states can be illustrated by plotting the energy level for the 4 lowest quantum dot states as a function of the Mn position. This is shown in figure 5.11a for positions 1 to 5 and 5.11b for positions 6 to 9. Only quantum dot states which have a non-zero LDOS at the position of the Mn impurity potential interact with the Mn. The amount of interaction depends on the value of the LDOS of the unperturbed quantum dot state at the Mn position. For Mn positions 1 to 5, the Mn is moving along the central axis of the quantum dot. Figure 5.11a shows that the presence of Mn in or near the quantum dot is lowering the energy levels of the quantum dot states. The biggest effect of the Mn occurs on the s-like quantum dot ground state, which has the biggest LDOS at the central axis of the quantum dot. Also the p-like (E=180 meV) and the d-like (E=241 meV) empty quantum dot states show a drop in their energy level because of their non-zero LDOS at the central axis of the quantum dot. For Mn positions 6 to 9, similar effects are taking place. Because the Mn is moving along a diagonal of the quantum dot, all 4 of the confined states with the lowest eigenvalues are influenced by the Mn impurity potential because they have an LDOS at the diagonal of the quantum dot. Again the s-like ground state shows the biggest drop in energy because of its largest LDOS on the path of the Mn.

Localization:
The Mn impurity potential not only influences the energy levels of the quantum dot states but also their probability density. The second effect concerns the localization of states around the Mn impurity potential. As mentioned before, the Mn impurity potential must be considered as a perturbation to the quantum dot potential. The influence of the Mn impurity...
potential on the unperturbed quantum dot states depends on the LDOS value of these states at the Mn position. In figures 5.12 to 5.14, the cross section plots of the normalized probability densities show that for Mn at positions 1, 2 and 3, the ground state in the quantum dot is strongly localized around the Mn. Also the 1'st and the 3'rd excited states are strongly localized around the Mn. These are exactly those states which have a non-zero LDOS at the Mn positions 1, 2 and 3. The p-like state which has a node in the middle of the quantum dot barely reacts to the presence of the Mn. The cross section plots for Mn at position 6 show that all of the depicted states are localized around the Mn. The corresponding isosurface plots show that these states are empty quantum dot states which are strongly modified by the Mn impurity potential. Similar effects occur for Mn at position 7. The cross sections plots show that the states are mainly localized around the Mn. The ground state however also shows a significant presence inside the quantum dot. The isosurface plots again show that all of the depicted states are strongly modified quantum dot states. In literature, the localization of Mn inside a quantum dot is a controversial issue. A localized Mn state [131] and a Mn state which is similar to a quantum dot state [132] are both considered. Our calculations show that for Mn inside a quantum dot, the probability density of the ground state is localized around the Mn in favor of [131].

**Coupling:**
For Mn outside of the quantum dot, we speak of coupling between the Mn and the quantum dot states. The strength of the coupling depends on the distance between the Mn and the quantum dot and the energetic alignment between the two states. For Mn at positions 7 and 8 (see figures 5.18 and 5.19), the coupling of the quantum dot state with the Mn state happens at increasingly higher energies for an increasing Mn-quantum dot distance. The importance of the energetic alignment for coupling can be illustrated with the results for Mn at position 8 (see figure 5.19). The p-like state at 180 meV and the d-like state at 239 meV both have similar LDOS at close proximity (spatially) to the Mn. However, only the d-like state couples strongly with the Mn. This is explained by a nearly resonant energy alignment between the Mn in bulk GaAs and the d-like state of the empty quantum dot. Simulations where strain was turned off (not presented in this thesis) showed that the main mechanism for breaking of symmetry of the Mn wavefunction outside of the quantum dot is the coupling with the quantum dot states.
Figure 5.11: Energy level of the 4 confined states with the lowest eigenvalues as a function of the Mn position in a quantum dot (see figure 5.6). Mn positions 1 to 5 along the central axis are plotted in a) and Mn positions 6 to 9 along the diagonal are plotted in b).
Figure 5.12: Isosurfaces and cross sections in the (110) plane of the normalized probability density for Mn at position 1. The quantum dot has a baseline of 10 nm and a height of 2.8 nm.
Figure 5.13: Isosurfaces and cross sections in the (110) plane of the normalized probability density for Mn at position 2. The quantum dot has a baselength of 10 nm and a height of 2.8 nm.
Figure 5.14: Isosurfaces and cross sections in the (110) plane of the normalized probability density for Mn at position 3. The quantum dot has a baselength of 10 nm and a height of 2.8 nm.
Figure 5.15: Isosurfaces and cross sections in the (110) plane of the normalized probability density for Mn at position 4. The quantum dot has a baselength of 10 nm and a height of 2.8 nm.
Figure 5.16: Isosurfaces and cross sections in the (110) plane of the normalized probability density for Mn at position 5. The quantum dot has a baselength of 10 nm and a height of 2.8 nm.
Figure 5.17: Isosurfaces and cross sections in the (110) plane of the normalized probability density for Mn at position 6. The quantum dot has a baselength of 10 nm and a height of 2.8 nm.
Figure 5.18: Isosurfaces and cross sections in the (110) plane of the normalized probability density for Mn at position 7. The quantum dot has a baselength of 10 nm and a height of 2.8 nm.
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\[ \lambda_{1,2} = 111 \text{ meV} \]
\[ \lambda_{3,4} = 180 \text{ meV} \]
\[ \lambda_{5,6} = 181 \text{ meV} \]
\[ \lambda_{7,8} = 239 \text{ meV} \]

Figure 5.19: Isosurfaces and cross sections in the (110) plane of the normalized probability density for Mn at position 8. The quantum dot has a baselength of 10 nm and a height of 2.8 nm.
Figure 5.20: Isosurfaces and cross sections in the (110) plane of the normalized probability density for Mn at position 9. The quantum dot has a baselength of 10 nm and a height of 2.8 nm.
5.5 Conclusion

Simulations based on the effective mass approximation are performed for Mn impurities in bulk InAs, in and near an InAs/GaAs quantum well and in and near an InAs/GaAs quantum dot. The calculations for bulk InAs show that the characteristic bow tie shape, as observed in the (110) plane cleavage plane in X-STM experiments [135], is reproduced in our calculations. The Mn simulations in and near a quantum well show that the ground state is localized around the Mn position. The localization around the Mn decreases as the Mn moves away from the quantum well. The presence of a Mn in or near a quantum well causes a decrease in the energy level of the ground state.

Simulations of Mn in and near a quantum show that the Mn impurity potential acts as a (strong) perturbation on the quantum dot potential. There are three main effects of the Mn impurity potential on the empty quantum dot states. The first effect is the shift in energy level of the quantum dot states when a Mn is present in or near a quantum dot. This shift has been found to be more pronounced for empty quantum dot states which have a higher value of the LDOS at the position of the Mn impurity potential. The second effect concerns the localization of states for Mn inside the quantum dot. The ground state and some of the excited states have been found to show significant localization around the Mn for all positions of Mn inside the quantum dot. The amount of localization around the Mn position is proportional to the value of the LDOS of the empty quantum dot state at the position of the Mn impurity. Our results are in favor of the description of the Mn acceptor wavefunction inside a quantum dot as being localized around the Mn impurity itself as was suggested in [131]. The last effect concerns the coupling of Mn states to quantum dot states for the cases of Mn outside the quantum dot. States with a LDOS both at the Mn position and inside the quantum dot have been found. The coupling of the quantum dot states with the Mn state happens at increasingly higher energies for an increasing Mn-quantum dot distance. Resonant energy alignment between the Mn in bulk GaAs and the quantum dot state is an important factor for the coupling between the two states.
Chapter 6

Incorporation and Spectroscopy of Mn in and near InAs/GaAs Quantum Dots

In this chapter, the experimental analysis of Mn doped InAs/GaAs quantum dots by X-STM will be presented. First a short introduction is given to Mn doped quantum dots and the experiments that have been performed with them up to now. Segregation during growth and incorporation of Mn atoms inside InAs/GaAs quantum dots are investigated by means of X-STM on samples created at different growth temperatures. After the description of 3 sets of samples that have been investigated, the results on the incorporation, which are obtained with an RT-STM and an LT-STM (77 K), are presented\(^1\). Scanning Tunneling Spectroscopy (STS) measurements which allow for energy resolved imaging, will be discussed in the next part. An overview is given of the STS results in which the Mn acceptor wavefunction is mapped in different environments: Mn in bulk GaAs, Mn in the InAs/GaAs WL and Mn at different positions in and near InAs/GaAs quantum dots. We are especially interested in the observation of the Mn acceptor wavefunction inside a quantum dot. The X-STM measurements and the analysis were performed by me for this thesis.

6.1 Introduction to Mn Doped Quantum Dots

Diluted Magnetic Semiconductors (DMS’s) such as GaMnAs have attracted a lot of attention in the past decade because of their interesting magnetic properties and their applications in future devices. The origin of ferromagnetism in bulk GaMnAs is attributed to the p-d exchange between the electrons populating a half filled d-shell of the Mn atoms and the p-like valence band holes of the Mn acceptor. Therefore DMS nanostructures such as Mn doped InAs/GaAs quantum dot’s are expected to exhibit a combination of magnetic, electronic

\(^1\)Published in *APL 96* 042108 (2010)
and optical properties which makes them interesting as building blocks for spintronic devices. The most spectacular work in this field up to now concerns the analysis of quantum dots doped with a single magnetic impurity [129, 136]. The growth of magnetic II/VI quantum dots is well established in contrast to the situation for III/V magnetic quantum dots. Although several groups [137, 138, 139, 140] have reported on the growth of Mn doped InAs quantum dots in GaAs there is hardly any evidence that these Mn doped structures are truly magnetically active and that Mn is incorporated in the structures. Although many characterization techniques have been employed to study these magnetically doped dots the research is severely hampered by the lack of a proper technique to visualize the incorporation of Mn in InAs quantum dots. This lack of high resolution data often leads to a high degree of speculation in the interpretation. In the past, X-STM was used successfully to analyze individual Mn impurities in detail [120] and thus X-STM is an ideal tool to study the incorporation of Mn in InAs quantum dots. Such analysis should be able to resolve several controversies that exist in this young field of the growth of magnetic II/V quantum dots. It is for example still not clear whether Mn acts as a surfactant or as nucleation point for quantum dot formation [138, 139]. Also on other issues like the influence of Mn doping on PL emission of quantum dots, different experiments [141, 142, 143] have shown contradicting results. This makes an analysis of Mn doped quantum dots at atomic scale necessary and interesting. Several questions about the behavior of the Mn acceptor wavefunction inside the quantum dot still need to be answered. A Mn inside the quantum dot can either form localized states or can hybridize with the quantum dot states to form delocalized states. Both possibilities have been considered in literature [132, 131] and our theoretical analysis in chapter 5 have shown that the ground state of a Mn doped InAs/GaAs quantum dot is strongly localized around the Mn impurity in agreement with [131]. Using the STM in spectroscopy mode might provide more experimental insight since the spectroscopic measurements distinguish between different states with different energies.

6.2 Sample Description

The experiments have been performed on 3 sets of samples which will be called set A, B and C. They are all grown by MBE on (001) GaAs n-type substrates. The 2D-3D transition related to quantum dot formation was monitored with RHEED. For the first two sets, the growth temperature was measured carefully with a BandiT® [144] system. For the third set, the temperature was monitored by a thermocouple and a pyrometer.

Set A was designed to find a suitable growth procedure to incorporate as many Mn atoms as possible in the InAs quantum dots. This set consisted of 4 wafers in which the Mn has been incorporated in the InAs quantum dots in 4 different ways: Mn deposition on the GaAs surface prior to the growth of 2.1 ML of InAs, the growth of 0.1 ML of InMnAs followed by 2.0 ML of InAs, the growth of 0.1 ML of InMnAs sandwiched between two 1.0 ML of InAs layers and finally termination of the GaAs buffer layer with GaMnAs before 2.1 ML of InAs was deposited. The growth temperature for set A was put at T=450 °C to limit segregation and still obtain optically active quantum dots. The total amount of
deposited Mn in all four cases was about $10^{11}$ cm$^{-2}$ corresponding to 0.016%. The same MBE setup was used to grow set B which was designed to characterize the segregation behavior of Mn δ-layers in GaAs at temperatures of $T=350$ °C and $T=400$ °C.

Set C was grown in a different MBE setup where more extreme conditions were used to incorporate Mn in InAs quantum dots. In this sample 6 quantum dot layers were grown with intended amounts of Mn ranging from 0% to 5% at a further reduced growth temperature of $T=320$ °C. A total of 2.4 ML of InAs was deposited to form the quantum dot layer with the Mn cell open only during the deposition of the last 1.4 ML of InAs.

6.3 Mn Incorporation in InAs/GaAs Quantum Dots

In figure 6.1 a typical image of a sample from set A is shown. The quantum dot size and shape are poorly defined due to the low growth temperature. The Mn atoms in the image, recognizable by their characteristic bowtie shape [120], have segregated in the growth direction. Only occasionally, Mn atoms are observed in the wetting layer and no cases were found where a Mn atom is visible inside the quantum dot. A similar behavior was found in all the respective samples in set A. Thus irrespective of the growth procedure of the samples in set A, segregation of the Mn atoms dominates the Mn distribution and consequently limits the incorporation of Mn in the quantum dot layer.

Because of the high resolution of X-STM, we were able to study the Mn distribution in more detail. In figure 6.2, Mn distribution profiles are shown which were obtained on samples from set B. The profiles for the two different growth temperatures show a similar fast decay in the Mn distribution in the layers im-

![Figure 6.1: Typical X-STM image obtained on one of the samples from set A. The image is taken at $V=+1.5$ V and $I=32$ pA and size of the image is 43x79 nm.](image)
Immediately above the intended doping layer. This fast decay ends at about 40 nm away from the intended doping layer. In the interval ranging from 40 nm to 150 nm the Mn concentration is constant and finally drops to zero beyond this interval. The relatively fast decay is related to segregation of the deposited Mn as reported before [145]. The second part of the profile with the constant Mn concentration is probably caused by Mn desorption from the sample holders and walls of the growth chamber and subsequent deposition on the sample. This memory effect of the growth chamber stops after the growth of about 150 nm GaAs which corresponds to approximately 25 minutes growth time after the Mn cell was opened. It must be noted that the amount of Mn in this second part of the graph is below the SIMS detection limit [146]. Furthermore, the lower concentration of Mn at a growth temperature of $T=400 \, ^\circ\text{C}$ compared to a growth temperature of $T=350 \, ^\circ\text{C}$ is probably due to Mn desorption from the growth front which is more important at higher growth temperatures.

![Figure 6.2: Segregation graphs for different temperatures. The lines for T350 and T400 are only to guide the eye.](image)

In order to maximize the Mn incorporation in InAs quantum dots it is very important that segregation is minimized even further by decreasing the growth temperature. Furthermore, we have increased the doping concentration considerably. The low growth temperature is however a major problem for the quality of the grown quantum dots. Lower temperatures result in smaller less well defined quantum dots having a larger number of internal defects causing very poor optical properties. Nevertheless the samples of set C are grown at a temperature of 320 $^\circ\text{C}$. In this sample the total amount of deposited InAs is 2.4 ML and the intended Mn doping is increased stepwise up to 5%. In the samples of set C we observed that even at $T=320 \, ^\circ\text{C}$, segregation of Mn in the growth direction is very important. However because of the high amount of Mn deposited, the chance of finding a Mn atom inside a quantum dot is highly improved. In figure 6.3, a topographic image and the current image (which resembles a spatial derivative of the topography image) of a quantum dot with several Mn atoms in and around it are shown. Mn features are indicated by the characters A to E.
The Mn feature A represents an example of a single Mn atom in GaAs. The bowtie shape of the deep Mn acceptor in bulk GaAs with a binding energy of 113 meV is well understood [120] and is due to the charge distribution of the hole bound to the Mn acceptor. Similar features have been observed in Mn doped InAs [135] where Mn behaves as a shallow acceptor with a binding energy of about 28 meV. Feature B represents a Mn atom in the wetting layer and its shape seems to be marginally affected by the strain and confinement potential of the InGaAs wetting layer. Mn C is located exactly at the interface of the InAs quantum dot and the GaAs matrix. The contrast of a Mn atom at the interface shows part of the bowtie in the GaAs area whereas the contrast in the quantum dot is absent. It is not yet clear why the Mn contrast is absent in the quantum dot. We observed that the number of Mn atoms residing at the interface is far larger than the number of Mn atoms in the quantum dot. The high number of Mn atoms residing at the quantum dot interface has also been observed in other experiments [147]. We think that this is related to the formation energy for the incorporation of a Mn acceptor in an InAs nanostructure as calculated by a DFT method [148]. These calculations show that the formation energy also increases for smaller InAs nanocrystals (300→500 meV). We suggest that this formation energy drives Mn atoms towards the quantum dot interface. Next to segregation this process further complicates the Mn doping of quantum dots. The Mn features D and E are related to Mn acceptors.
in the quantum dot. Their contrast is strongly modified compared to Mn in GaAs. Several mechanisms such as strain [120], potential confinement and position near to the cleaved surface [149] are expected to have an impact on the wavefunction of the Mn acceptor. Unfortunately within a quantum dot all these mechanisms play a complicated role and thus it is very difficult to explain at the moment why we see these specific Mn features in the dot. The same applies for the missing part of wavefunction in the dot for Mn atoms at the InAs/GaAs interface of the dot. Spectroscopy measurements, which will be presented in the next part of this thesis, will provide more insight in the behavior of Mn in and near quantum dots.

We thus have shown that Mn segregation strongly limits the incorporation of Mn atoms in a quantum dot. Even at a low growth temperature of T=320°C segregation still dominates the Mn distribution. However in strongly doped structures we have observed large numbers of Mn acceptors present in the wetting layer and a limited number of Mn atoms in a quantum dot. Mn incorporation in quantum dots is possibly further complicated by strain induced self-purification of the quantum dot.

6.4 Spectroscopic Analysis of Mn in and near a Quantum Dot

For the investigation of both nanostructures and single impurities, STM is usually operated in the constant current mode. As was explained before in section 2.5, for constant current mode, the tunneling current stems from a range of states available for tunneling. All of these states contribute to the tunneling current and thus this technique is not capable of addressing individual states appearing at different energies. This limitation of constant current mode is illustrated in figure 6.3. The Mn acceptor indicated with C is located exactly at the interface of the quantum dot. As can be seen in the topography image in figure 6.3a, no details of the Mn wavefunction can be seen inside the quantum dot. Even the current image in figure 6.3b, which can be considered as the spatial derivative of the topography image, does not show any details about the part of the Mn wavefunction inside the quantum dot. One possible explanation is that the tunneling to the quantum dot states is so dominant in comparison with tunneling to the Mn state, that the Mn wavefunction inside the quantum dot is difficult to see. Scanning Tunneling Spectroscopy measurements which resolve the energy scale could resolve this issue. The Mn doped InAs/GaAs quantum dot sample used in this part of the thesis is the same as the strongly Mn doped sample described in the previous part of this chapter.

An appropriate area with relatively large quantum dots and high Mn concentration was chosen for the spectroscopic measurements. Figure 6.4a shows this area which was scanned at a negative voltage. At a voltage of -2.10 V, the Mn atoms in this area are invisible except the ones that are 3-4 layers below the cleavage surface. These Mn atoms look like round, bright features as was reported earlier [119]. Figure 6.4b shows the current image of the same measurements where it can be seen more clearly that the Mn atoms close to the surface are visible.
Figure 6.4: Topography (a) and current (b) images taken at -2.10 V showing the area’s where STS measurements have been performed. Images c) and d) show the topography and current images taken at a voltage of +1.45 V. The Mn acceptors are visible in their ionized state in images a) and b) and in their neutral state in images c) and d).

In figure 6.4c, the same area is measured at a positive voltage of +1.45 V. The wavefunctions of the Mn acceptors in their neutral state are visible. Especially the presence of Mn atoms near the quantum dots makes this area very interesting for spectroscopy measurements. The baselength of the cleaved quantum dots in this sample, which is grown at 320 °C, is approximately 7 nm. These dots are small in comparison to dots grown at higher temperatures.

The areas indicated by the dashed squares in figure 6.4 have been analyzed by spectroscopy measurements. The stabilization setpoint settings for these spectroscopy measurements are respectively -1.8 V and 3.0 nA for Area 1 and -2.1 V and 3.0 nA for Area 2 which is close to the voltage settings for the topography measurements shown in figure 6.4. At these setpoints, the topography image shows minor contrast for Mn atoms except for those close to the surface indicating that some topography cross talk in the STS measurements can be expected in these cases. However we will neglect this issue in the further course of this thesis.

Figure 6.5 shows that many Mn atoms are visible in both areas where the spectroscopy measurements have been performed. We group them as Mn atoms in bulk GaAs (B), in the InAs/GaAs wetting layer (W), near the quantum dots (N) and inside quantum dots (I).
The previously reported properties on Mn in bulk GaAs are reproduced in our measurements. First of all, we recognize the bow tie shape in bulk GaAs \cite{119} for the Mn atoms indexed with B1-B5 which are located in a bulk like environment away from quantum dots and the wetting layer. Furthermore, the previously observed depth dependent asymmetry of the bow tie shape is also present in our measurements as can be seen in figures 6.4 and 6.5 \cite{121}. The multiple peak structure of each Mn acceptor in the dI/dV measurements at positive voltages was also present in our measurements \cite{122}.

In the dI/dV measurements, the Mn acceptors in bulk GaAs appear sequentially with different features. Going through the dI_{V}(x,y)/dV images from -1.8 V to +1.7 V for the measurement in Area 1, the Mn acceptors close to the surface (B2-B4 which are about 4 to 5 MLs deep below the surface) show a feature at negative voltages which we suggest stems from the Mn resonance deep in the valence band.

In figure 6.6, the dI_{V}(x,y)/dV image taken at -1.11 V, shows a weak contrast
Figure 6.6: $dI/V(x,y)/dV$ images of Mn in bulk GaAs in Area 1 at different voltages. The overview at the bottom shows the appearance of each feature as a function of the bias voltage. The dark areas indicate the voltages at which a dark contrast is observed.

due to the Mn resonance in the valence band for Mn acceptors B2, B3 and B4. Only B2 will be treated in detail. The tunneling process in this situation corresponds to the situation depicted in figure 6.7c where the Mn resonance, lying in the valence band [117] contributes most strongly to the tunneling current.

The next feature of the Mn acceptors becomes visible at -0.31 V. At this voltage, the Mn acceptors are imaged in their ionized state. The main contribution to the contrast in the tunneling current stems from the electrons extracted from the valence band which is influenced by the Coulomb field of the Mn ion. The Mn acceptors are visible as roundish bright protrusions as reported before [119]. In figure 6.6, the $dI/V(x,y)/dV$ image at -0.31 V also shows a dark contrast for Mn B1 which we do not understand yet. Figure 6.7b shows the alignment and band bending for this situation.

When we increase the voltage in the $dI/V(x,y)/dV$ data further, we observe the familiar bow tie shape of the Mn acceptors at voltages of around -0.15 V. At this voltage, the Mn acceptors are ionized (thus available for filled state tunneling) and the Mn contrast dominates over the Coulomb contrast seen at -0.31 V (see figure 6.7b).

Finally, the Mn state is imaged at positive voltages. At +0.38 V tunneling into the neutral Mn acceptor state dominates the image. The characteristic bow tie shape of the Mn acceptor is well visible. In figure 6.7, this corresponds to the tunneling mechanism depicted in image e: the Mn is in its neutral state and
tunneling occurs into the hole bound to the Mn core. At the bottom of figure 6.6, an overview is given of the appearance of Mn acceptors B1 and B2 at different voltages. A dark contrast is observed sometimes in the $dI/dV(x,y)$ images which will not be discussed further.

Figure 6.7: Different tunneling mechanisms for a Mn acceptor in a p-type semiconductor. a): At low negative voltages, the Mn is in its neutral state and tunneling occurs from the top of the VB. b): At high negative voltages, the Mn acceptor is ionized and causes a current in two ways: via the acceptor itself and via an increased amount of VB states available for tunneling. c): At even larger negative voltages, the main effect of the ionized acceptor is the effect of the Coulomb field on the VB. d): Usually, the flat band condition is reached at positive voltages for p-type semiconductors. The ionization of the acceptor depends on the position of the local Fermi level under the tip. e) At positive voltages, the top of VB is pulled above the Fermi-level of the sample and a tunneling current will appear due to injection of electrons in the empty state of Mn because it is in a neutral state. e): At higher positive voltages, also tunneling to the CB becomes possible.
Mn in InGaAs Wetting Layer

Next we discuss Mn acceptors in the InGaAs wetting layer. As in the case for Mn acceptors in bulk GaAs, the appearance of the Mn acceptors in the InGaAs WL depends on the charge state of the Mn which in turn depends on the bias voltage between tip and sample. Again we go through the $dI/dV$ measurements starting with large negative voltages.

The first features appearing at large negative voltages are rings of ionization which are not observed for the Mn acceptors in bulk GaAs. Similar rings have been observed before for Si donors in GaAs [27] and Mn in InAs [135]. These rings are visible in the $dI(x,y)/dV$ images at voltages where the Mn level is locally pulled down below the Fermi level by which it is ionized. The ionization of the Mn acceptor depends on the applied voltage and the spatial distance of the tip to the Mn acceptor. Upon ionization, the Coulomb field of the ionized acceptor causes an increase in the tunneling current as explained in figure 6.7a and 6.7b. At the moment of ionization, an increased $dI/dV$ signal is observed. For a fixed bias voltage, ionization happens at a fixed lateral tip-acceptor distance which in the case of a symmetric tip results in a ring in the spatial $dI(x,y)/dV$ map. An image of the ionization ring around Mn acceptor W3 is shown in figure 6.8, in the $dI(x,y)/dV$ image taken at -1.30 V. The voltage at which the ring closes is the voltage at which the impurities can no longer be pulled below the

![Image of Mn ionization rings](image-url)

**Figure 6.8:** $dI(x,y)/dV$ images of Mn W3 in InGaAs wetting layer in Area 2 at different voltages. The overview at the bottom shows the appearance of each feature as a function of the bias voltage. The dark areas indicate the voltages at which a dark contrast is observed.
Fermi level with the applied voltage even with the tip right on top of the acceptor. This voltage is related to the energetic position of an impurity with respect to the Fermi level in the sample. Thus for acceptors deeper in the bandgap, a more negative voltage is found at which the ring closes.

In figure 6.9a, the threshold voltage at which the rings close are plotted for different Mn acceptors in the wetting layer. Also the Mn acceptors inside a quantum dot (I1 and I2) show clear ionization rings. The energetic position of the Mn acceptor state in bulk GaAs is 113 meV above the valence band edge. It has been reported that for a quantum well the Mn acceptor level is positioned above the valence band edge [150] with an energy separation of 107 meV between the Mn level and the hole ground state in the quantum well. What happens in a wetting layer is yet unclear but will depend on the local In concentration which shows an exponential decay in the growth direction due to segregation and local variations in the xy-plane. The order in which the rings close does not show a relationship with the depth of the different Mn acceptors below the cleaved surface as reported for Si in bulk GaAs [151]. Typically, the Mn acceptor energy level changes in the order of a few percent as a function of depth below the cleaved surface [122]. However in the case of Mn in the InGaAs wetting layer, the variation seems to be larger than a few percent as can be seen in figure 6.9. We think that this large variation in the energetic position of the Mn acceptor is caused by local inhomogeneity of the In concentration in the InGaAs wetting layer.

![Figure 6.9](image)

**Figure 6.9:** a) Voltages at which the ionization ring closes for different Mn acceptors in the wetting layer (W) and the quantum dot (I). b) Schematic dependence of the Mn acceptor energy level as a function of its position in and near a quantum dot and a wetting layer. In [131], it was assumed that the Mn level is lower in energy than the unperturbed quantum dot ground state. In [150], optical spectroscopy on Mn doped quantum wells showed that the Mn energy level is in the gap.
After the closing of the ionization ring, the Mn acceptor level is positioned above the Fermi level and it is not available anymore for tunneling in filled states imaging. However, the Mn acceptor still shows a feature in the $dI/V(x,y)/dV$ image at negative voltages after the ring has closed as can be seen in figure 6.8, see for instance the $dI/V(x,y)/dV$ image taken at -0.51 V. We attribute this feature to the Mn excited states which can be observed by filled state imaging.

At positive sample voltages, Mn acceptors in the WL are imaged in their neutral state. Figure 6.8 shows the $dI/V(x,y)/dV$ image taken at +0.57 V. W3 appears as an atomically resolved structure instead of the more smooth envelope we observe for Mn in bulk GaAs deeper below the surface. Just like in bulk GaAs, the appearance of the Mn acceptors in the wetting layer in their neutral state depends on the depth below the cleaved surface. This can be seen in figure 6.5 where the $I/V(x,y)$ image at positive voltages is clearly showing the different shapes for different depths. Mn acceptors close to the surface have a more atomically resolved contrast whereas the deeper Mn acceptors are more smooth in their appearance. Just like in bulk GaAs, they have an asymmetric shape in the 001 direction with a stronger lower part compared to the upper part. W3 and W4 belong to this class of Mn acceptors in the wetting layer. W1 and W5 are Mn acceptors in the wetting layer which lie deeper below the cleavage surface and they have the shape of an atomically resolved cross which is more symmetric. Mn acceptors even deeper below the surface like W6, W7 and W8 show a smooth envelope like the bow tie in bulk.

In some cases, the features seen at positive voltages are also visible at negative voltages and they remain visible when the voltage is swept across 0 V during the spectroscopy measurement. We discuss two possible mechanisms for this:

1): At negative voltages, the Mn acceptor state can be positioned above the Fermi level of the sample (i.e. neutral Mn) and thus it is not available for tunneling in filled states imaging. However, other states related to Mn like resonant states in the VB or excited states caused by the presence of Mn are still below the Fermi level of the sample and they are available for filled states tunneling at negative sample voltages. At positive voltages, tunneling to the neutral Mn state takes place. In this situation, the Mn feature will be visible both at negative and at positive voltages.

2): If at 0 V, the Fermi level of the tip, the Mn acceptor state and the Fermi level of the sample are all aligned, then the Mn acceptor state is available for tunneling both in filled state imaging and empty state imaging at all voltages. We consider this mechanism as highly improbable.

**Mn near Quantum Dots**

Next, Mn acceptors close to quantum dots will be discussed. In figure 6.5, two examples are indicated with N1 and N2. Case N1 is the most frequently observed type of Mn at or close to the quantum dot interface. Mn atoms have a tendency to end up at the quantum dot interface during growth because of segregation [152, 147] and self-purification of quantum dots. Calculations have shown that there is a formation energy involved in the incorporation of Mn near the center of InAs/GaAs nanocrystals [148] and thus Mn atoms tend to go to the quantum dot exterior during the quantum dot formation process where they
stay during the capping process. The spectroscopy data of Mn N1 shows that at negative voltages of around -0.27 V, N1 looks like a complete bow tie which starts to take the form of a half bow tie at around -0.20 V with a weaker spatially more extended part inside the quantum dot. This is illustrated by the $\text{d}I/\text{d}V_{(x,y)}$ images in figure 6.10. We suggest that around this voltage of -0.20 V, tunneling to a different state starts to take place. This state is composed of a part that is localized at the Mn position and a part inside the quantum dot which is spatially more extended. The interaction of the Mn states with the quantum dot states has been treated theoretically in the previous chapter within the effective mass approximation. It was shown that Mn acceptor states outside the quantum dot can couple with the quantum dot states. The ground state for the case with Mn at position 7 in figure 5.18 shows a probability density which is concentrated on the Mn but also has a spatially extended part leaking into the quantum dot. The excited states show features which are localized at the Mn position. This situation probably corresponds to the case of Mn N1 where we suggest that a transition from an excited state imaging to the ground state imaging takes place at a sample voltage of around -0.20 V. A comparison of the experimental image of the ground state and the result of effective mass calculations is shown in figure 6.11. Mn acceptor N2 is located at the upper right corner of a quantum dot. This situation is similar to a case that was investigated before in topography mode [120]. At positive tunnel voltages, a deformation of the Mn acceptor feature was observed which was attributed to strain induced by the quantum dot. In the STS measurements presented here however, we observe that the Mn starts with a symmetric bow tie shape at negative voltages. At around -0.2 V, it becomes asymmetric as was reported before in [120] where the asymmetric shape was attributed to influence of strain. In our case however, strain can not be the reason for the breaking of symmetry since the strain distribution should not depend on the applied voltage. Instead we suggest that in this case the Mn acceptor wavefunction is coupling with a quantum dot hole state as observed for Mn N1. This has also been observed in the simulations for Mn at position 7 in figure 5.18 in the previous chapter. The transition from a symmetric to an asymmetric feature is shown in figure 6.10 where the $\text{d}I_{(x,y)}/\text{d}V$ images of -0.27 V and -0.13 V are plotted. At positive voltages, Mn acceptor N2 again shows up as an asymmetric feature. Coupling is thus a mechanism for symmetry breaking in addition to earlier reports where a Mn wavefunction deformation was attributed to strain [120]. Just like for the case of Mn N1, the effective mass calculation for Mn at position 7 in figure 5.18 is also applicable for this case of Mn N2 showing a clear similarity between the experiment and the simulation as can be seen in figure 6.11. The STM images of both Mn acceptors N1 and N2 show that the majority of their LDOS is located outside of the quantum dot and only a weak presence inside the quantum dot is observed due to coupling to the quantum dot states.
Figure 6.10: \(dI/V(x,y)/dV\) images of Mn acceptors N1 and N2 near a quantum dot in Area 1 at different voltages. The overview at the bottom shows the appearance of each feature as a function of the bias voltage. The dark areas indicate the voltages at which a dark contrast is observed.
Figure 6.11: a) $dI/(x,y)/dV$ image of Mn N1 and N2 near a quantum dot at -0.13 V. It is clear that probably coupling is taking place between the Mn acceptor holes and the quantum dot hole states. b) similar results were obtained with effective mass calculations for an off-center Mn.
**Mn inside quantum dots**

Finally, Mn acceptors inside a quantum dot are discussed. Two Mn atoms indicated by I1 and I2 in figure 6.5, which are clearly located inside a quantum dot, are investigated in detail. Their locations inside the quantum dots are shown in figure 6.5. Mn I1 is located at a central position inside the quantum dot on the right. This Mn is probably located close to the cleavage surface because there is a high degree of similarity between Mn I1 and Mn W3 and W4 in the wetting layer which were considered as being close to the cleaved surface. At negative voltages, a peculiar bright shape is visible in the dI/dV(x,y)/dV image taken at -0.48 V. At this voltage, the Mn looks like a small triangle which points in the 001 direction. This feature of the Mn is probably related to the ionized state of the Mn inside the quantum dot since it appears in the voltage range where an ionization circle is observed around this Mn (see figure 6.9a). The observed shape belongs to the hole that was being occupied by the electron before it was injected into the tip.

When we increase the voltage, this feature associated with the ionized Mn disappears at about -0.4 V. At -0.2 V, another more symmetric shape of the Mn appears which remains visible up to positive voltages without any interruption. In figure 6.12, this feature is depicted in the dI/dV(x,y)/dV image taken at +0.31 V. At negative voltages, the observed feature is probably caused by excited states of Mn inside the quantum dot such as the strongly modified quantum dot p and d like states that were observed in the effective mass calculations in the previous chapter for Mn at position 2 at the center of the quantum dot (see figure 5.13). At positive voltages we attribute the observed feature to the wavefunction of the neutral ground state of the Mn acceptor inside the quantum dot. Most importantly, the observed Mn states inside the quantum dot are well localized as was shown by the effective mass calculations in the previous chapter. This also solves the controversy about the nature of the Mn state inside a quantum dot. In literature, both possibilities of a localized and a delocalized Mn state are considered [132, 131]. The assumed localized Mn state is considered to have the character of Mn impurities in bulk [131] while the assumption of a delocalized [132] Mn state considers the Mn impurity as a perturbation to the quantum dot states. Thus the ground state of the Mn in an InAs/GaAs quantum dot still has the symmetry of the quantum dot state according to [132]. We show here that the Mn state inside the quantum dot has a localized feature. We discuss 2 arguments that are involved in the understanding of the observed shape:

1): At positive voltages, the shape is very similar to the shape of Mn acceptors in the wetting layer as can be seen for W3 and W4 in figure 6.5. This indicates that confinement in the z-direction might play a substantial role in the resulting shape.

2): Mn acceptors in bulk GaAs close to the surface have a clearly broken symmetry in the (001) direction due to surface induced strain [121]. A similar effect of the surface on the Mn acceptor inside the quantum dot should contribute to the observed shape.

We expect that all mechanisms contribute to the observed shape but we can not determine at the moment which one dominates.

Mn I2 is located near the edge of the quantum dot. The spectroscopy data is presented in figure 6.12. This Mn acceptor is visible at negative voltages in the
Figure 6.12: $dI/V(x,y)/dV$ images of Mn acceptors I1 and I2 in a quantum dot in Area 1 at different voltages. The overview at the bottom shows the appearance of each feature as a function of the bias voltage. The dark areas indicate the voltages at which a dark contrast is observed.

d$I$/d$V$ data, for instance in the image taken at -0.25 V. At these voltages, it appears in the normal bow tie shape which we also observe for the Mn acceptors in bulk GaAs deep below the cleavage surface. When we increase the voltage, the feature disappears at a negative voltage of about -0.1 V. The question is of course which state is visible at this negative voltages since this Mn acceptor shows an ionization ring which closes at around -1.5 V (see figure 6.9a) which means that the Mn ground state itself is not available for tunneling at negative voltages of about -0.2 V since that state is already above the Fermi level of the sample. This suggests that we observe a Mn excited state inside the quantum dot. As was shown by the effective mass calculations for Mn at position 6 (see figure 5.17), the first excited state is a strongly modified quantum dot p-like state which becomes strongly localized at the Mn position.

At positive voltages, Mn I2 shows up with a completely different feature. This is shown in the $dI/V(x,y)/dV$ image in figure 6.12 which is taken at +0.49 V. At this voltage, the Mn acceptor is imaged in its neutral state and the feature looks like a big cross which resembles the Mn acceptors in the InGaAs WL (see Mn W1,
W5 and W6 in figure 6.5). Interestingly, the arm of the cross that sticks out of the quantum dot has a much weaker contrast than the other arms of the cross suggesting that the confinement inside the quantum dot is playing a role in the observed feature.

6.5 Discussion and Conclusion

X-STM measurements in topography and spectroscopy mode have been performed on Mn doped InAs/GaAs quantum dots. The incorporation and behavior of Mn in and near quantum dots has been investigated. We focus on 4 major conclusions of the work:

- **Incorporation of Mn in quantum dots:**
  We have shown that Mn segregation strongly limits the incorporation of Mn atoms in a quantum dot. Even at a low growth temperature of $T=320^\circ C$ segregation dominates the Mn distribution. However in heavily doped structures we do observe large numbers of Mn acceptors in the wetting layer and a limited number of Mn atoms inside the quantum dots. Mn incorporation in quantum dots is possibly further complicated by strain induced self purification by which the Mn is pushed during growth towards the upper InAs/GaAs interface of the quantum dot.

- **Coupling of Mn and quantum dot related states:**
  For a Mn acceptor near a quantum dot along the diagonal (Mn N2), coupling between the Mn states and the quantum dot states has been observed. The coupling depends on the energy level of the different Mn states. A relatively unperturbed Mn state, obtained at large negative voltages, is observed in the $dI(x,y)/dV$ images followed by Mn states observed at less negative voltages which show a larger coupling with the quantum dot states. At positive voltages, only Mn states which show a coupling with the quantum dot states are observed. The localized Mn states visible at large negative voltages are the excited Mn states and the delocalized Mn state observed at voltages closer to zero is the Mn ground state. The ground state is also observed at positive voltages. A similar case of Mn near the quantum dot interface along the diagonal was simulated in the previous chapter (Mn at position 7). It was shown that the Mn impurity near the interface has excited states which are more localized than the ground state which shows coupling with the quantum dot s-like ground state. Thus our spectroscopy measurements, which show a delocalized Mn ground state due to coupling with quantum dot states and more localized Mn excited states, are in excellent agreement with our theoretical modeling.

For Mn N2, we observe a voltage depending symmetry breaking. We observe a finite LDOS in the quantum dot at the moment of symmetry breaking suggesting that coupling is the source of symmetry breaking. Thus we observe a mechanism for symmetry breaking in addition to previous results that suggested strain as the cause of symmetry breaking \[120\].
• **Half bow-tie shape of the Mn state at the quantum dot interface:**
  For a Mn impurity located at the quantum dot interface (Mn N1), breaking of symmetry at specific voltages has been observed in the \( dI(x,y)/dV \) images. At negative voltages, the Mn appears as a complete bow-tie shape and it takes the form of a half bow-tie at less negative voltages. At positive voltages, only a half bow-tie shape is visible. From the spectroscopy measurements, we consider this half bow-tie shape, which shows coupling with the quantum dot ground state, as the Mn ground state. There is a strong LDOS at the position of the Mn and a much weaker LDOS inside the quantum dot. Just like Mn N2, this case is supported by the effective mass simulations of Mn at position 7 along the diagonal of the quantum dot. Thus the characteristic half bow-tie shape that we see in many experiments for the Mn at the interface, is due to coupling with the quantum dot states.

• **Strong localization of Mn wavefunction inside the quantum dot:**
  For Mn inside a quantum dot, the spectroscopy measurements show a contrast which is localized around the Mn impurity, having a similar size as the contrast for Mn acceptors in bulk GaAs. For Mn in the middle of the quantum dot, at large negative voltages, the ground state is imaged in its ionized state. At smaller negative voltages the excited state is imaged because at these voltages the ground state is shifted above the Fermi level (closing of the ionization ring). At positive voltages the ground state of the Mn is observed. In all cases, we observe a strong localization at the Mn impurity site. These experimental observations resolve a controversy about the nature of the Mn state in a quantum dot discussed in two previous studies [131, 132]. In the first study [131], the Mn LDOS in a quantum dot is considered to be concentrated around the Mn with similar spatial size as in bulk GaAs or InAs. In the second study [132] however, the Mn impurity is considered as a weak perturbation to the quantum dot attractive potential and thus the Mn ground state is assumed to have the character of the unperturbed quantum dot ground state. This means that the state related to Mn should be spatially more extended inside the quantum dot. We show here that the localization of the Mn state inside the quantum dot is in agreement with the first study [131]. Localization of the Mn is also in agreement with the analysis of the photoluminescence of single Mn doped InAs/GaAs quantum dots performed by Kudelski [129] and Van Bree [130]. In these studies [129, 130], the localization of the Mn wavefunction at the Mn impurity site was used to support the assumption that the Mn complex can be treated as a single spin object consisting of the Mn d-electrons spin (5/2) and Mn acceptor hole spin (3/2).
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Abstract

In this thesis, a Cross Sectional Scanning Tunneling Microscope (X-STM) is used to investigate nanostructures in III-V semiconductors and single Mn impurities in bulk GaAs. The atomic resolution which can be achieved with X-STM makes it possible to link structural properties of nanostructures to growth conditions and to properties obtained in other experiments. Furthermore, X-STM is very well suited to investigate the effect of a quantum dot on single Mn acceptors both in terms of potential confinement and in terms of strain.

In recent years, quantum dots have emerged as essential components of new generation optical devices. The use of Sb has proven to be a way of tuning the emission wavelength of quantum dots. X-STM measurements have been performed on samples with InAs/GaAs and InAs/InP quantum dots where Sb has been used in different ways during capping to tune their emission wavelength. We have found that Sb can act as a strain reducing layer for the InAs/GaAs quantum dots if it is used in the capping layer in the form of GaAsSb which results in reduced quantum dot decomposition during capping. The same reduction of quantum dot decomposition has been achieved by soaking the quantum dots with Sb before capping. In this case the Sb has been found to act as a surfactant which limits the in plane mass transport of material from the quantum dots. Similar results have been obtained for InAs/InP (311B) quantum dots.

Another subject that has been investigated with X-STM is the incorporation and the behavior of single Mn acceptors in and around InAs/GaAs quantum dots. Single Mn doped quantum dots are potential building blocks for future spintronic devices in which electric, magnetic and optical properties can be utilized. X-STM measurements have shown that segregation of Mn during growth makes it very difficult to incorporate Mn in InAs/GaAs quantum dots. Furthermore, Mn acceptors in and around the quantum dots have been investigated with Scanning Tunneling Spectroscopy (STS). For Mn outside the quantum dots, we have found that the wavefunction is strongly influenced by coupling between the quantum dot states and the Mn states. There is a much smaller influence of strain field of the quantum dot. For Mn atoms inside the quantum dot, the shape seems to be determined by the potential confinement.
List of Publications

   *Shape and size control of InAs/InP (113)B quantum dots by Sb deposition during the capping procedure*
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   *Shape control of QDs studied by cross-sectional scanning tunneling microscopy*

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4. Bozkurt, M., Grant, V.A., Ulloa Herrero, J.M., Campion, R.P., Foxon, C.T., Marega, E., Salamo, G.J., Koenraad, P.M.
   *Atomic scale characterization of Mn doped InAs/GaAs quantum dots*

5. Ulloa Herrero, J.M., Gargallo-Caballero, R., Bozkurt, M., Moral, M. del, Guzman, A., Koenraad, P.M., Hierro, A.
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PAPERS IN PROGRESS

18. J. M. Ulloa, M. del Moral, M. Bozkurt, P. M. Koenraad, A. Guzmán, and A. Hierro
Analysis of the modified optical properties of GaAs1-xSbx-capped InAs/GaAs quantum dots
To be submitted

Scanning Tunneling Spectroscopy and Effective Mass Calculations of Mn acceptors in and around InAs/GaAs QDs
In preparation

20. M. Bozkurt, P.J. van Veldhoven, R. Nötzel and P.M. Koenraad
Effect of a thin GaAs layer on the formation of InAs/InP QDs
In preparation

21. M. Bozkurt, P. Studer, B. Bryant, S. Schofield, N. Curson, C. Hirjibehedin and P.M. Koenraad
X-STM Observation of Mn acceptors in GaAs in the presence of a B-field
In preparation

22. S.J.C. Mauger, M. Bozkurt, P.M. Koenraad, A.D. Giddings, R.P. Campion, and B.L. Gallagher
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PAPERS DURING TRAINEESHIP (not part of this thesis)

23. S.M. Orbons, L. van Dijk, M. Bozkurt, P.N. Johnston, P. Reichart, D.N. Jamieson
   *Focused ion beam machined nanostructures depth profiled by macrochanneling ion beam analysis*

24. Leon van Dijk, Murat Bozkurt, Andrew Alves, Peter N. Johnston, Tim J. Davis, Patrick Reichart, David N. Jamieson
   *Macrochanneling: Characterisation of nano-structures by ion beam analysis*
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Curriculum vitae

Murat Bozkurt, born 27 July 1980 in Gaziantep

2007-2011:

Ph.D. project, Atomic Scale Study of Intrinsic and Mn-Doped Quantum Dots in III-V Semiconductors.
Photonics and Semiconductor Nanophysics, Department of Applied Physics, Eindhoven University of Technology, promotor Prof. Dr. P. M. Koenraad.

1999-2007:

Master study in Applied Physics, Eindhoven University of Technology.

Master project: STARS Overlay Measurements on Processed BOOH Wafers and RCWA Simulations.
ASML & Photonics and Semiconductor Nanophysics, Department of Applied Physics, Eindhoven University of Technology, supervisors: Prof. Dr. P.M. Koenraad, Dr. M. van der Schaar, Dr. M. Tenner and Dr. A. den Boef.

Externship: Ion Beam Micromachining with PMMA and Imaging of Microstructures using RBS.
Royal Melbourne Institute of Technology & University of Melbourne, supervisors: Dr. L.J. van IJzendoorn, Prof. D.N. Jamieson and Prof. P.N. Johnston.

Internship: Absorptie en Polarisatie Spectroscopie met Fe-atomen in een Fe-He Holle Kathode Ontlading.
Experimental Atomic Physics and Quantum Electronics, Department of Applied Physics, Eindhoven University of Technology, supervisors: Prof. Dr. H.C.W. Beijerinck and Prof. Dr. K.A.H. van Leeuwen.

1993-1999:

Gymnasium, Kruisherken Kollege in Uden and Mondriaan Lyceum in Amsterdam