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Atomically precise formation of Mn doped semiconductor nanostructures

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus prof.dr.ir. F.P.T. Baaijens, voor een commissie aangewezen door het College voor Promoties, in het openbaar te verdedigen op woensdag 15 februari 2016 om 16:00 uur

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Chapter 1

Introduction

Over the last 40 years the importance of systems with a size in the nanometre scale has increased enormously. The field that studies the properties and the formation of these nanostructures is called nanotechnology, a multidisciplinary field where solid state physics, surface science, material science and chemistry are connected with each other. The interest in this field is motivated by the intriguing new properties observed in these nanostructures, often originating from quantum mechanical phenomena or from surface effects, which become more relevant when the structures are small.

The techniques used to create nanostructures can be classified in two different families: the bottom-up and the top-down approach. With the bottom-up approach nanostructures are created starting from a group of small building blocks, which could be atoms or molecules. Many bottom-up processes rely on the interaction between these small units to create a larger and more complex structure preferably through a self-organized process. This process is commonly called self-assembly and is observed in many natural processes. The advantages of this approach are that it does not require advanced techniques to control precisely the exact assembly of the nanostructures, but the system spontaneously evolves towards the formation of nanostructures. This make this approach scalable and potentially cheap. On the other hand the properties of the obtained nanostructures depend on the interaction between the building blocks, which can be difficult to control and expose the system to statistical variation in size and properties. The top down approach instead uses external stimuli to modify a large system and create a nanostructure. In this approach the nanostructures are created with more control on their structure, but the control is limited by the length scale at which the external stimulus can be applied. Moreover the scalability of this process depends on the characteristic of the technique used to define the structure.

Semiconductor nanostructures are a particularly interesting system. When the size of these nanostructures is in the range of few nanometres, quantum confinement effects can be observed. This effect has a crucial influence on the electronic properties of the material, causing a redistribution of the semiconductor density of states. The electronic properties of the nanostructures become dependent on
its size and morphology, which allows scientists to change the property of the material by controlling the nanostructures’ structural properties. Thanks to their versatile properties semiconductor nanostructures have many interesting applications, for example in the fields of nano-optoelectronics, nanophotonics, quantum computation and energy conversion. The connection between electronic properties and morphology made the control on the structural properties of semiconductor nanostructures a fascinating and important challenge, which caused the flourishing of advanced microscopy techniques. Scanning Tunnel Microscopy (STM) is a particularly interesting technique, where topographic and electronic properties of a conducting surface can be explored at the atomic scale, allowing researchers to ”see” the single atoms in the material’s surface. But the possibility to probe nanostructures at the atomic scale is not the only contribution of this technique to nanotechnology. A few years after its discovery it has been shown that not only scientists can ”see” atoms with this technique, but they can also ”touch” them, move and position them with atomic precision on the surface. This process, commonly called atom manipulation, can potentially be used as a new approach to build nanostructures atom by atom. This process is a bottom-up approach, where the structure is created starting from small building blocks. However this method has some characteristics typical of a top-down approach: atoms can be deterministically placed on the surface and the assembly of a nanostructure needs to be guided by an external influence, which in this case is the STM tip. The issue in this case is that it is difficult to implement an atom manipulation process for any atom-surface combination. In some systems the interaction between atom and surface can be stronger than in others, and a careful optimization of the manipulation process is necessary.

The scope of this thesis is to use STM to investigate some semiconductor nanostructures created by a bottom-up approach and to develop further the capability of STM as a tool to create semiconductor nanostructures. In chapter 2 the theoretical background of the STM technique will be presented, focusing on the application of this technique on semiconductor materials. The properties of dopants in semiconductors will also be introduced, treating in detail the case of Mn in GaAs. In chapter 3 an overview will be given for the STM atom manipulation methods, which have been implemented over the last 30 years for various atom-surface combinations.

In chapter 4 we present a study on the morphology of the first nanostructure considered in this work, semiconductor quantum dots (QDs) created with a bottom-up approach. QDs are small clusters of semiconductor material where the carriers present in the semiconductor can be confined in three dimensions. The QDs studied in this work are obtained by epitaxial growth of InAs on GaAs. The lattice mismatch between the two materials induces the formation of small three dimensional clusters of InAs, following a Stranski-Krastanov growth mechanism. In order to integrate these nanostructures in a functional device and protect the QD from oxidation an overgrowth step is necessary, where the nanostructures are covered with a semiconductor capping layer. During the overgrowth the strain introduced by the lattice mismatch between the capping layer and the QDs can modify the morphology of the dots. The strain introduced during capping can be
engineered by carefully choosing the material used in this step. In this work we investigate the effects of different InGaAs capping layers on the QDs morphology, using a combination of STM measurements and Kinetic Monte Carlo simulations. Our results show that by the strain engineering of the capping layer, the final height of the QDs can be controlled.

In chapter 5 the atom manipulation process of Mn atoms on the \{110\} GaAs surface is investigated. Previous work demonstrated the possibility to move Mn atoms on this GaAs surface using an STM tip and showed that the incorporation of a Mn atom inside the GaAs surface layer can also be induced. It is known that Mn in GaAs behaves as an acceptor, an atom which can bind a hole present in the semiconductor. Mn is also a magnetic atom and it has been used to introduce magnetic properties in GaAs. For this reason a nanostructure built from Mn atoms could be an interesting structure to study the magnetic properties in semiconductor at the nanoscale. In this chapter the state of the art of the atom manipulation technique for Mn atoms is discussed and a possible way to enhance the control on this process is presented. Moreover a new manipulation technique is developed, based on the self-assemblies of Mn atom in complexes of a few atoms, aligned in a specific crystallographic direction. Using this new bottom up approach assemblies as large as 4 atoms were created. In chapter 6 we study by STM spectroscopy the electronic properties of the Mn nanostructures, created with the bottom-up approach described in the previous chapter. Mn assemblies in GaAs are an interesting system to understand the properties of magnetic semiconductors and Mn pairs in the surface of GaAs have already been investigated. In our study new insight is obtained on the magnetic interaction in Mn pairs. We show that our results can be explained considering the influence of the surface on the pairs, which cause substantial deviation with respect to the properties predicted for Mn pairs in the bulk.

In chapter 7 we investigate the morphological properties of another semiconductor heterostructure, composed of a GaAs/InGaA/GaAs Quantum Well (QW) coupled to a nearby Mn delta layer. The QW is a nanostructure where the carriers from the semiconductor are confined, but only in the growth direction. The Mn delta layer should localize the Mn atoms in a very thin region. In this heterostructure the free carriers confined in the QW will be coupled to the Mn delta layer, which is only 3 nm away, and they will enhance the magnetic interaction between Mn atoms. The coupling and therefore the enhancement of the magnetic properties strongly depends on the spatial distribution of Mn atoms. Our STM measurements show that the Mn distribution is heavily affected by diffusion and segregation processes during growth, providing an explanation for the complex magneto-optical properties of these structures.
Chapter 2

Experimental and Theoretical Background

2.1 Introduction

In this chapter the principles of Scanning Tunneling Microscopy (STM) will be summarized and the phenomena observed in STM measurements on semiconductors are introduced. The role of dopants in semiconductors is described and the properties of Mn dopants in GaAs will be reviewed, since this system will be investigated in several chapter of this dissertation. A technical description of the experimental setup and the steps necessary to prepare an STM measurement will also be given.

2.2 STM working principles

Scanning Tunneling Microscopy (STM) is an experimental technique developed in 1981 by Binning and Rohrer [10]. The discovery of this experimental technique allowed researchers to study a wide range of conducting and semiconducting surfaces with an atomic resolution. This made STM a essential tool for the study of nanostructures and in general for the investigation of the physics at the nanoscale. Schematically the STM is composed of a sharp metallic tip, controlled by a piezoelectric scanner, which is brought in close proximity to the sample’s surface, at about 1 nm distance. When a bias is applied between sample and tip some electrons tunnel through the vacuum barrier between tip and sample and a tunneling current is detected, approximated by:

\[ I_t \propto e^{-2kd}. \]  

(2.1)

In this equation \( d \) is the tip-sample distance and \( k \) is the inverse decay length in vacuum, around 1 Å\(^{-1}\). The exponential dependence of the tunneling current from the tip-sample distance allows a precise detection of variations in the distance: a
CHAPTER 2. EXPERIMENTAL AND THEORETICAL BACKGROUND

Figure 2.1: Simplified scheme of an STM. A sharp metallic tip is placed in proximity of the sample’s surface (tip-sample distance below 1 nm). When a bias is applied between tip and sample a tunneling current flow through the system and is recorded. The \((x, y, z)\) position of the tip is regulated with a piezoelectric scanner and a feedback loop is used to adjust the \(z\) position of the tip, in order to maintain the tunneling current constant while the tip is moved over the surface.

change of distance of 1 Åcorrespond to a decrease of the tunneling current by a factor 7.

The extreme dependence of the tunneling current on the tip-sample distance guarantees that the contribution to the tunneling current only comes from a very localized region. This is the origin of the extreme resolution characteristic of the STM technique, which allows the experimentalists to visualize atomic features smaller than 1 nm. When the tip is moved over the surface using the piezoelectric scanner the tunneling current will change according to the morphology and the electronic properties of the material. During the movement of the tip a feedback loop is used to adjust the distance between tip and sample, in order to keep the current constant. The profile followed by the tip during the movement across the surface contains information about the topography and the electronic properties of the surface.

2.3 STM on semiconductors

The STM is a powerful tool to study the material properties at the nanoscale. One of the main limitations of this experimental technique is the fact that it can be applied only to conductive systems with an almost flat surface, allowing to detect the tunneling current without damaging the STM tip. In the case of zinc-blende semiconductors, such as III-V or II-VI semiconductor materials, it is possible to obtain a clean, oxide free and atomically flat surface simply by cleavage along a \(\{110\}\) surface. In order to maintain the surface clean and prevent the oxidation, which would suppress the conductivity of the semiconductor surface, the sample
CHAPTER 2. EXPERIMENTAL AND THEORETICAL BACKGROUND

Figure 2.2: Schematic representation of the (110) GaAs surface. In a) the top view of the surface is shown, where atomic rows along the [110] direction are observed, with alternating Ga and As atoms. In b) and c) the side view of the surface, respectively with and without surface relaxation, is represented.

is cleaved under Ultra High Vacuum (UHV) conditions \( (p \sim 10^{-11} \text{ mbar}) \). This variation of the STM technique is called Cross Sectional STM (X-STM).

2.3.1 Zinc-blend \{110\} surface

The X-STM measurements in this work have all been performed on a \{110\} semiconductor surface. In zinc-blende semiconductors, such as GaAs for example, this surface presents zig-zag rows along the [110] direction, composed by alternating anions (As) and cations (Ga) as shown in Fig.2.2. This surface is non polar and undergoes only a small surface relaxation, during which the group III atoms (Ga) are moved inwards, while the group V atoms (As) relax outwards \[29, 136\], as shown in Fig.2.2. This relaxation process hardly changes the size of the surface cell or the length of the bonds in the system, but mainly affects the angles between bonds through a buckling process. The movement of the surface atoms is accompanied by a charge transfer between cations and anions in the zig-zag row. As a result of this process As dangling bonds will be filled with an electron and the Ga dangling bonds will be empty. In the band structure picture this means that the As and Ga surface state are pushed outside the energy range of the bandgap and will be, respectively, filled and empty of electrons. The lack of half filled surface states within the bandgap gives rise to an unpinned Fermi level on the (110) surface \[15\].

2.3.2 Tip Induced Band Bending

An important aspect to take into account in STM measurements on semiconductors is the influence of the bias applied with the STM tip on the band structure of the material. On metals the high density of free carriers will effectively shield the electric field applied by the tip. The same will happen in materials where the Fermi level at the surface is pinned within the bandgap by the surface states, as in the case of the Si (001) surface. If there are no surface states in the semiconductor bandgap, there are no free carriers available and the electric field will penetrate deep inside the semiconductor. These three configurations are shown in Fig.2.3a,b,c respectively. In panel c) it can be observed that in the case of
unpinned Fermi level the electric field bends the bands in the material, giving rise to the phenomenon called Tip Induced Band Bending (TIBB). In the case of the (110) GaAs surface the Fermi level is unpinned, as in the system represented in Fig. 2.3c. When we consider the isolated semiconductor and the isolated metal tip, their bands are flat and the position of the Fermi level with respect to the vacuum level is different for the two systems. The energy difference between the Fermi level and the vacuum level at the surface of the material is called the work function. In Fig. 2.4 the work function for the tip is marked as $\Phi_t$, while the work function of the sample is given by $\Phi_s = \chi + E_g - E_f$, where $\chi$ is the electron affinity and $E_g$ is the bandgap of GaAs. It should be noticed that for semiconductor materials the work function is affected by the doping of the semiconductor. When the tip and the sample are brought in tunneling contact the two systems will exchange carriers to reach a new equilibrium, where the Fermi energy is constant over the whole tunneling junction. This equilibrium condition is represented in the left panels of Fig. 2.4 for p- and n-doped GaAs. The difference in energy between the work function of the tip and the work function of the sample give rise to a non zero tip-induced band bending. The value of this quantity, schematically represented in Fig. 2.4, cannot be trivially extracted from an STM measurement [82, 94] and is highly dependent on the tip’s shape and size [35]. The presence of TIBB introduces complications in the interpretation of the spectroscopic analysis: this phenomenon is responsible, in example, for the apparent difference in bandgap between two regions with a different dopant concentration [140], for the offset in the energy of the dopant’s levels in the semiconductor bandgap [141] and for an apparent shift in energy of the dopant levels due to the change in the local electrostatic potential during an STM measurement.

In Fig. 2.4 two regimes of tunneling are presented, taking into account the presence of TIBB. The main classification of the tunneling regimes is based on the polarity of the bias applied to the sample. When the voltage has negative polarity, the bands of the semiconductor are pulled downwards in proximity of the
Figure 2.4: Representation of different TIBB regimes for p- and n-doped semiconductors. The two panels on the left represent the equilibrium situation reached when tip and sample are in tunneling contact and no bias is applied. The evolution of band bending when a voltage with positive or negative polarity is applied to the sample is schematically depicted in the remaining panels.

<table>
<thead>
<tr>
<th>Equilibrium ((V_s = 0 \text{ V}))</th>
<th>Filled states ((V_s &lt; 0))</th>
<th>Empty states ((V_s &gt; 0))</th>
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<td><strong>n-doped</strong></td>
<td><strong>p-doped</strong></td>
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<tr>
<td>Sample</td>
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Surface. This imaging condition is called filled state imaging, since the states in the bandgap of the semiconductor contributing to the tunneling current are below the Fermi level and are filled with an electron. Conversely when the voltage applied to the sample has a positive polarity, the bands will be pulled upwards close to the surface and the states in the band gap will be lifted above the Fermi level. Therefore these states are empty and this imaging condition is called empty state imaging. Different states of the semiconductor bands are involved in the tunneling process in these two imaging regimes. It has been reported that under filled state conditions the main contribution to the tunneling current arises from the semiconductor valence band, while in empty state conditions the major contribution comes from the conduction band [21]. In the case of GaAs the electronic states close to the edge of the valence and the conduction band are dominated, respectively, by As and Ga related states. Therefore it is a common approximation to assume that the group V sublattice is visualized under filled state conditions, while the group III sublattice is probed with empty states imaging conditions [30, 53].

### 2.4 STM measurements: topography vs spectroscopy imaging

The tunneling current measured in a STM experiment depends on the width of the vacuum barrier, but also on the number of states available for tunneling. The
The exact expression for the tunneling current between the sample and the STM tip is given by the Bardeen formula [5, 129]:

\[
I_t = \frac{4\pi}{h} \int_0^{eV} \rho_s(E_{F,s} + E')\rho_t(E_{F,t} - eV + E')|\hat{M}|^2dE',
\]

where \(\rho_s, \rho_t\) are the Local Densities of States (LDOS) for sample and tip respectively, \(E_F\) is the Fermi level position and \(|\hat{M}|\) is the matrix element for the tunneling of electron between tip and sample. This general equation can be simplified assuming that the LDOS associated to the metallic tip is flat and that its electronic wave function is \(s\)-like. Under these assumptions, which prove valid in many cases [129], \(|M|^2 = e^{-2kd}\) and the formula for the tunneling current becomes:

\[
I_t \propto e^{-2kd} \int_0^{eV} \rho_s(E_{F,s} + E')dE'.
\]  

In this formula the tunneling current is factorized in two terms: the first is an exponential dependence of the tunneling current on the tip-sample distance. The second term depends on the density of the states of the sample, integrated over the energy interval where tunneling can occur. These two terms contain information on both the local electronic structure of the sample and the morphology of the surface. As a result every STM image encompasses topographic and electronic information. It is possible, however, to partially separate these two contributions by choosing an appropriate voltage for the STM experiment: if the bias applied is large many states will participate to the tunneling process. Therefore the influence of local variation of the LDOS on the total tunneling current will be less relevant, and the image obtained will mainly contain topographic information [21].

Two examples of STM images acquired on the same area at different voltage conditions are shown in Fig. 2.5. In a) the contrast observed at negative voltage \((V = -2.5V)\) for a single Mn atom in the GaAs surface layer is shown. On the surface of GaAs the atomic corrugations are observed and the Mn appears as a small dumbell feature [71]. The protrusion introduced by this feature is about 20 pm high. In b) the same area is imaged under low positive voltage condition \((V = 1.5V)\), where the Mn gives rise to a crab-like feature. In this case the protrusion observed in our measurements is much higher, above 0.4 nm. These images show that the information about topography and electronic properties of the surface can be separated to a large extent by carefully choosing the imaging voltage and performing the STM measurements at high voltage.

The dependence of the tunneling current on the local electronic properties can be exploited to study the LDOS of the system with an atomic resolution. In order to extract this information the derivative of the tunneling current can be studied:

\[
\frac{dI_t}{dV} \propto \rho_s(E_{F,s} + E')e^{-2kd}.
\]  

If the tip sample distance is kept constant, the voltage can be varied and the information about the LDOS of the sample \(\rho_s(E)\) can be obtained. The standard approach to measure this quantity is to place the tip at the desired position on the
surface and record the tunneling current as function of the bias voltage. During the measurement the tip-sample distance is kept constant by keeping the feedback loop off. This measurement technique, which is called point spectroscopy, can be repeated over a two dimensional grid of points. This technique, called Current Imaging Tunneling Spectroscopy (CITS) [49], allows the researchers to study the variation of the LDOS on the sample with an atomic resolution. It is a drawback that a measurement on a typical 100 × 100 points grid can take up to 12 hours, making the reduction of the thermal drift and of the piezo creep a crucial point in these measurements. The value of $dI/dV$ can be obtained calculating the numerical derivative of the $I(V)$ curves, but it can also be simultaneously measured with a lock-in technique during the spectroscopy measurements. In these measurements an small AC modulation (typical amplitude $V_{pp} = 30$ mV, frequency 1 KHz) is added to the bias voltage applied in the STM measurements. The tunneling current will also be modulated with the same periodicity and we can measure with a lock-in amplifier the amplitude of the first harmonic signal. This quantity is directly related to $dI/dV$ and the lock-in provide an additional filtering of the signal.

An example of the STM spectroscopy measurements is reported in Fig.2.6. In Fig.2.6b the result of a point spectroscopy measurement, performed near the centre of a Mn atom in the GaAs surface, is shown. The plot is obtained from the numerical derivative of the $I(V)$ curve and applying a Savitzky-Golay low pass filter. In Fig.2.6c a cut obtained from a CITS map is shown. Also in this case the $dI/dV$ information is obtained by numerical derivation and the same low pass filter is applied. The cut reported is through the centre of the Mn atom along the [001] direction. In both measurements the bandgap of GaAs is observed (around 1.5 eV) and the states introduced by the Mn within the band gap are detected.
Figure 2.6: Different techniques of spectroscopic analysis. In a) the topographic image of a Mn atom in the surface of GaAs is shown, taken under high voltage conditions ($V = -3.0V$, $I = 50pA$). In b) the $dI/dV$ point spectra measured in the centre of the Mn is shown. In c) a colormap shows the variation of $dI/dV$ along the [110] direction.

The CITS measurements in particular combine the electronic and the spatial information, allowing to measure the extension and the shape of the states probed. An important issue regarding the interpretation of spectroscopic data is related to the quantification of the electronic contribution to the image of the surface. A flat surface, as shown in Fig.2.5, can appear non-flat due to local modification of the LDOS, originated for example from an interface between different materials or from the preference of defect (Fig.2.5). During a CITS measurement this effect, called topographic cross-talk, can introduce artefacts in the measurements. A possible way to reduce this effect is to perform the topographic measurements at high voltages ($V \geq 2.5V$), reducing the contribution of the electronic contrast to the image.

### 2.4.1 Dopants in Semiconductors

Defects and impurities have a key role in influencing the semiconductor properties, and STM has been used to study the properties of many impurities at the atomic scale, such as vacancies and antisites [77, 29, 14, 36, 80]. Dopant atoms are an important class of impurities, which can be used to introduce carriers in the semiconductor: if the dopant has one valence electron more than the atom it substitutes for, it will be able to donate an electron to the semiconductor and it will be called a donor. Conversely, if the dopant has an electron less, it will be able to capture one, introducing a hole in the semiconductor; in this case the dopant is called an acceptor. The energy necessary to remove the excess carrier from the dopant and inject it into the semiconductor bands is called Binding Energy ($E_b$). Based on this important quantity, dopants can be roughly classified in two groups: there are shallow dopants, for which the binding energy is smaller than the thermal energy at room temperature (around 26 meV), and deep dopants where the binding energy is higher. This classification is useful to understand the role of dopants from the technological perspective: if a dopant is shallow at room temperature the carrier will be found in the semiconductor bands, while if it is a deep dopant the carrier will be trapped around the dopant. Several dopant systems have been in-
vestigated by STM over the past decades, such as Si [26, 134, 46, 139, 127], Te [44], C [83], Zn [146, 82] and Be [62, 63] in GaAs, Zn [31] and Cd in InP and GaAs [20], Zn [87] and S [88] in InAs. In the last 20 years the study of transition metal (TM) impurities in semiconductor has been an active field of research, thanks to the prospect of using these impurities to obtain semiconductor with magnetic properties at room temperature [101, 23, 64, 25]. One of the main goal of the experimental studies in this field is to increase the Curie temperature ($T_C$) of these materials, to make them useful for spintronic applications [25]. Magnetic TM atoms, such as Mn, Fe and Co, introduce a deep acceptor level in III-V semiconductors. The electronic properties of these dopants have been widely studied by STM, with a particular emphasis on Mn doped GaAs.

**Mn in GaAs**

Mn is a particularly interesting TM dopant due to its relatively low binding energy (113meV). Just as most of the transition atoms, Mn in GaAs substitutes for a Ga atom and is expected to share three valence electrons with the semiconductor crystal, remaining in a Mn$^{3+}$ state with a 3$d^4$ electronic configuration. However, electron paramagnetic resonance experiments have shown that the most favourable configuration is a Mn$^{2+}$ charge state [79], with the Mn 3$d$ shell which remains half filled in the 3$d^5$ configuration. As a result the Mn ion is negatively charged with respect to the GaAs environment and it can bind a hole, creating a $A^- + h^+$ complex. In order to understand the electronic properties of the hole bound to the Mn atom the effects of the GaAs crystal on the Mn electronic levels need to be considered. These effects, as discussed in the literature [145, 120], are summarized in Fig.2.7. The occupied Mn 3$d$ levels are split from the 3$d$ states with opposite spin due to exchange interaction. When the Mn is placed in a crystal, the position of the atoms surrounding the Mn will affect its electronic properties. The influence of the lattice is described with a crystal field potential, which leads to a further splitting of the d states: the three d states with $t_{2g}$ symmetry will be lifted in energy respect to the remaining 2 states with $e_g$ symmetry. The d states with $t_{2g}$ symmetry point towards the 4 neighbouring As atoms, positioned at the vertices of a tetrahedron. The $t_{2g}$ states hybridize with the p-like states of the neighbouring As. As a result three degenerate states are found close to the valence band edge, occupied by only two electrons. The remaining electronic state host the hole bound to the Mn atom.

STM measurements show the wavefunction of the hole bound to a Mn acceptor [141, 13, 71], which is reported in Fig.2.7. The spatial extension of the Mn hole wavefunction observed in the measurements depends on the depth of the Mn below the surface, and it evolves from a crab-like feature for a Mn in the GaAs surface layer to a bow-tie feature for subsurface Mn. The shape of the hole wavefunction has also been reproduced and explained in Tight Binding studies [141, 142, 13, 11, 119]. The hole bound to the Mn has an important influence on the magnetism observed in DMS. In the commonly accepted theory for the magnetism in Mn doped GaAs the hole, which is antiferromagnetically coupled to the Mn core electrons by a p-d exchange mechanism, behaves as an itinerant
Figure 2.7: In panel a) a schematic representation of the energy levels of Mn in GaAs is shown, from the work of Strandberg et al. [119]. In b) an STM image of Mn atoms in GaAs is reported, from the work of Celebi et al. [13]. The feature introduced by a Mn atom changes with the depth of the Mn below the surface. The numbers indicated in the image refer to the depth of the Mn atom with respect to the GaAs surface, where 1 is a Mn in the surface layer.

carrier which couples the spin of Mn atoms in the system [23]. The interaction between Mn atoms has been investigated by STM in the work from Kitchen et al. [70]. In this study Mn atoms were placed in the GaAs surface with atomic precision, using an atom manipulation procedure developed for STM. Despite the fact that the Curie temperature for Mn-doped GaAs remains too low for application in spintronics (the highest value achieved is 185 K [137]), this material is still an interesting system where magnetic phenomena in semiconductors can be investigated. Atom manipulation techniques can be exploited to create complex Mn structures with interesting magnetic properties.

2.5 Experimental Method

In the following sections the technical details of the experimental setup and the experimental procedures required to perform X-STM measurements will be presented.

2.5.1 Setup description

The STM experiments described in this work have been performed with a commercial Omicron Low-Temperature STM setup. This setup is composed of three Ultra-High-Vacuum (UHV) chambers: the load lock, the preparation chamber and the STM chamber. The UHV system is designed to achieve pressures as low as \(1 \cdot 10^{-11}\) mbar in proximity of the STM. The load lock is a small chamber where samples and tips are loaded at ambient pressure condition. The load lock is connected to a turbo pump and when the pressure is around \(5 \cdot 10^{-9}\) mbar it is possible
to transfer samples and tips to the preparation chamber. Inside the preparation chamber some steps of in-situ preparation for samples and tips are performed, which will be described in the next sections. When the pressure in the chamber is below $3 \cdot 10^{-9}$ mbar samples and tip can be transferred to the STM chamber. This chamber contains the STM scanner and is always kept at extremely low pressure, which never raises above $1 \cdot 10^{-10}$ mbar. The STM scanner is located directly below a cryostat. The cryostat is composed of two concentric baths. The outer bath is always filled with liquid Nitrogen during the measurements, while the inner bath can be filled with liquid Nitrogen or liquid Helium, allowing to keep the sample at temperatures of 77 K or 5 K respectively, as required for the specific measurement.

There are some advantages performing the measurements at liquid He temperature. Under this condition it is possible to study several phenomena that are not observed at room temperature and also the energy resolution of the STM technique is improved. Moreover at liquid He temperatures undesired effects in the movement of piezoelectric elements, such as creep or thermal drift, are greatly reduced. This is important especially for long measurements such as the CITS maps, which can last for several hours. The drawback of measuring at low temperature is a reduced conductivity of the semiconducting sample, which can constitute an issue during the measurements, especially on wide gap semiconductors or on samples containing a large heterostructure barrier, where the carrier can be frozen and trapped in certain region of the sample. In these cases it is often convenient to perform the measurements at liquid nitrogen temperature, which can be a useful compromise between the conductivity of the system at room temperature and the stability of the measurements at low temperatures.

### 2.5.2 Sample preparation

The samples used in a X-STM experiment are in general a $4 \times 8$ mm rectangle, obtained from a $\{100\}$ GaAs wafer. The first step in the sample preparation is the evaporation of metallic contacts, which improve the conductivity of the measured sample. The contacts are deposited by means of a thermal evaporator: in the case of n-doped semiconductors a Ge-Ni-Au contact is used, while for p-doped samples a Ni-Zn-Au contact is deposited. A commercial wafer is typically 350 $\mu$m thick and in order to obtain an atomically flat surface after cleavage it is necessary to thin the sample down to 120 $\mu$m, which is done by mechanical polishing. Afterwards a scratch 1 mm long is made on the surface of the sample, which will promote the cleavage in a precise position. The sample is then clamped in a sample holder, as shown in Fig. 2.8 with the scratch lying slightly above the clamping bars. Two small disks of In, with a diameter of approximatively 1 mm, are place between the sample and the clamping bar, in order to mechanically fix the sample and improve the electrical contact. The samples are subsequently loaded in the Ultra-High-Vacuum (UHV) setup, where the sample is heated at a temperature around 150°C for 30 minutes, in order to remove water and other organic residuals that have been left on the sample.
2.5.3 Tip preparation

In this work the STM tips were obtained by electrochemical etching of a 99.9% pure, polycrystalline W wire with a diameter of 0.25 mm. The solution used during the etching step is a 2M KOH solution in water. The tip and a Pt/Ir counter-electrode are immersed in the solution, a bias of 6V is applied and the etching process is started. The etching rate at the water meniscus, created where the tip enters the solution, is higher respect to the rest of the wire. This is because the products of the redox reaction, $\text{WO}_4^{2-}$, fall from the meniscus along the wire, partially inhibiting the reaction. When the wire at the meniscus becomes too thin, the weight of the wire in the solution causes a rupture and induces a drop-off. The tip is then loaded in the UHV system and it is heated to a temperature of 200°C for around 30 min, in order to remove possible sources of contamination. Subsequently the tip is sputtered with Ar ions, which removes the oxide layer present on the tip and increase its mechanical stability. In this step an ion energy of about 1keV is used, and the sputtering process lasts around 20 minutes. The tips obtained with this procedure have a curvature radius of about 50nm and are terminated with small and atomically sharp micro-tips. The micro-tip which is the closest to the sample will be involved in the tunneling process, allowing us to probe the surface in the STM measurement with atomic resolution. During an STM measurement a tip crash event can occur, if the tip gets too close to the sample or if the tunneling current becomes too high damaging the tip. After these events it is still possible to obtain a stable tip simply applying some short voltage pulses during the measurements, with a duration of 10ms and an amplitude between 5 and -8 V. This process, called tip conditioning, causes a rearrangement of the atoms on the tip by an electro-migration process. After a few tip conditioning events a new stable tip can be obtained.
2.6 Electron beam Evaporator

An important tool which has been added to the STM setup is the Electron Beam Evaporator EFM 3i from Omicron. This evaporator has been used in our work to deposit Mn atoms on a clean and freshly cleaved surface. Since the evaporation occurs inside the STM chamber, two important requirements need to be satisfied by the evaporation technique: the first is that only a few atoms should be deposited on the surface, the second is that the pressure in the STM chamber should be kept below $p \sim 10^{-10}$ mbar during the evaporation. A scheme of the Electron beam evaporator used in this study is shown in Fig. 2.10. The evaporation in our evaporator is induced by an electron beam, which ensures that the evaporation occurs only in a localized part of the source. This allows a very controlled and low evaporation rate ($10^{-4}$ ML/s). The electron beam is realized running a current of about 1.5 A through a thoriated W wire. In the presence of a high electric field an emission current can be extracted from the filament and it can be focused on the source rod. The local heating induces the desorption of atoms from the rod, which will be able to reach the sample. As a result of the excitation by the electron beam some ions will be formed, which are accelerated by the electric field and

![Figure 2.9](image_url) Image of the tip holder used in our STM experiments. In b) the scheme of the setup used for electrochemical etching is shown. Picture taken by Ineke Wijnheijmer.

![Figure 2.10](image_url) Schematic representation of the evaporator and its components.

Figure 2.10: Schematic representation of the evaporator and its components.
damage the sample. In order to prevent damage to the semiconductor surface an electromagnetic lens is used to deflect those ions. A water cooling shroud is used to keep the temperature and the background pressure low during the evaporation step \((p \sim 10^{-11} \text{ mbar})\). Typical parameters used for the Mn evaporation are an electric field of 850 V, an emission current of 3 mA which give a ion flux of about 0.85 nA. Under these conditions an evaporation time of 20 s will give a Mn coverage of about 0.001 ML on GaAs. The cleanliness of the evaporation is a crucial point for the success of the STM experiments. In order to have a clean evaporation a degassing of the source is necessary before every evaporation step, and the evaporator should be baked using an internal heather to high temperatures (up to 275°C), every time after it has experienced a high pressure condition.
Chapter 3

Atom Manipulation Methods

The invention of Scanning Tunnel Microscopy in 1980 \[10\] gave scientists a new powerful tool to investigate the properties of surfaces. About ten years later the capability of this technique to interact with surfaces at the atomic scale was successfully employed to control the position of atoms on a surface \[34\]. Eigler and Schweizer opened this field and positioned a few Xe atoms on a (110) Ni surface with atomic precision, creating precise structures. After this discovery the STM technique, on top of being a refined microscopy technique, became a tool to move single atoms, which allowed the scientist to use surfaces as atomic playgrounds. Researchers can potentially build atom by atom any 2D structure they can design and directly investigate their properties afterwards. In this way simple model systems based on few atoms can be realized and studied to test theoretical predictions and the results of computational simulations, where the limitation in the size of the system can still be important. Moreover new devices can be realized and characterized, exploiting the quantum mechanical phenomena observed at the nanoscale \[66\] and using the single atoms as building blocks with reliable and robust electronic properties \[39, 37\].

At the present time, however, experiments on single atom manipulation are only possible in a limited amount of systems; moreover it is a difficult experiment, where a deep control on the properties of the tunneling junction needs to be achieved \[57\]. Atom manipulation is a complex process and its outcome depends on the delicate balance between three fundamental contributions:

- the interaction between the atom adsorbed (in short \textit{adatom}) and the surface itself, which can be a simple Van der Waals interaction (physisorption) or it can induce a local re-hybridization between the adatom and the surface states (chemisorption) \[92\];
- the interaction between the tip and the adatom, which can be a Van der Waals interaction or a Coulomb interaction between the adatom’s dipole and the applied electric field \[122\];
- the perturbation of the local environment due to the electric field applied by the tip or due to the tunneling current. The electric field can change the
potential landscape and induce the movement of the adatoms while the tunneling current can provide the energy required to move the adatom, thanks to electron-phonon coupling in the sample \cite{123} or to direct excitation of an electronic transition in the adsorbate \cite{118}.

Depending on the physical properties of the system considered, one of these different interactions can dominate and drive the atom manipulation process. The implementation of highly controlled single atom manipulation experiments in a certain material often requires an understanding of what is the dominating interaction. With this information a suitable manipulation process can be designed. An important limitation to take into account during an atom manipulation process is related to the stability of tip and sample: it is important that the adatoms adsorbed on the surface have a stable position when they do not interact with the STM tip. For this reason many atom manipulation experiments are performed at low temperatures. However the conditions required to manipulate the atoms must be compatible with the range of parameters accessible without inducing tip crash or tip instability events.

In the next sections some systems where STM manipulation technique has been implemented will be discussed, as an example of the different manipulation techniques used in diverse materials and to show the contributions given to different fields.

### 3.1 Single atoms on metals

The first demonstration of single atom manipulation was achieved using Xe atoms on a Ni (110) surface \cite{34}. The choice of the system took into account two crucial aspects very important for the development of an atom manipulation process: the atoms deposited on the surface should be relatively loosely bound, so that the adatom can be moved on the surface, but the adatom position should be stable at low temperature under the STM measurement conditions. In this case Xe atoms interact with the surface only by weak Van der Waals interaction, while the (110) Ni surface has a corrugation sufficiently high to keep the Xe adatom in a stable position at low temperature. It was possible to move Xe atoms on the surface by reducing the tip-sample distance, which increases the tip-adatom interaction, and allows dragging the atoms on the surface with the tip. The force driving the atom manipulation process originates from the Van der Waals interaction: by decreasing the tip-adsorbate distance the interaction can be increased until it overcomes the surrounding potential barriers. A similar manipulation method was applied to other adatom-metal systems and it was exploited to build more complex atomic structures. However, different systems require modifications to the atom manipulation technique with respect to the dragging method implemented for Xe on Ni. In general it was found that the dragging method is possible only for a limited set of adatom-surface combinations, but the manipulation can occur only above a tunneling current threshold \cite{59}. This indicates that the tunneling current has an important role in exciting the adatom-substrate bond, through inelastic scattering phenomena for example.
CHAPTER 3. ATOM MANIPULATION METHODS

Figure 3.1: In a) the STM image of a quantum corral [59]. The electrons confined in the structure form a standing wave pattern in the quantum corral. In b) the scheme of a logic gate based on a single atoms is shown, as proposed by Khajetoorian et al [69]. This structure was realized experimentally through atom by atom assembly using an STM tip.

A famous example of an interesting structure created by atom manipulation is the Quantum Corral, created for the first time in the work by Crommie, Lutz and Eigler [18]. In their work Fe adatoms deposited on a Cu (111) surface were used to confine electrons in a circular well. The atom manipulation technique used to build these structure has been described in detail in other interesting works [59]. Quantum Corral structures have been used as a model system to investigate the complex physics of many body interaction, giving new insight in Kondo physics [109] and the Quantum Mirage phenomenon [86]. An example of a Quantum Corral is shown in Fig.3.1a. Atom manipulation on metals has also been employed to realize tailored nanomagnets [68], in which a careful choice of the distance between magnetic atoms allows the scientists to control the coupling by RKKY interaction and tune the magnetic properties. With a similar approach even all-spin based logic gates were realized and tested [69](see Fig.3.1b), showing the enormous progress in the control of matter at the atomic scale and a first example of an atomic scale spintronic device.

3.2 Molecules on metals

The manipulation processes developed for a single atom adsorbed on a metallic surface are also applicable to molecules. The first demonstration of single molecule manipulation was realized by Meyer, Neu and Rieder [91]. The system considered in this study was composed of CO molecules on a Cu (211) surface, for which a pull and drag manipulation was initially implemented, mimicking the process developed for metal surfaces. Soon a new method was developed, based on the vertical transfer of a molecule from the substrate to the tip and vice-versa [6]. This approach made the manipulation process more flexible: the molecule could be picked up by the tip, the tip was moved to the desired position and the molecule could be deposited on the surface. In this manipulation process the electric field
applied between the tip and the sample has an important role, because it changes the electrostatic potential for the adsorbed molecule and favours the transfer of the molecule to the tip. The inverse process, in which the molecule is transferred back to the substrate can be obtained by using the opposite voltage polarity \[^{[6]}\]. Also in this atom manipulation process the tunneling current has an important role in exciting the adsorbed molecule, making the transfer process possible. The level of control achieved in this system is so high that CO molecules have been used to realize complex domino-like structures on metallic surfaces \[^{[52]}\]. In this system, composed of many CO molecules positioned close to each other on the surface, the manipulation of one molecule triggered a cascade of effects on the position of the other CO molecules in the structure. It was shown that it is possible to operate such structures as a logic gate. An example is shown in Fig. 3.2b.

After the success in manipulating CO molecules, atom manipulation was demonstrated also for bigger and more complex molecules \[^{[56, 17]}\], including for example fullerene \[^{[47]}\] or graphene nanoribbons \[^{[133]}\]. An example of the degree of control achieved by STM on such a system is the work from Hla et al.\[^{[58]}\], where the steps of a chemical reaction were controllably induced at the atomic level by exploiting the perturbation introduced by an STM tip. Some molecules are too mobile on the surface to be controllably manipulated by STM even at low temperatures; as a solution to this issue it has been shown that for some systems a reaction between molecule and substrate can be induced using the STM tip, which anchors the molecule in a specific position \[^{[133, 58]}\]. The process of vertical transfer of a molecule to the tip was also exploited in several studies to controllably functionalize the STM tip, giving the possibility to provide chemical \[^{[6]}\] or magnetic \[^{[55]}\] sensitivity to the STM measurements. A comparison between an image taken with and without a CO molecule adsorbed on the tip is shown in Fig. 3.2.
3.3 Atoms on insulators

Recent development demonstrated that atom manipulation experiments can be performed also on insulating substrates. The most common system where this experiments have been performed consisted in islands of CuN on a Cu substrate, grown by ion implantation of $N_2$ ions [55]; during the sub-monolayer growth $N$ spontaneously forms islands of insulating material on which other adatoms can be placed. The first report of atom manipulation on this system is the work from Hirjibehedin et al. [55], where a vertical transfer manipulation technique was implemented for Mn atoms adsorbed on CuN and it was exploited to create chains of magnetic atoms, as the one shown in Fig. 3.3a. The vertical transfer method is similar to the method described for molecules on metals, where the transfer of the atom to and from the tip is induced by opposite voltage polarity (positive and negative voltages respectively). This system is particularly interesting for the study of the magnetic interaction between individual atoms, because they are decoupled from the metallic substrate by the insulating layer while retaining the magnetic properties of the isolated atom [55]. For this reason the system has been used to create magnetic structures and to study their magnetic properties in depth [54].

Another interesting example of atom manipulation on a partially insulating systems is described in the work from Kalff et al. [65]. The system consists of a Cu (100) surface terminated with Cl, where the coverage is not complete and several vacancies of Cl are left on the surface. The manipulation procedure is based on the hopping of the Cl vacancies atoms, induced by the local heating from the injected tunneling current. This process was optimized and successfully employed to build a kilobyte of memory based on an array of more than 8000 vacancies, giving an impressive demonstration of the level of control and reproducibility that can be achieved in an atom manipulation process. The process of writing and erasing a group of 64 single atom bits is shown in Fig. 3.3b.
3.4 Atoms on semiconductors

In the last 60 years semiconductor materials played a central role in technological progress thanks to an unparalleled control achieved over their properties [84]. Several STM studies have been performed on this important class of materials, including experiments on atom manipulation. The first example of atom manipulation on semiconductors has been shown on a Si (111) surface, where single atoms were successfully desorbed from the surface under the influence of an STM tip [130]. However, as discussed in the previous chapter, semiconductor surfaces can have complex electronic properties, due to the presence of surface states within the bandgap. This issue delayed the progress of atomic manipulation techniques on these surfaces, especially for group IV semiconductors where it is difficult to prepare a flat surface suitable for STM measurements. The situation is different for III-V and II-VI semiconductors, where an atomically flat and unpinned (110) surface can be obtained by cleavage under Ultra High Vacuum conditions, as described in the previous chapter.

One of the first examples of atom manipulation on a GaAs (110) surface is the work from Whitman et al. [138] with Cs atoms. In their work it was shown that these adatoms organize in mono-atomic rows, under the effect of the electric field generated by the STM tip. After this example atom manipulation was implemented for other defects, such as As-vacancies in the GaAs surface layer [76]. It is interesting to notice that in this system the atom manipulation does not occur with the dragging method implemented for metal substrates, but only through an highly asymmetric hopping process, where an As vacancy is moved preferentially along the [001] direction. There is no report in the literature about the implementation of the dragging method on semiconductor surfaces. This indicates that adatoms on semiconductor’s surface are more tightly bound or experience a potential landscape with higher corrugations. This characteristic of semiconductor’s surfaces implies a lower hopping rate for an adatom on the surface. In order to overcome the potential barrier for the movement the tip sample distance should be so small that the tip is effectively crashed into the sample, which makes the lateral manipulation implemented for metals more challenging or not applicable.

An interesting example of atom manipulation where the adatoms are sufficiently mobile is constituted by Ga adatom on GaAs. These atoms can be easily moved while scanning an area with an STM tip at a specific polarity of the voltage, as shown in the work from Gohlke et al. [45] (Fig. 3.4a). However the movement of the atoms is still constrained by the symmetry of the surface, resulting in a highly asymmetric movement which occurs preferentially along the [001] direction. More success in creating structures of Ga adatoms was obtained when a vertical transfer manipulation was developed [45]. The observation that the manipulation of vacancies and Ga adatoms on III-V materials preferentially occurs at a specific voltage polarity indicates that in this system the manipulation occurs when a specific electronic state of the defect is involved in the tunneling process. Under these tunneling conditions the transfer of energy from the tunneling electron to the defect via inelastic scattering can be more efficient.

Vertical transfer manipulation has also been implemented in some other sys-
Figure 3.4: In a) the manipulation of Mn and Ga adatoms on the (110) GaAs surface is represented, and the possibility to modify the electronic landscape is demonstrated with the creation of regions with high Ga concentration [45]. In b) the results for the work of Pan et al. [103] are shown: chains of In adatoms are created on a (111) InAs surface and can be used as configurable QD molecules. By controlling the size of the QDs the electronic states can be tuned and reshaped.

Dopants, in particular for In adatoms on a (111) InAs surface [38]. In the work from Folsch et al. [37] several complex structures (such as chains, squares and other shapes) were realized with In adatoms on the InAs (111) surface. In this study it is demonstrated that In adatoms interact through substrate mediated interactions and chains of atoms show molecular orbital like features. Atomic chains realized with this method behave similarly to semiconductor QDs, with the advantage that they can be assembled and placed with atomic precision, eliminating stochastic variations in their size that are often an obstacle for the study of fundamental physics problems with QDs [103]. An example of these QDs is given in Fig.3.4

3.5 Dopant manipulation on semiconductors

Dopants are impurities which are able to accept or donate an electron to the semiconductor. They have a key role in semiconductor technology since they are used to tune the opto-electronic properties of the semiconductor and are necessary to realize semiconductor devices. The possibility to control the position of dopants in semiconductor materials at an atomic level is very appealing, since it would give the possibility to create new devices based on the combination and the interaction between a few doping atoms [72]. In the case of dopants in semiconductors, additionally, the single atom is partially decoupled from the semiconductor electronic states, since its electronic state is found within the bandgap. This means that in semiconductors a single dopant can retain some atomic-like properties but it can also be manipulated by using an electric field or it can be involved in transport experiments, unlike single atoms on completely insulating systems [72]. The most impressive example of a semiconductor device based on a single atom is the Single Atom Transistor, implemented and described in the work of Fueschele et al. [39], where a single P atom is positioned with atomic precision on a Si surface. The experimental technique used is called STM lithography and uses an STM tip to
Figure 3.5: (a) Image of a single atom transistor, based on a single P atom placed with atomic precision between 2 contacts in silicon. This device was realized in the work of Fueschele et al.[39]. In b) the steps in the manipulation process leading to the incorporation of a Mn dopant in a GaAs surface are shown. After the incorporation process Mn is found in the surface layer in a position where it substitutes for a Ga atom, while the Ga atom which has been replaced is found on the surface as an adatom. This process was reported for the first time in the work of Kitchen et al. [70].

desorb H from an H-terminated Si surface. Subsequently P precursor molecules are deposited and adsorbed at the position without H. With a similar procedure also the contacts are created, after which the structure is overgrown with Si at low temperature. The fabricated device, shown in Fig.3.5a, behaves as a single electron transistor where the electrons are transferred between the leads and the P atom. This work can potentially initiate further progress in the field Quantum Computation in semiconductors [66].

In III-V materials the research on dopant manipulation is not yet as developed. The first example of dopant manipulation is in the study from Kitchen et al. [70]. In this work a set of transition metal atoms, specifically Fe, Co and Mn were deposited on the (110) GaAs surface. These transition metal atoms behave as an acceptor when incorporated in GaAs and all have a net magnetic moment. The combination of these two properties made them an interesting test system that can be used to study magnetic interaction in semiconductors. These interactions are at the basis of Diluted Magnetic Semiconductor systems studied in the last 20 years [101, 32, 74]. In GaAs, which is a well known system suitable for STM studies, Mn atoms are an interesting case. Mn is a relatively shallow acceptor (binding energy in bulk $E_b = 113\,\text{meV}$), which makes it an interesting dopant for III-V materials and a well known system in STM studies [141]. Atom manipulation of the three transition metal adatoms on GaAs was demonstrated. Two different processes were shown: the movement of an adatom by hopping to a neighbouring position or the incorporation of the dopant in the surface layer, where it can
substitute for a Ga atom. As a result of this process the Ga atom is found as an adsorbate on the surface and can be readily moved on the surface, as shown in Fig3.5. The inverse process in which a Ga adatom exchanges its position with a substitutional Mn dopant in the surface is however very unlikely. The atom manipulation technique developed will be described in chapter 5 This method was used by Kitchen et al.[70] to assemble Mn pairs along different crystallographic directions and to study the anisotropy of the Mn-Mn interaction. In chapter 5 we will present new manipulation methods which allowed us to build larger Mn assemblies on the GaAs surface.
Chapter 4

Height control of self-assembled quantum dots by strain engineering during capping

Strain engineering during the capping of III-V quantum dots has been explored as a means to control the erosion of strained self-assembled quantum dots. Results of Kinetic Monte Carlo simulations are compared with cross-sectional Scanning Tunnel Microscopy measurements performed on InAs quantum dots grown by Molecular Beam Epitaxy. In the first part of our investigation we considered QDs which have been first partially capped by In_xGa_{(1-x)}As; in the second stage of the capping the QD are completely covered by pure GaAs. The KMC model shows the details of the QDs’ erosion process, which has an important influence on the final shape of the dots. In the second part of our work we study InAs quantum dots which are completely capped by In_xGa_{(1-x)}As layers of different indium compositions. Both from our realistic 3D Kinetic Monte Carlo simulations and the X-STM measurements on real samples a trend in the height of the capped quantum dot is found as a function of the lattice mismatch between the quantum dot material and the capping layer. Results obtained experimentally on additional material combinations show a generic role of the elastic energy in the control of the quantum dot morphology by strain engineering during capping.

4.1 Introduction

The epitaxial growth of Stranski-Krastanov Quantum Dots (QDs) has been extensively studied in the last decades [61, 135]. In this growth process the strain, due to the lattice mismatch between the deposited material and the substrate, controls to

\footnote{Part of this chapter has been published in Applied Physics Letter 105, 143104,(2014)}
a large extent the formation of self-assembled QDs. The three dimensional confinement of carriers in these nanostructures makes them interesting for applications like QD lasers [9], single photon sources [144] and single electron transistors [147]. The optoelectronic properties of QDs are determined by the confinement of the carriers [48] and are therefore directly connected to their morphology, which is the result of a delicate interplay between the elastic relaxation and the surface energy [8].

In many studies only the shape obtained after the QD growth process is investigated [89, 61]. In order to be used in an actual device, however, the QDs need to be overgrown with a capping layer and in this process the morphology and the properties of the QDs can dramatically change [99, 81]. The choice of the capping material thus has an important influence on the final properties of these nanostructures. For instance tuning of the capping layer’s composition makes it possible to control the strain field inside the QDs [51] and the QDs erosion process [131]. This means that in order to control the structural properties of the nanostructures strain engineering during capping is just as important as during the formation of the QDs. In this Chapter we use a Kinetic Monte Carlo (KMC) model [22] to investigate the role of the strain in the control of the morphology of the QDs during capping. The considered system consists of InAs QDs grown on GaAs which are capped with In$_x$Ga$_{(1-x)}$As.

In the first part of our study the KMC model is used to investigate the effects of a complex capping structure on the QD morphology. First the QDs are partially covered with a In$_x$Ga$_{(1-x)}$As, leaving the QD’s top exposed. Subsequently a second capping layer of pure GaAs is deposited, which completely covers the dots. The erosion’s process of the dot is investigated by comparing the results for systems with different In concentration in the first capping layer ($x = 0$, 0.05, 0.1). The result of the simulations are compared with previous experimental results, which reported a similar erosion process for the QDs [99].

In the second part of this work the QDs are overgrown with a In$_x$Ga$_{(1-x)}$As capping layer 5 nm thick, which completely covers the dots. The lattice mismatch between the QDs and the capping layer can be engineered by tuning the In concentration in the capping layer [98]. Five systems with five different values of In concentration in the capping layer are considered ($x = 0$, 0.05, 0.1, 0.15, 0.2). The effects on the QDs morphology are studied and the results obtained from the simulation are compared with cross-sectional Scanning Tunnel Microscopy (X-STM) measurement on QD samples grown by Molecular Beam Epitaxy (MBE) [67].

### 4.2 Computational and Experimental Methods

The experimental results on the QDs’ morphology, obtained by X-STM, are compared with the outcome of a KMC model. The details of the model and the experimental methods will be described in the following sections.
4.2.1 Kinetic Monte Carlo model

The KMC model which I used in this study has been developed by Smereka et al. [116, 7, 22]. It efficiently describes the hetero-epitaxial growth of semiconductors, allowing to simulate large systems (up to $90 \times 90 \text{nm}^2$) which can be directly compared with the experimental results.

In this model each pair of III-V atoms in the system is represented as a cube, as shown in Fig. 4.1. Since a zinc-blend unit cell contains 4 pairs of III-V atoms, the volume of the cubes is chosen to be $1/4$ of the unit cell volume. The chemical interaction between the different cubes is divided into two components: a short range term, related to the strong chemical bonds between the neighbouring atoms, and a long range term, which describes the elastic effects introduced by the lattice mismatch between two different semiconductors. In particular the short range interaction between each cube and its neighbours is described using a bond-counting model, while a ball and spring model is used for the description of long range elastic interaction.

In the model only the surface atoms are considered to be mobile, since their mobility is much higher than the bulk mobility [93], but a certain degree of intermixing is allowed by the thermal roughening of the surface. Through this process atoms deposited on the surface can be incorporated in subsurface layers. In the simulation each cube at the surface can jump to one of his neighbouring sites with a hopping rate given by:

$$R = R_0 \exp \left( -\frac{B - \Delta W}{k_B T} \right),$$

(4.1)

where $R_0$ is the hopping attempt frequency, $k_B T$ is the thermal energy, $\Delta W$ is the elastic energy and $B$ is the bonding energy.

There are different bonds in the system, depending on the type of ”atoms” involved. In this work the system studied is composed of InAs QDs grown on GaAs and capped with $\text{In}_x\text{Ga}_{(1-x)}\text{As}$. Therefore the possible bonds in the system are: GaAs-GaAs, GaAs-InAs and InAs-InAs bonds. The bonding energy for a generic cube is given by:

$$B = B_{Ga-Ga} + B_{Ga-In} + B_{In-In}.$$ 

(4.2)

Figure 4.1: Representation of an InAs ”adatom” on a GaAs surface in the KMC model. The interaction of the ”adatom” with the adjacent cubes, which correspond to the first, second and third nearest neighbours (marked in progressively darker blue), is described with a bond counting model.
CHAPTER 4. HEIGHT CONTROL OF QUANTUM DOTS BY STRAIN ENGINEERING

The three terms count the number of bond that an "atom" has of each type and are given by:

\[ B_\alpha = (aN_{\alpha I} + bN_{\alpha II} + cN_{\alpha III}) \gamma_\alpha , \]  \hspace{1cm} (4.3)

where \( \alpha \) identifies the type of bond, \( N_{\alpha I}, N_{\alpha II}, N_{\alpha III} \) are the number of \( \alpha \)-type bonds with the first, the second and the third neighbours and \( \gamma_\alpha \) is the energy of a single bond. The three parameters \( a, b \) and \( c \) are chosen to reproduce the anisotropy of the zinc-blend crystal and the different surface energies. In our simulation we choose \( a = 0.3, b = 0.5 \) and \( c = 1.0 \), which give rise to realistic pyramidal QDs. For the other parameters we take \( \gamma_{Ga-Ga} = 0.2506 \) eV, \( \gamma_{Ga-In} = 0.2217 \) eV and \( \gamma_{In-In} = 0.2169 \) eV \[67\].

The elastic energy \( \Delta W \) is the change in the total elastic energy given by the removal of the "atom" considered. The elastic interactions in the system are calculated with a ball and spring model, using two spring constants, \( k_L \) and \( k_D \), and the misfit \( \mu \) between InAs and GaAs. We take \( k_L = 2.89 \text{ eV}/l_1^2 \) and \( k_D = 9.64 \text{ eV}/l_1^2 \), where \( l_1 \) is the lattice constant of GaAs, and a misfit \( \mu = 0.075 \). This set of parameters gives a decent approximation for the bulk and surface properties of GaAs \[90\].

The key approximation of the model, which has been thoroughly tested \[116\], is that the movement of an "adatom" is not influenced by the elastic field. In this model a cube is treated as an adatom when there are less than 10 "atoms" around it, considering the I,II and III nearest neighbour positions. An isolated "atom" on the surface has only 9 "atoms" in its neighbouring positions; therefore it is considered as an "adatom" and it is not necessary to recalculate the elastic field after its movement. Thanks to this approximation the code is 10-15 times faster, since the movement of an adatom does not require the recalculation of the elastic field, which is computationally very expensive. This allow us to simulate systems on a realistic time scale that are as big as \( 90 \times 90 \) nm\(^2\) which can be directly compared to experimental observations.

4.2.2 Cross-Section Scanning Tunnel Microscopy

The QDs for the X-STM analysis were grown by MBE on a n-doped (100) GaAs substrate. The growth process is initiated with the deposition of 350 nm GaAs at 580°C as a buffer layer. The sample contains 4 layers of capped QDs, grown by deposition of 2.7 ML of InAs at 450°C and with a growth rate of 0.04 ML/s. Every QD layer is overgrown with 5 nm of \( \text{In}_x\text{Ga}_{(1-x)}\text{As} \), with \( x = 0.00, x = 0.05, x = 0.10 \) and \( x = 0.15 \) respectively for the first, second, third and fourth layer of QDs. A growth rate of 0.75 ML/s and a growth temperature of 450°C were used for the \( \text{In}_x\text{Ga}_{(1-x)}\text{As} \) layer. The QDs layers are separated by GaAs spacer layers of 50 nm, grown at 580°C and with a growth rate of 0.7 ML/s. Finally a QD layer is grown on top of the sample for the analysis of uncapped QDs by Atomic Force Microscopy (AFM). The growth parameters used in the simulation match the ones used for the MBE grown sample, except for the growth rate for the QD layer, which is set as 0.15 ML/s in the simulations, roughly four times bigger than the experimental value.
Another set of simulations is performed, considering the same QD ensemble and depositing first a $\text{In}_x\text{Ga}_{(1-x)}\text{As}$ capping layer 2.8 nm thick, which does not completely cover the dots. Three different In concentrations are considered, in particular with $x = 0.00$, $x = 0.05$, and $x = 0.10$. Subsequently the dots are fully covered with a second capping layer, consisting of pure GaAs grown at 580°C. X-STM analysis was performed at 77 K under Ultra High Vacuum (UHV) conditions on a (110) surface obtained by in-situ cleaving. The measurements were all done at high negative bias voltages and low tunneling currents ($V = -3$ V, $I = 20$ pA). The X-STM measurements have been performed by Joris Keizer.

4.3 Results

Several well known phenomena occurring during the QD growth are captured with our model. In Fig. 4.2 some important steps in the QDs growth process are shown. As expected in a Stranski-Krastanov growth mode [78], first a wetting layer of InAs is formed, as observed in 4.2a. Subsequently QDs are formed, initially as small islands with irregular shape, called prepyramids, which can evolve into larger QDs with pyramidal shape. A similar evolution of the QDs’ shape has been also observed experimentally [125]. The ensemble of QDs represented in Fig. 4.2c is obtained after the deposition of 2.7 ML of InAs, and it will be used as the starting system for all the capping simulations presented in the rest of our study.

4.3.1 Control on the QD’s erosion by partial capping

In this section we present the results from our KMC simulations for a system where the QDs have been overgrown with two different capping layers: first an $\text{In}_x\text{Ga}_{(1-x)}\text{As}$ layer 2.8 nm thick is deposited, which does not completely cover the dots; the overgrowth is then completed with a second capping layer of pure GaAs. The images of the QDs obtained after the complete capping process are shown in Fig. 4.3. In the figure the capped QDs are represented using the isosurfaces corresponding to an In concentration of 66%. Three systems with different In concentration in the first capping layer ($x = 0$, 0.05, 0.1) are presented.

![Figure 4.2: Steps observed during the QD growth. In panel a) the formation of an InAs wetting layer is observed, for a coverage equal to 0.6 ML. Further InAs deposition initiates the QD nucleation, as observed in panel b). The final ensemble of QDs, obtained after the deposition of 2.7 ML of InAs, is shown in panel c).](image-url)
Figure 4.3: Comparison between the QD ensembles obtained after the QD growth and after the capping process. Panel a) shows the ensemble before capping. Three different capping layer were considered, with 0, 5, 10 % In concentration in b), c) and d) respectively. Ring-like features are observed as a result of the erosion process and interestingly fewer dots are preserved when a capping layer with higher In concentration is used.

During the overgrowth the QDs are eroded, due to the lattice mismatch between the dots and the capping layer. The erosion causes the disgregation of several dots and ring-like features are formed. The evolution of Stranski-Krastanov QDs into ring-like shape after capping is a phenomena experimentally observed [81]. This process is the result of the lateral compression exerted by the capping layer on a QD, which causes the In to flow out of the center of the dot. It is interesting to notice that fewer dots are preserved when the first capping layer has a higher In concentration. This result is surprising, since the lattice mismatch between the dots (InAs) and the capping material (In$_x$Ga$_{(1-x)}$As) is lower and a reduced erosion would be expected. With respect to the initial system, where 45 QDs are present, at the end of the overgrowth only 18, 17 and 12 QDs are preserved, for the system where the first capping had an In concentration of respectively 0%, 5% and 10%. The number of rings increases with the In concentration in the capping layer, going from 7 rings for the 0% In concentration to 10 and 13 rings for In concentrations equal to 5% and 10%.

These observations can be understood considering the size of the QDs obtained after the growth of the first capping layer, illustrated in Fig. 4.4. In these images it can be observed that after the growth of the first capping layer more and larger QDs are obtained when the In concentration in the capping layer is the highest (x = 10%). This result is expected since between the systems considered, this system has the smallest lattice mismatch between QDs and capping layer.
I capping layer

GaAs/GaAs

<table>
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<tr>
<th>GaAs/GaAs</th>
<th>In\textsubscript{\textit{x}}Ga\textsubscript{1-x}As/GaAs (x = 0.05)</th>
<th>In\textsubscript{\textit{x}}Ga\textsubscript{1-x}As/GaAs (x = 0.10)</th>
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Figure 4.4: Comparison between the QD ensembles at the end of the first capping layer growth and during the first stages of the growth of the second capping layer. Three different capping layer were considered, with 0.5, 10% In concentration. We show both the top view and a cross section of the systems, taken along the red dashed line. InAs ”atoms” are depicted as yellow and GaAs ”atoms” as blue. It can be observed from the images that the surface at the end of the first overgrowth step is relatively flat, but it becomes unstable and rougher as the deposition of the second capping is started. This phenomenon becomes more pronounced increasing the In concentration in the first capping layer.

When the second capping layer deposition is initiated, the erosion of the QDs is enhanced by the increased lattice mismatch and the higher temperature. These two factors increase the movement probability for surface atoms, as described by Eq. 4.1. Since the dots partially capped with material having an higher In concentration are bigger, they will remain more exposed at the end of the first capping. Therefore these dots will be more affected by the erosion process occurring during the growth of the second capping.

The ring-like features observed in our simulation are a result of this erosion process. The shape of these features can be understood considering the strain distribution inside the QD. The InAs ”atoms” at the side of the dots are constrained by the surrounding capping layer, which has a smaller lattice parameter and introduces additional elastic energy in the dot. Conversely InAs ”atoms” in the center of the dot can partially relax this elastic energy, expanding along the growth direction for example. When the second capping deposition is initiated, the ”atoms” in a QD will experience additional strain. Since the ”atoms” in the center of the
dot are partially relaxed, the lattice mismatch with the capping layer material will be maximum for them. As a result these “atoms” will have the highest hopping probability and they will move from the centre of the dot, leaving a ring-like feature behind.

This particular erosion mechanism has been observed also in a few experimental studies [81, 99], confirming the capability of this model to qualitatively reproduce the processes taking place during Stranski-Krastanov growth. It should be noticed however, that this erosion process has been reported only in a few cases, while it is often observed in our simulations. An explanation for the enhanced probability of ring formation in our simulations could be the fact that in our system intermixing is taken only partially into account. Therefore in a real system intermixing contributes more in reducing the elastic energy in the system and the formation of rings is hindered.

4.3.2 Height control of QDs by strain engineering

In the next section we present the results for the same ensemble of QDs shown in Fig. 4.2, but in this case the dots are fully covered with an $\text{In}_x\text{Ga}_{(1-x)}\text{As}$ capping layer 5 nm thick. The effects of different In concentration in the capping layer on the QD morphology is investigated in this section. In the figure the capped QDs are represented using the isosurfaces corresponding to an In concentration of 66%.

![Figure 4.5: Top view of simulated capped QDs, represented as the isosurfaces corresponding to an In concentration of 66%.](image)

From the comparison between the images shown in Fig. 4.5 a number of trends can be observed when the indium concentration in the capping layer is increased: 1) the average height of the QDs increases 2) the number of QDs preserved after capping increases and 3) the number of ring-like features decreases. The observed
trends are all related to the strain induced destabilization of the QDs. If the lattice mismatch between the dot materials and the capping layer is large the dot erosion will be strong, reducing the average height of the QDs and desolving more QDs. A capping layer with a higher In concentration has a smaller lattice mismatch with the QD, which means that the compressive strain applied to the QD will be lower, and this explains the lower number of rings that are formed. Our observation that the number of ring structures decreases when the capping layer has a higher In concentration supports the proposed mechanism for the ring formation.

In order to show the effect of the composition of the capping layer on the height of the QDs more quantitatively, the height distribution of the capped QDs obtained in the simulation is shown in Fig. 4.6. The average height for QDs capped with a higher In concentration is shifted to higher values, confirming that the strain engineering during capping plays a central role in determining the final height of QDs in our KMC model.

In order to confirm this trend observed in the simulation the results are compared with the X-STM analysis on MBE grown QDs. Three layers of QDs, overgrown with In$_x$Ga$_{(1-x)}$As with an indium concentration of $x = 0.00$, $x = 0.05$ and $x = 0.10$, are analyzed and the average height of the QDs is determined to be 3.9 ± 0.4 nm, 4.6 ± 0.4 nm, 5.1 ± 0.4 nm respectively. With the AFM the average height of uncapped QDs is also measured, giving $h = 5.6 ± 0.7$ nm. The cross-section of a capped QD obtained in the simulation is shown in Fig. 4.7, where we can see a good qualitative agreement between the morphological features of a real QD and one obtained in the simulations. The average height results obtained from the simulation are compared with the results obtained by X-STM measurement in Fig. 4.8.

There is a qualitative agreement between the trend observed from the experimental data (red open symbols) and the results of the simulation (black filled symbols) which confirms that a smaller mismatch between QD and capping layer...
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Figure 4.7: (a) Cross-sectional view of a QD capped with GaAs obtained with X-STM. (b) X-STM image after the application of a high-pass filter to enhance the contrast of In atoms over Ga atoms. (c) Color map of the indium density obtained for a QD capped with pure GaAs in the simulation, where the In concentration varies from 0\% (black) to 100\% (white).

Figure 4.8: Average height of capped QDs as a function of the lattice mismatch between the QD and the capping layer. The average height of the QDs increases when the lattice mismatch between the QD material and the capping layer is reduced. Both the average QD heights obtained in KMC simulations and the X-STM measurements are presented in this graph (respectively the black filled and red open symbols). Furthermore experimental results from X-STM measurements performed on samples where InAs QDs grown were capped with GaAsSb (blue open symbols) are also shown in this graph.
reduces the dot erosion process [67] and will result in QDs with a larger height. In Fig. 4.8 additional experimental points are shown (blue open symbols), obtained by X-STM measurements on other InAs QD samples that are capped with GaAsSb instead of InGaAs [132, 131].

The qualitative agreement with the trend found for the systems studied in this chapter and the points obtained for different InAs QDs systems is striking, in spite of the differences between the systems considered (i.e. different capping and different morphology of the uncapped QDs). This suggests that the morphological properties of uncapped QDs are of secondary importance with respect to the misfit between the QD and the capping layer material. Therefore the offset in the trend obtained for the simulation and the experimental result is not attributed to the difference in height between the uncapped QD studied (5.6 ± 0.7 nm for the real system and 5.1 ± 0.5 nm for the simulations), but can be explained considering the different level of intermixing in the real and simulated QDs.

In the KMC model the intermixing is taken into account only at the surface during the growth, whereas bulk intermixing is not considered. This is an underestimation with respect to a real system where both types of intermixing occur. The intermixing increases the Ga content in the InAs QD, reducing the misfit with the In$_x$Ga$_{(1-x)}$As capping layer. Therefore a real QD will have a higher Ga content and a smaller mismatch with the capping layer than a QD obtained in the simulations under the same conditions. This argument is supported by the result shown in Fig. 4.7, where a filtered STM image and a map of the In density for a simulated QD are shown. In the STM image the In atoms appear as bright spots, and a fluctuation in In content inside a real QD can be seen. The map of the In density for a QD obtained from the simulations, instead, shows an internal region of high and uniform In concentration, confirming that in these QDs a smaller degree of intermixing has occurred. A 10% higher Ga concentration in the real QDs as compared to the simulated QDs nicely explains the shift between the curves describing the QD height vs. mismatch dependence for the simulated and measured QDs, shown in Fig. 4.8. The observation that all the experimental points qualitatively follow the same trend found in the simulations suggest that the relation between the mismatch of the QDs with the capping and their final height can be general for many strained QDs systems.

### 4.4 Conclusions

In conclusion strain engineering during capping by tuning the mismatch between capping layer and QDs makes it possible to effectively control the height of QDs. The good qualitative agreement between the simulated QDs obtained by KMC modelling and those observed by X-STM in MBE grown samples confirm that the KMC model can be successfully used, in combination with experimental techniques like X-STM, to gain a deeper understanding in growth processes occurring during hetero-epitaxial growth.
Chapter 5

Study and manipulation of Mn adsorbates.

In this chapter the study of Mn atom manipulation on the \{110\} GaAs surface is presented. The position of the Mn adsorbate (adatom) is extracted from STM measurements, and the contrast observed is explained considering its electronic properties. The adatom's properties are investigated in different doping environments and the differences in behaviour between Mn on n- and p-doped substrates are explained. For Mn adatoms on p-doped GaAs three atom manipulation techniques are presented. The influence of several parameters on the outcome of the manipulation process is investigated.

5.1 Introduction

Manipulation of single atoms by STM, as discussed in chapter 3, is commonly performed on metallic or insulating surfaces [60, 55, 122]. Atom manipulation on semiconductor surfaces instead, and in particular the manipulation of dopant atoms, remains a less explored field.

Dopant atoms are particularly interesting because they effectively influence the electronic and magnetic properties of the semiconductor [115], which give them great technological importance. Complexes of dopants, controllably built by STM, represent the ultimate limit in the miniaturization of semiconductor devices [72, 39] and they can be used as quantum structures with robust properties [72, 103]. These structures are potentially interesting for the realization of qubits based on a single atom [66] and they can give important insight into the interaction between dopants, which ultimately regulates the properties of semiconductor materials [101, 70].

The first example of atomic manipulation for dopant adatoms has been shown for a small set of transition metal atoms (Mn, Fe, Co) on a \{110\} GaAs surface by Kitchen et al. [70]. In their work two different manipulation processes have been studied: the first is the movement of an adatom on the surface by hopping to a neighbouring position; the second is an exchange process between the Mn adatom
CHAPTER 5. STUDY AND MANIPULATION OF MN ADSORBATES.

and a Ga atom in the surface, which results in the creation of an embedded Mn dopant, substituting for Ga in the GaAs surface, and a Ga adatom. By employing these two processes is possible, in principle, first to build a desired structure with Mn adatoms and then to embed the adatoms in the GaAs surface layer, preventing further manipulation.

The main issue in this approach concerns the lack of control on the manipulation process’ outcome. Both the movement and the embedding process are triggered under similar conditions [70, 45], which limits our capability to move Mn adatoms over the surface without inducing an embedding event. This issue has limited the size of the structures built with this method to pairs of Mn atoms, oriented along different directions on the surface [70]. In this work the behaviour of Mn adatoms on the GaAs \{110\} surface is studied in depth by STM. The influence on the manipulation outcome of several parameters, such as the bias voltage and the tunneling current applied by STM or the doping environment, is investigated. Furthermore new atom manipulation techniques are developed, which made it possible to build larger structures like trimers and tetramers of Mn atoms.

5.2 Experimental Methods

The experiments are performed with a Low Temperature Omicron STM, at a temperature of 5 K. Electrochemically etched W tips are used for the STM measurements and a clean and atomically flat \{110\} GaAs surface is prepared by cleavage under UHV condition (around 2 \cdot 10^{-11} mbar). All the measurements are taken in constant current condition, using a feedback loop to adjust the tip-sample distance and maintain the tunneling current constant. The voltage indicated in the STM experiments is applied to the sample.

The sample consists of a p-doped GaAs wafer (10^{19} at/cm^{3}) on which three layers have been grown with different Be doping concentrations, ranging from 10^{16} to 10^{18} at/cm^{3}. A similar n-doped sample is also used, grown on a n-doped GaAs substrate (10^{18} at/cm^{3}) with three layers of different Si doping concentrations. The deposition of Mn on the cleaved GaAs surface is performed in-situ with an Omicron EFM3s electron beam evaporator. For the evaporation a beam of electrons is used, corresponding to a current of 3 mA, accelerated by an electric field of 800 kV onto the target, a rod of pure Mn, for a time between 20s and one minute. Under these conditions a low Mn coverage is obtained, between 10^{10} and 10^{11} at/cm^{2} (corresponding to 0.001 ML). In order to prevent damage to the surface an electrostatic lens is used to deflect any Mn ions created in the electron bombardment of the target and allowing only the neutral atoms to reach the surface.

5.3 Adsorbate properties

The capability of the STM to image with atomic resolution is employed to study Mn atoms adsorbed on the GaAs surface. The identification of the Mn feature is possible by comparing images of the surface before and after the Mn evaporation. A study of the Mn adsorbates and how their properties are affected by the
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Figure 5.1: STM images for a Mn adatom. In a) the filled state image is shown, measured with $V = -2.0\, V$ and $I = 100\, pA$. In b) the empty state image is shown, taken with $V = 1.05\, V$ and $I = 15\, pA$. The red cross mark again the position of the Mn adatom. In c) the schematic GaAs surface is shown with the estimated location of the Mn adatom.

surrounding doping environment are reported in the following sections.

5.3.1 p-doped GaAs

On p-doped GaAs the Mn is adsorbed as an adatom on the surface. Two STM images of the adatom, taken in filled ($V_s < 0$) and empty state ($V_s > 0$) imaging condition, are shown in Fig.5.1. The contrast observed in filled state condition is consistent with the feature reported in previous studies [70, 45]. Furthermore the manipulation processes that have been previously described for Mn adsorbates are also observed, confirming that the feature is associated to a Mn adatom.

The contrast observed in the filled state condition, displayed in Fig.5.1a for a (110) surface, consists of a faint bright protrusion surrounded by a dark depression, slightly elongated and pointing in the [001] direction. In Fig.5.1b the empty state image is shown where the Mn appears as a bright star-like feature, which has not been reported in previous studies. The protrusion in this case is very high (6 Å) and is surrounded by an extended contrast with two mirror planes and elongated along the [110] direction.

The origin of this contrast can be qualitatively explained considering the electronic properties of the adsorbate. Several metallic adsorbates, including Mn, are
known to introduce donor states within the bandgap of GaAs and other semiconductors [92]. In p-doped samples the Fermi energy lies close to the valence band and the electronic state introduced by a Mn adsorbate is located above the Fermi level position. Therefore the Mn donor state is empty and positively charged, and the Coulomb potential bends the bands downwards close to the surface. When the Mn concentration is sufficiently high the presence of donor states will pin the Fermi level position [92]. However, our STM measurements show that the low coverage of Mn is not sufficient to reach this condition in our samples.

It is well established that a Mn atom incorporated in the surface layer at a substitutional Ga position behaves as an acceptor [41]. In experiments with a clean \{110\} GaAs surface two different contrasts are observed for this feature, depending if the Mn level is filled with an electron or it is empty [107]; the electric field of the tip is used to move the Mn level above or below the Fermi level. In our experiments, when Mn adatoms are on the surface, it is still possible to observe both features for the substitutional Mn, indicating that the Fermi level is not pinned by the Mn adatoms nearby. A scheme qualitatively describing the tip induced band bending and its effect on the charge state of the Mn adatom is shown in Fig. 5.2.

As it can be observed in Fig. 5.2b, in empty state imaging condition the adatom’s energy level lies above the Fermi level and the Mn has a positive charge. The empty state of the adatom constitutes an additional path for the electron tunneling from the tip to the sample, enhancing the total tunneling current and resulting in a bright feature in the STM image (Fig. 5.1b). Moreover the Coulomb potential bends the bands downwards in proximity of the surface, increasing the number of states from the GaAs conduction band available for tunneling. This contribution increases the tunneling current causing the feedback loop to retract.
the tip farther away from the sample, in order to maintain the current constant. This results in a long range and circular symmetric contribution to the Mn feature in the topography image. The extension of the contrast, which is spread over several nanometres, and the complex symmetry of the feature indicate that the Mn states are hybridized with the surface states. This suggest that the Mn strongly interacts with the surface, forming a partly covalent and directional bond, as it has been reported for Mn on InAs \cite{117}. Conversely under filled state imaging conditions (Fig. 5.1a) the Mn donor state is filled with an electron and is neutral.

We argue that the contrast originates from two contributions \cite{113}: the first component is a dark depression, which is due to the interaction of the adatom with the GaAs surface states. This effect can be understood comparing two situations: when the tip is on the bare GaAs the surface states contribute to the tunneling current, giving rise to the atomic corrugation of the (110) surface in the STM image. When the tip is in proximity of the adsorbate, the surface states are perturbed by the adatom and are shifted out of resonance with respect to the unperturbed surface states \cite{113}. As a consequence the contribution to the tunneling current arising from the surface states is reduced in proximity of the adsorbate, resulting in a depression. The second component is due to tunneling of electrons out of the adatom state, which gives rise to the protrusion present in the centre of the feature. This process however does not seem to be efficient under the filled state condition and the feature is very weak. An analogous analysis has been used to explain the contrast associated to adatoms on metal surfaces \cite{113}.

The comparison between the two images in Fig. 5.1 allows us to determine the precise position of a Mn adatom on the GaAs surface. If the growth direction is assumed to be the [001], the surface obtained after cleavage can be identified using the orientation of the Be wavefunction at positive voltage \cite{85}. From Fig. 5.1a the position of the adatom with respect to the As sub-lattice, which is probed under filled state imaging \cite{30}, is extracted. The position of the adatom is taken as the local maximum of the faint bump present in Fig. 5.1a. A schematic representation of the surface is shown Fig. 5.1c. The position found for the Mn in the surface unit cell is \[ x/a = 0.61 \pm 0.1 \] and \[ y/b = 0.54 \pm 0.04 \], where \( a, b \) are the lattice parameter for the surface cell. In the empty state image instead the Ga sub-lattice is probed \cite{30} and under these conditions the Mn adatom wavefunction has two mirror planes, across the [110] and the [001] directions. This observation suggests that the Mn adatom is sitting exactly in between two surface Ga atoms along the [001] direction, giving as expected position for the adatom \( x/a = 0.68 \) and \( y/b = 0.5 \). Since it is obtained from purely geometric arguments, this result has no uncertainties and it is in agreement with the position obtained from the analysis of the filled state image.

The accurate knowledge of the adatom position is an important starting point for a deeper understanding of the properties of an adatom and of the atom manipulation phenomena. Our result for the Mn adatom position is in agreement with the position predicted by means of the DFT+U method \cite{45}, which is in contrast with previous simulations not taking into account the correlation correction \cite{12}. The information obtained in STM experiments provide a valuable confirmation of results based on DFT simulations \cite{12, 121, 45} and can be used as a starting point.
point for the modelling of the manipulation process and its underlying reaction mechanism [117].

5.3.2 n-doped GaAs

The influence of the doping environment on the properties of Mn adatoms is investigated by depositing Mn on a n-doped GaAs substrate. Important differences in behaviour are observed with respect to Mn on p-doped samples, discussed in the previous section. The first difference is that the features introduced on the GaAs surface after Mn evaporation could not be moved under the influence of the tip. Furthermore the shape of the features is compatible with the contrast originating from a Mn in the substitutional Ga position [107]. These experimental observations suggest that the Mn deposited on a n-doped substrate become spontaneously embedded in the GaAs surface layer, as it has been reported for the case of Mn in InAs [117].

The different incorporation’s probability for Mn adatoms in n and p-doped environment can be qualitatively explained considering the different position of the Fermi level in the two systems. A simple schematic representation of the band bending configuration is depicted in Fig. 5.3.

As previously discussed metal adatoms, such as Mn and Ga, introduce a donor state in the bandgap of GaAs [92]. In p-doped GaAs the adatom state is above the Fermi level, thus empty and positively charged, and the Coulomb potential bends the bands downwards in proximity of the surface [128]. A Mn atom in the surface layer of GaAs instead introduces an acceptor state, still located above the Fermi energy but neutral. When a Mn adatom is embedded it becomes a neutral acceptor [43] and a Ga adatom, which as previously discussed is a positively charged donor, is extracted. As a result the bands are still bended downwards and the Fermi level position at the surface is not substantially changed.

In the case of n-doped environment the energy level introduced by metal adsorbates is below the Fermi level, and the related donor state is filled and neutral. Conversely, when the Mn is embedded, the acceptor level that is introduced is negatively charged and bends upwards the semiconductor bands. Considering a system where the Mn is initially found as an adatom, the formation energy for a Mn impurity in the substitutional Ga position is given by

\[ E_{\text{for}}(q) = (E_M + \mu_Ga) - (E_0 + \mu_{Mn}) + qE_f, \]  

where \( E_{\text{for}} \) is the formation energy, \( E_M \) is the total energy of the system including the Mn defect in substitutional position, \( E_0 \) is the total energy of the system without the Mn and \( \mu_{ad} \) is the chemical potential for the adsorbate \((ad = Mn, Ga)\).

The last term describes the electrostatic contribution, where \( E_f \) indicates the Fermi energy in the system, measured with respect to the valence band maximum.

In the p-doped environment a Mn acceptor is neutral and the electrostatic background is not changed after the Mn embedding: the positively charged donor state of the Mn-adatom has been replaced by a positively charged Ga donor. Thus the formation energy for a Mn acceptor depends only on the difference between the first two terms. In the case of n-doped samples instead the Mn acceptor state is
negatively charged, so the last term will give a negative contribution to the formation energy, stabilizing the system. Intuitively the stabilization can be understood as the result of the removal of one electron from the Fermi level and its placement in the lower energy Mn level. This additional energy gain explains the more favourable embedding of Mn in n-doped with respect to p-doped environments and why we do not observe Mn adatoms in n-doped samples. Since it is not possible to move Mn adatoms on the surface of n-doped GaAs we will focus, for the rest of this study, on the manipulation of Mn on the surface of p-doped GaAs.

5.4 Atom manipulation process

At the moment the main challenge in the field of dopant manipulation in semiconductor is the lack of control on the manipulation outcome. A possible route to overcome this limitation is to explore new atom manipulation techniques. In this work three different manipulation techniques have been successfully implemented for Mn adatoms: the first one, which we call ‘Point Mode’, has been applied by Kitchin et al. [70]. In this manipulation technique the tip is placed close to or on top
of the adatom; then the feedback loop is turned off and the voltage is swept, while
the tip-sample distance is kept constant. During this process the manipulation of
the adatom occurs. The second method is called 'Scanning Mode' manipulation,
it has has been developed for Mn in this work and consists in scanning an area
with Mn adatoms at positive voltage. Unlike in the Point Mode manipulation,
the feedback loop is kept active during the manipulation process, controlling the
tunneling current involved in the manipulation event. An additional advantage of
this technique is the possibility to manipulate several adatoms in a single image,
increasing the number of adatom sampled in similar condition, which is important
to build reliable statistics. The last method used in this study is called 'Pulse
Mode' manipulation; in this manipulation technique a single high voltage pulse
\( V = 4V, t = 20pA \) is applied at any point during a scan of the surface at positive
voltage. This step is quite delicate, since the same procedure is used for the condi-
tioning of the tip: if the tip is not sufficiently stable, it can even desorb and deposit
small W clusters on the surface; if the voltage is too low the manipulation will not
take place. When the process is successful several Mn adatoms are simultaneously
manipulated, over an area of several tens of nanometres. The behaviour of Mn
adatom in these three different manipulation processes will be now investigated.

A deeper insight in the process taking place during the Point Mode manipula-
tion is obtained recording the tunneling current during the voltage sweep \[ \text{[70]} \]. If
the tip is in proximity to an adatom, a spike in the tunneling is observed between
\( V = 0.7V \) and \( V > 1V \). This feature originates from the fact that the Mn adatom
has moved, and its state, which was an available tunneling path, is not access-
ible any more, causing an abrupt decrease of the tunneling current. Two possible
outcome are reported for this atom manipulation process:

1. Movement: the Mn adatom hop to a neighbouring position on the GaAs
surface. This movement is highly directional and, considering a (110) surface,
it seems to occurs preferentially along the [001] direction \[ \text{[70, 45]} \].

2. Embedding: the Mn adatom exchange its position with a Ga atom from
the surface layer and, as a result, a Mn dopant is included in the surface
layer, while a Ga adatom is extracted as an adatom on the surface. The
Ga adatom can be moved similarly to the Mn atom \[ \text{[45]} \], but the reverse
process of exchange between the Ga adatom and the surface Mn has a very
low probability to occur.

In both cases, as a result fo the manipulation process, the Mn is moved to a
new position. The distribution of the final Mn position after a manipulation event
is represented in Fig.5.4. For this plot a data set including 37 movement and 28
embedding events is considered, where different tip-sample relative position are
chosen to ensure that the outcome is independent from the positioning of the tip
with respect to the adatom.

The plot in Fig.5.4 shows the initial Mn position (red dot) and the probability
to find the final Mn location in one of the neighbouring surface unit cells for the
movement and the embedding process. It can be observed, from Fig.5.4a, that the
most probable movement event is a single hop of the Mn adatom along the [001]
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Figure 5.4: Distribution of the Mn position probability on a (110) GaAs surface after a movement and an embedding event. The red dot marks the initial position of the Mn adatom and $N_x$, $N_y$ are the indices the unit cells on the surface. For both the movement and the embedding process the most likely outcome is to find the Mn in the neighbouring surface cell along the [001] direction, showing the strong anisotropy for both processes.

direction, when a (110) surface is considered. Long range movement is also possible and can be interpreted as the result of sequential single hops. The movement probability along the [110] direction instead is much lower and symmetric with respect to the initial Mn position. The outcome of the embedding process is shown in Fig. 5.4b, where the final position of the embedded Mn is marked again in red. The most probable outcome of the process is to have a Mn embedded in the next surface cell along the [001] direction.

The strong anisotropy along the [001] direction for both processes is an indication that the Mn adatom form strong covalent bonds with the underlying substrate. This observation suggests that during a manipulation event the Mn adatom goes through several intermediate steps of a chemical reaction, in which old bonds are broken and new bonds are formed, giving a precise and reproducible outcome. The possibility to induce similar processes by STM has been demonstrated for other systems, such as vacancies on InP [76] or embedding of Mn adatoms in InAs [117].

It has been reported [70] that the position of the tip with respect to the adatom has some influence on which manipulation process is triggered (embedding or movement), but this weak dependence does not allow enough control to build structures larger than two atoms. The probability to embed the adatom while attempting to move it across the surface is high and the embedding process is not reversible. The combination of these two factors is a substantial obstacle in the realization of structure of dopants larger than a pair.

The experiments performed with the Scanning Mode manipulation presents the same outcomes and anisotropy in the movement of Mn adatoms as the Point Mode, but this method has the advantage to be more controlled and to provide a larger statistical sampling within a single measurement. The steps of the manipulation process are described in detail Fig. 5.5. In the first step an area with Mn adatoms is imaged at negative voltages, as shown in Fig. 5.5a. Under this condition the manipulation does not occur (passive condition) and the position of the adatoms
can be determined. In the next step, shown in Fig. 5.5b, the surface is scanned under positive voltage condition. When the STM tip is close to a Mn adatom, a manipulation event can take place, inducing a change in the contrast in the STM image (active condition). Both an embedding and a movement of the adatom can take place. Finally in Fig. 5.5c the outcome of the manipulation processes is checked with a scan at negative voltage.

This additional control on the manipulation process allows a more systematic study of the manipulation events and their dependence from the voltage and the tunneling current involved with the STM measurement, which will be performed in the next section.

The last manipulation technique introduced in this work is called ‘Pulse Mode’ manipulation. Also in this case both embedding and movement events are observed as outcome of the manipulation, but many atoms are simultaneously manipulated and the movement occurs preferentially along the [110]/[110] direction, in this case. These differences with the manipulation methods previously described suggest that another mechanism is behind the Mn movement, maybe related to the excitation of phonons in the GaAs lattice or to the injection of a large number of minority carrier\(^{29}\), which recombining could provide the energy necessary for the manipulation to distant Mn adatoms.

Interestingly, several pairs of neighbouring Mn atom are formed using this manipulation process. The formation of pairs with the Pulse Mode manipulation is investigated by statistical analysis. This manipulation technique is applied on 16 different \(50 \times 50 \text{nm}^2\) areas, and as a result 6 different pairs and 1 triplet of Mn atoms are formed. This result indicates that there is a clear difference between the distribution of Mn adatoms and the distribution of substitutional Mn obtained after the manipulation process. Using combinatorial calculus we can calculate the probability to find these atoms disposed in a configuration where no first or second neighbour pair are present, assuming a random distribution of the atoms and a low surface coverage of Mn. In an area of \(50 \times 50 \text{nm}^2\) there are on average \(n_{\text{Mn}} = 24\) Mn adatoms and there are about \(N = 11603\) available sites for the Mn adsorbates. The probability for not finding any pair in the 16 images considered is \(P = 0.818\), which means that the probability to find a pair or a larger cluster composed of neighbouring Mn atoms is \(P = 0.182\).

From this result we would expect to observe a Mn adatoms’ pair every 5-6 \(50 \times 50 \text{nm}^2\) images. No nearest neighbour pair of Mn adatoms is observed instead in the 16 images considered, which put this result outside the 2\(\sigma\) confidence interval and indicates that the distribution of Mn adatoms on the surface is not random. In previous studies \(^{75}\) the presence of a Coulomb potential around the Mn adatom has been demonstrated, which could explain the reduced probability to find adatoms’ pairs. As soon as a Mn adatoms becomes embedded the atomic state turns from a donor character to an acceptor character. The acceptor’s state is above the Fermi level in p-doped GaAs and will remain empty and neutral, as shown in Fig. 5.3. There is no Coulomb interaction between a neutral Mn acceptor in the GaAs surface layer and a negatively charged donor introduced by a Mn adatom: hence pairs composed of a Mn adatom and a Mn in the GaAs surface can be formed. Therefore we argue that the formation of a pair of Mn atoms in
Figure 5.5: STM images of the different steps in the manipulation procedure. In a) the initial positions of Mn adatoms are revealed at negative voltage ($V = -2V$, $I = 50pA$), when no manipulation events take place. In b) the image of the same area at positive voltage is shown ($V = 1.1V$, $I = 50pA$). Under these condition embedding and movement of the adatoms take place. The changes in the adatoms’ positions are verified by another image taken at negative voltage, shown in c) ($V = -2V$, $I = 50pA$).
the GaAs surface is the result of a two step process: first the excitation induced by the voltage pulse cause the movement and the embedding of the first adatom, then a second Mn adatom can be moved to a neighbouring position and become embedded.

In our experiments many pairs have been created with this manipulation method, around 100 considering also larger Mn assemblies. This observation suggests the existence of a mechanism favouring the formation of Mn pairs in the GaAs surface. There are several physical processes which could be responsible for this effect: it could be a sort of chemical interaction between the Mn adatom and the Mn acceptor, which favours the formation of a donor-acceptor pair. Another explanation could be related to an enhancement of the structural stability of the surface. It has been shown in the work from Richardella et al. [107] that a Mn atom embedded in the surface layer can induce a change in the GaAs surface reconstruction. It is possible that the presence of Mn pair reduces the total energy of the system, with respect to the configuration with two isolated Mn atoms, through a complex relaxation process. A deeper investigation of this phenomenon is required to determine the origin of this pairing effect.

5.5 Control on the manipulation outcome

The most direct approach to improve our control on the manipulation processes is to study in detail the outcome’s dependence on the parameters involved in the manipulation process. In this part of our work the Scanning Mode manipulation, described in the previous section, is employed to study the influence on the manipulation’s outcome of two parameters: the bias voltage applied between the STM tip and the sample and the tunneling current. This experiment is performed on the p-doped (Zn) substrate, with a doping concentration around $10^{19} \text{at/cm}^3$. A schematic representation of the manipulation process is shown in Fig.5.5.

We are interested in finding two distinct sets of manipulation conditions for which either the movement or the embedding of the Mn adatom is favoured. The manipulation events are classified considering only the initial and the final state of the adatom: if a Mn adatom becomes embedded, the event is classified as embedding, even if the adatom has also been moved over the surface before the incorporation. The event is counted as movement only if the Mn remains on the surface as an adatom. We choose this classification in order to optimize the manipulation process for building structures of dopants. When a Mn adatom is incorporated in the surface, the probability of the reverse process is very low, preventing further manipulation of that Mn atom. The embedding process then a limit to our capability to move a Mn adatom across the surface and this classification ensures that Mn adatoms which has been moved remain available for further movement.

The results obtained for the manipulation probability as function of voltage (Fig.5.6a,b) and tunneling current (Fig.5.6 c,d) are shown in Fig.5.6. In Fig.5.6a) the outcome of the manipulation process is studied under low current condition ($I = 15\text{pA}$). The probability for embedding or moving the adatoms are very low for voltages below 1.1V; between 1.1V and 1.2V a steep increase in the em-
Figure 5.6: Probability for embedding and moving an adatom as function of voltage and current, applied by STM during the manipulation process. In a) and b) the voltage dependence is shown for two different current conditions, 15 and 30 pA respectively. In both series a threshold is observed between 1.1 and 1.2 V for the embedding probability, which dominates at high voltage. In c) and d) the dependence of the manipulation probability on the current is reported for voltages below and above the embedding threshold.

Another observation from the plots in Fig. 5.6 is that for voltages above the embedding threshold the movement probability stays low. For \( V \geq 1.2V \) the embedding probability dominates and is the most probable process. In Fig. 5.6b) the result of the manipulation processes with an higher tunneling current (\( I = 30 \text{pA} \)) is shown: at low voltage the probability for the embedding process is still low, while an higher movement probability is reported. The embedding probability rises and dominates over the movement at higher voltage conditions. In panel c) the manipulation probability under a voltage of 1.1V is reported. It is clear that an increase in the current does not have a large influence on the embedding and the movement probability, in contrast with the highly non-linear dependence of the embedding probability on the voltage. In panel d) finally the manipulation probability for a voltage above the threshold (\( V = 1.2V \)) is shown. Under these conditions the change in the current does not affect much the manipulation probability, which is dominated by the embedding process.

Another observation from the plots in 5.6 is that for voltages above the embedding threshold the movement probability is generally low. This is a consequence of our classification of the manipulation event: above the embedding threshold a Mn adatom can still be moved on the surface remaining available for a new manipulation event. Since the embedding probability is high it is likely that an embedding event will eventually occur, and the manipulation process will be classified as an embedding event. The presence of a threshold voltage for the embedding
probability can be explained in two ways:

- the embedding process occurs when the tip is able to efficiently inject electrons in the empty state of the Mn adatom. The electrons lose their energy by inelastic scattering and some energy is transferred to the lattice as phonons. The excitation of vibrational modes of the adatom brings the system in an excited state, where the energy barrier for the exchange between the Mn adatom and the surface Ga can be overcome. Since this process requires the tunneling of electrons in the Mn state, it can occur only when the tip is positioned in proximity to the adatom (within 1-2 nm).

- the embedding process occurs when the voltage applied on the tip is sufficient to bend the potential landscape of the sample and reduce the barrier for the embedding process. Under positive voltage conditions (when the manipulation occurs), the Mn adatom is positively charged (empty donor) and the Coulomb interaction with the negatively charged STM tip would be attractive. The Coulomb interaction between the tip, the sample and the adatoms extends over several nm ($\approx 10$ nm or more) [35].

Our results can be explained only with the first model, since the embedding process always take place when the tip is in proximity to the Mn adatom, regardless of the magnitude of the positive voltage applied. In the second model if the applied voltage is sufficiently high, the embedding process should take place also when the tip is further away from the Mn adatom. The probability for the movement of Mn adatoms increases linearly with the current when the voltage applied is below the threshold for embedding. At voltages above the threshold for embedding the movement probability is low, arguably due to the fact that also the embedding process is now available for the adatoms.

In conclusion we have found a set of parameters for which the embedding is the favoured manipulation process (high voltage, low current) and another set of parameters which promotes the movement instead (low voltage, high current). It should be noticed that these experiments are performed on the highly p-doped substrate ($10^{19}$ at/cm$^3$). These results represent the first step towards more refined atom manipulation techniques, where the atom manipulation process is combined with an atom-tracking technique [124]. This technique could potentially improve the efficiency of the Mn adatom movement process.

### 5.6 Conclusion

The study of Mn atoms deposited on a {110} GaAs surface indicates that the doping environment has a decisive influence on the adatoms’ behaviour. It is shown that in a n-doped environment the Mn is spontaneously incorporated in the surface layer after the deposition. We argue that the acceptor level introduced by the surface Mn is filled with an electron from the Fermi level, lowering the total electronic energy of the system and driving the incorporation process. In p-doped environment it is observed that the Mn is adsorbed on the surface. The adsorption
position is estimated from the STM images obtained, both under filled and empty state imaging conditions, is reported and explained qualitatively.

Two new atom manipulation techniques are developed, in order to overcome the limitations of the existing manipulation process. The first method, called Scanning Mode, is employed to gain a deeper insight into the dependence of the manipulation’s outcome on the most important STM parameters (V,I). Two regions in the parameter space are identified, one where the incorporation of a Mn adatom is the most likely process and the other where the movement of the adatom on the surface is favoured. The second method, called 'Pulse Mode' manipulation, is successfully employed to build assemblies of Mn in the GaAs surface layer such as pairs, trimers and tetramers, which are larger than the structures previously reported. The investigation of the electronic properties of these structures will be presented in the next chapter.
Chapter 6

Properties of Mn assemblies.

In this chapter the electronic properties of Mn assemblies, created by STM, are investigated. STM spectroscopy measurements provide a combination of electronic and spatial information, which will prove to be crucial for the understanding of the magnetic interaction between Mn atoms. The analysis of Mn pairs aligned along different crystal directions shows an anisotropic Mn-Mn interaction, which is nicely reproduced in Tight Binding (TB) simulations taking into account the surface of GaAs \[119\]. More complex assemblies, with up to four Mn atoms, are created and analysed in this chapter. The observed Mn-Mn interactions obtained in larger structures follow the results obtained for Mn-Mn pairs.

6.1 Introduction

The STM manipulation techniques developed in the previous chapter, together with the insight in the manipulation process, allow us to build Mn assemblies, where two or more Mn atoms substitute for Ga atoms in the surface layer in neighbouring positions. As discussed in section 2.4.1, Mn is a magnetic acceptor and in GaAs it retains an electronic spin \(S = \frac{5}{2}\). The magnetic interaction between Mn atoms can be exploited to create ferromagnetic semiconductors \[101\]; in order to control and enhance the magnetic properties of the material the nature of the coupling between Mn dopants has been investigated.

Nowadays it is commonly accepted that the magnetic coupling between the Mn core electrons is mediated by the holes, injected and spin polarized by the Mn acceptor; the itinerant holes interact with the core level by a p-d exchange mechanism\[24\]. This interaction has been explored with STM measurements performed on Mn pairs by Kitchen et al. \[70\], which demonstrated that Mn atoms show ferromagnetic coupling only when the pair is aligned along specific crystallographic directions. In this study the ferromagnetic coupling between two Mn atoms was detected in the STM analysis as a splitting of the Mn acceptor state. A toy model of the Mn-Mn interaction \[119\] clarifies the origin of the splitting: when the electronic spin of the two Mn atoms are aligned, also the spin states of the holes bound to the Mn will be the same. The two holes, having an identical set...
of quantum numbers, will interact forming a bonding and an antibonding state. Conversely, if the two Mn are antiferromagnetically coupled, the two holes have different spin states and the two Mn levels will remain degenerate. This model is very useful to interpret our experimental result and shows that we can probe the magnetic coupling in a Mn pair even without a spin polarized tip or a magnetic field.

In this chapter we study in depth the Mn-Mn coupling in pairs oriented along different crystallographic directions. The electronic properties of the pairs combined with spatial information on the extent of the states introduced in the GaAs bandgap give insight into the magnetic interaction in these structures. Complexes with more than two atoms will also be investigated and their electronic properties are compared to Mn pairs.

6.2 Experimental methods

The Mn complexes in GaAs are created by STM using the ‘Pulse Mode’ manipulation, described in the previous chapter. The atom manipulation and the STM measurements are performed at 5 K on a \{110\} GaAs surface. The electronic properties of the Mn assemblies are investigated by STM spectroscopy, exploiting the direct proportionality between the Local Density of States (LDOS) and the derivative of the tunneling current with respect to the voltage \(\frac{dI}{dV}\) \[129\].

Two spectroscopy techniques have been employed in this study: the first is simply called Scanning Tunnel Spectroscopy (STS) and allow us to measure the LDOS in one specific point. In the STS analysis first the tip is placed on top of the Mn assembly, then the voltage is varied and the I(V) curve is recorded, while the tip-sample distance is kept constant. Before the acquisition of an I(V) curve the tip is approached to the sample (typically \(\Delta z = 0.2 \text{ nm}\)), in order to increase the signal to noise ratio and resolve better the states introduced by the Mn within the band gap. The derivative of this curve \(\frac{dI}{dV}(V)\) is subsequently calculated numerically. Current Imaging Tunneling Spectroscopy (CITS) is the second spectroscopy technique used in this study \[49\]. In this method a constant current STM image is acquired, using the feedback loop to maintain a constant tunneling current by adjusting the tip-sample distance. Simultaneously an STS measurement is performed for each point in the image. The result is a 4-dimensional matrix of data \(I(x,y,z,V)\) which contain a combination of electronic and spatial information. Also for this technique the \(\frac{dI}{dV}(x,y,z,V)\) is calculated by numerical derivation.

6.3 Results and discussion

Some examples of Mn assemblies created by ‘pulse mode’ manipulation are shown in Fig. 6.1. In filled state condition (Fig. 6.1 a,c) the contrast for a single Mn incorporated in the GaAs surface is a dumbbell-like feature with two lobes along the [110] atomic row \[107, 75, 71\]. The Mn is located in the centre of the feature and the two lobes correspond to the position of the neighbouring As atoms. In empty state imaging conditions the acceptor level introduced by the Mn is empty.
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Figure 6.1: STM images of different Mn pairs, created by Pulse mode manipulation. In a),c) the filled state images are shown, acquired with $V = -2.5 \, \text{V}$ and $I = 50 \, \text{pA}$ and in b),d) the empty state images are reported, taken with $V = 1.55 \, \text{V}$ and $I = 30 \, \text{pA}$. In a,c) a pair and a trimer of Mn atoms along the [001] direction can be observed. In c), d) the image of a pair along the [110] direction is shown.

and the wavefunction of the hole bound to the Mn can be imaged; as a result a crab-like feature is observed, asymmetrically elongated along the [001] direction [107, 41].

In Fig.6.1a,b a pair and a trimer of Mn atoms, aligned in the [001] direction, are shown. In Fig.6.1b the feature in the top right corner can be identified, by comparison with previous studies [70], as a pair where two Mn atoms are sitting in the nearest neighbour Ga position along the [110] direction. In these images a first hint of the difference in behaviour between the [001] and the [110] pair can be observed. When Mn atoms are aligned along the [001] direction, the Mn features remain identical in shape to the single Mn features, both for empty and filled states (Fig.6.1a,b). Conversely for a Mn pair along the [110] direction the contrast shows relevant changes, both at negative and positive voltages.

6.3.1 Single Mn spectroscopy

The results of a spectroscopy measurements on an isolated surface Mn are shown in Fig.6.2. The STM image of the Mn feature, used as a set point for the CITS measurements, is shown in a). In b) the $dI/dV$ curve, acquired in the centre of the Mn feature, is plotted as function of voltage, after the application of a Savitzky-Golay low pass filter. The GaAs band gap can be extracted from this measurement (around 1.5 eV); the states of the valence and conduction band are probed at negative and positive voltage, respectively [53]. The presence of a Mn acceptor introduces two peaks, one within the bandgap (Mn1, at around 0.8 eV)
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Figure 6.2: Spectroscopic analysis of a single Mn atom in the surface layer of GaAs. In a) the STM image of the dopant is shown, taken at $V = -2.5 V, I = 50 pA$. In b) the comparison between the $dI/dV$ curves obtained in the centre of the Mn (red circle in figure a) and the $dI/dV$ curve for bare GaAs is shown. The presence of the Mn introduces a small peak around $0.8 eV$, a shoulder around $1.2 eV$ and another peak around $1.75 eV$. In c) and d) two cuts of the CITS measurement, along the directions marked with the arrows, are shown.

and one close to the edge of the conduction band (Mn2, at around $1.75 \text{ eV}$).

In Fig.6.2c and d two color plots of the CITS data are shown, along the arrows displayed in panel a). The $dI/dV$ information is obtained by numerical derivation and the high frequency noise is removed by applying a low pass filter. In these measurements the spatial extension and the shape of the features introduced by Mn dopants can be explored. The states introduced by Mn appear asymmetrically elongated in the $[001]$ direction, in agreement with the symmetry of the crab-shaped wavefunction observed for a surface Mn in Fig.6.1b. Close to the edge of the valence band, around $V = -0.6 eV$, an unstable behaviour of the Mn atom is observed, characterized by local and irregular spikes in the $dI/dV$ plot. This observation is in agreement with the work from Richardella et al. [107], where it is shown that the dumbbell feature stems from the switching between two single-lobed features. These features originate from a spontaneous distortion of the bonds between Mn and the neighbouring As on the surface: one of the As will be buckled up with respect to its unperturbed position and the other As will be
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Figure 6.3: Representation of the tunneling paths accessible in the STM measurements. In the first tunneling path, observed at lower voltages, an electron is injected in the Mn level and can be transferred to other acceptor states from the impurity band of the p-doped substrate. In the second tunneling path, instead, the electron is injected in the Mn and is subsequently transferred to the conduction band of GaAs.

buckled down. When the voltage applied by STM is low, a switch to the specular feature is possible, which can be detected in CITS measurements as an instability in the tunneling current. Higher voltages will increase the switching rate until only the average between the two features will be observed, as shown in Fig.6.2a) [107].

Several theoretical studies [126, 119] predict that a Mn dopant introduces only one state within the GaAs bandgap. We attribute the presence of two peaks (around 0.8eV and 1.75eV) in the spectroscopy measurement to the existence of two different tunneling path involving the empty Mn state, schematically represented in 6.3. We argue that in the first tunneling path, observed when a low positive bias is applied, an electron is first injected into the Mn state and then diffuses in the p-doped GaAs impurity band through sequential tunneling into the states of other acceptors, as in the tunneling process proposed by Munnich et al. [94]. The second tunneling path is accessible at higher voltage and involves the tunneling of an electron into the surface states in conduction band, through the Mn state [43].

One issue that needs to be addressed in STM spectroscopy measurements is the influence of the tip work function [35]. Tips with different work function introduce a different Tip Induced Band Bending (TIBB, see section 2.3.2), which changes the potential landscape introduced by the tip and can shift the voltage position of the peaks [42]. The tip work function can also change as a consequence of tip modification events, since the work function depends on its microscopic structure, making the comparison between different experiments potentially challenging. Interestingly the voltage position of the first Mn peak is reproduced in several studies [70, 75, 119], and it has been reported that its position does not change with the tip work function [75]. This observation is only true for Mn atom inside the surface layer and does not hold for subsurface dopants [41]. The origin behind this effect is not well understood, but it allows us to compare results from the Mn1 peak even if they are obtained with different tips. The voltage position of the Mn1 peak is also used as a reliable link between the voltage and the energy scale: the presence
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of an offset between the two energy scales cannot be ruled out, but we assume that the features related to the Mn1 peak occur at the same energy.

Another feature observed in our spectroscopy measurements is the region of Negative Differential Resistance (NDR), which is found after each Mn peak. This feature is reported in several other STM studies [71, 83]. The origin of this feature is not completely understood and it cannot be explained in the framework of the Tersoff-Hamman approximation [129], but it is interpreted as the result of a resonant tunneling process between tip and sample. In the following part of our study we will use the spectroscopy on an isolated Mn atom as a reliable term of comparison for the spectroscopy measurements on a Mn assembly.

6.3.2 Mn pair spectroscopy

In this study 87 pairs of Mn dopants have been created by Pulse Mode manipulation. Two Mn atoms in the 1st or in the 2nd nearest neighbour position (considering the Ga sublattice) are treated as a pair. It has already been shown that the interaction between two Mn atoms greatly depends from the orientation of the pair [70]. In this section we will use STS and CITS measurements to reproduce these results, adding the spatial information obtained about the extent and the shape of the Mn pair's states. It should be noticed that in this study Mn is incorporated only at the Ga substitutional position in the GaAs surface. As a result Mn atoms can be found only on the Ga sublattice and in the following sections we will refer to this sublattice when we discuss first Nearest Neighbour (NN) and second Nearest Neighbour (2NN) pairs.

In Fig 6.4 the spectroscopy results for a pair of Mn aligned along the [001] direction are shown. In panel b) the STS spectra acquired in the centre of the pair is compared with the $dI/dV$ spectra for a single Mn. The position in energy of the two peaks introduced by Mn is not changed and the hole wavefunction related to this pair (reported in Fig. 6.1b) is simply the overlap of two single Mn, crab-like features. The plots from the CITS measurements (reported in panel c and d) also show that the state introduced by the Mn pair has two maxima, corresponding to the position of the two Mn.

A different behaviour is observed for a Mn pair along the [110] direction, shown in Fig 6.5. In the $dI/dV$ spectrum acquired in the centre of the pair (Fig. 6.5b), the mid-gap peak (around 1.1 eV) shows a substantial shift in energy with respect to the peak observed for Mn in the nearby [001] pair (around 0.8 eV, consistent with previous observation). Another spectrum taken on one of the lobes of the Mn pair feature reveals the existence of a second peak at lower energy (around 0.5 eV).

The presence of two peaks within the band gap is confirmed by the CITS measurements, reported in panel d) and e). In panel e) the difference in electronic properties between the [110] and the [001] pair are confirmed, clearly showing how the single mid-gap peak observed for the single Mn case is split into two states. In panel d) the cut of the CITS data along the [110] direction is plotted and it shows that the wavefunctions of the two levels differ in spatial extension and number of nodes. In panel c) and f) the map of the LDOS at the energy of
Figure 6.4: Spectroscopy analysis of a Mn pair along the [001] direction. In a) the filled state image of the pair is shown ($V = -2.5\,\text{V}$, $I = 50\,\text{pA}$). In b) the dI/dV spectra taken in the centre of the pair is shown in comparison to the single Mn and the substrate spectra. There is no appreciable difference in the position of the peaks between a single Mn feature and a pair. In c) and d) two cuts of the CITS measurements across the Mn pairs are shown. The two Mn states maintain the same spatial extension of a single MN state and also the position in energy does not show any appreciable change (Fig.6.2c,d).
the two mid-gap states \((dI/dV (x,y))_V\) is represented with a colormap. The low energy state (around 0.5 eV) has a nodal plane through the centre of the Mn pair, typical of an antibonding state, while the higher energy state does not show any nodal plane, resembling a bonding state. In panel f) also the state for the Mn [001] pair is included in the plot. It should be noticed that in these measurements the wavefunction of the holes bound to the Mn [110] pair is imaged, and for these carriers the ground state is the closest to the conduction band. This observation explains why the state closer to the conduction band has a bonding character.

An additional challenge in the CITS spectroscopy on the [110] pair is the unstable behaviour observed for this pair under condition of high current at positive voltage. A signature of the instability can be observed in Fig.6.5d,e, where irregular spikes in the \(dI/dV\) plot are reported in the Negative Differential Conductivity region. These instabilities can result in a local rearrangement of the surface atoms, causing a displacement of the Mn and the disruption of the pair. A similar behaviour is observed when the distance between two Mn is increased along the [110] direction. In Fig.6.6 the spectroscopy results are shown for a pair where the Mn
Figure 6.6: Spectroscopic analysis of a Mn pair along the [110] direction, where two Mn are in the next nearest neighbour position in the Ga sublattice. In a) the filled state image of the pair is shown ($V = -2.5\, V$, $I = 50\, pA$). In b) the STS spectra for this pair is acquired in the center of the pair and on top of one lobe, and is compared to the spectra of the single Mn nearby. In panels d) and e) the CITS result along two different directions is plotted. Two different electronic states are observed for the pair, with a very small energy splitting. The spatial extension of these states is shown in the $dI/dV$ maps in panel c) and f).

atoms are in the next nearest neighbour along the [110] direction (considering only the Ga sublattice). The position for the Mn is shown in the inset of panel a).

In point spectroscopy, shown in panel b), a small shift of the peak position is reported. The CITS confirm that two levels, very close in energy, can be found, and they can be visualized in the $dI/dV$ maps as shown in panel c) and f). The low energy state is shown in panel c) and a nodal plane through the centre of the Mn feature can be clearly observed, similar to the wavefunction observed for the nearest neighbour [110] Mn pair (Fig.6.5c). The higher energy state, plotted in panel f, shows three maxima, while for the nearest neighbour pair a single maximum is observed for the high energy state (Fig.6.5f). This apparent discrepancy can be understood considering the limitation in energy resolution for the STM. Even at 4 K the feature related to the electronic states are subject to a broadening of about 50 meV [41]. As a result when the high energy state is probed by STM, there is a contribution left from the low energy state, due to the small energy splitting between the two. Therefore the three maxima observed in the wavefunction of the first excited state have different origin: the two side maxima arise from the contribution of the low energy state and the central maximum is due to the high energy state.
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Figure 6.7: Spectroscopic analysis of a Mn pair along the [112] direction. In a) the filled state image of the pair is shown \((V = -2.5 V, I = 50 pA)\), with the position of the two Mn atoms schematically represented in the inset. In b) the point spectroscopy measurements, acquired in the center of the pair, show that the position of the energy levels is the same as for the isolated Mn, but an unstable behaviour can be observed around 1 V. This instability is confirmed in the CITS measurements, reported in panel c) and d).

Another pair that is considered in this study is the [112] pair. The spectroscopy analysis on this pair, reported in Fig.6.7, shows that the energy level of the Mn is not changed in position with respect to the single Mn case. The \(dI/dV\) spectra, instead, shows an unstable behaviour in the electronic properties around 1V and in proximity of the first Mn atom. We argue that this feature, likewise the instability observed at low negative voltages\[107\] and the one observed for [110] pairs, stems form a structural instability of the pair.

The energy splitting observed in our experiments for different pairs is summarized in Fig.6.9. The origin of this phenomenon can be understood by considering the magnetic coupling between Mn atoms, which is described with a toy model in the work from Strandberg et al. \[119\]. This model explains the origin of the splitting observed in the STM experiments and the magnetic coupling of the Mn atoms. The electronic levels for a Mn pair with antiferromagnetic and ferromag-
Figure 6.8: Schematic representation of the 12 energy levels close to the valence band edge for the case of antiferromagnetic (a) and ferromagnetic (b,c) coupling between the Mn atoms in a pair, from the work of Strandberg et al. [119]. In the antiferromagnetic configuration the Mn pair can bind two holes in a twofold degenerate level. In b) an example of ferromagnetic coupling is shown, where the holes bound to the pair have different energy and can be resolved by STM spectroscopy. In c) the ferromagnetic configuration in agreement with the experimental results is shown.

antiferromagnetic

ferromagnetic

\[ m_j = 0 \]
\[ m_j = -1 \]

\[ m_j = 1 \]

\[ m_j = 0 \]
\[ m_j = -1 \]

\[ m_j = 1 \]

\[ m_j = 0 \]
\[ m_j = -1 \]

\[ T^2/J_{pd} \]
\[ 2T + 1 \]
\[ 2T - 1 \]

\[ \xi \]

\[ \xi - 2T \]

\[ \Lambda E \]

\[ \text{a) b) c) } \]
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Figure 6.9: Plot of the splitting energy for pairs of Mn atoms formed along different crystallographic directions. An overview of the pair orientation is also shown. The only pairs which give a detectable splitting are the pairs along the [110] direction. Our results are in good agreement with Tight Binding (TB) simulations which include the effect of the surface [119]. A discrepancy with the result of previous experimental work [70] and bulk TB simulations is observed. The magnetic coupling between Mn atoms, as predicted by the Tight Binding model including surface effects, is also reported.

netically; if the hopping term is small the antiferromagnetic configuration is more favourable; and finally if there is no hopping between the holes’ states the pair will remain paramagnetic.

In our measurements, shown in Fig.6.9 a measurable splitting is observed only for the nearest neighbour and next-nearest neighbour [110] pairs, indicating that the ferromagnetic coupling between two surface Mn atoms occurs only along this direction. The absence of splitting for the other pairs implies the existence of an antiferromagnetic coupling or the lack of magnetic interaction between the two atoms, which results in a paramagnetic configuration. This result shows that the magnetic interaction between Mn atoms on the GaAs surface is highly anisotropic and we can conclude that only pairs in the [110] direction have a sufficiently high hopping parameter to give rise to a ferromagnetic coupling.

Our data show a good agreement with the TB calculation from the work of Strandberg et al. [119], where the effect of the surface on the Mn states has been taken into account. The simulations predict a ferromagnetic coupling for the [110] pairs and an antiferromagnetic alignment of the Mn in the [112] pair. For the other pairs no energy difference between ferromagnetic and antiferromagnetic configuration is reported, pointing towards a paramagnetic coupling between the Mn spins. This model of the magnetic interaction is in agreement with our results,
where the only two pairs which give rise to a detectable splitting are the nearest
neighbour and second nearest neighbour [110] pairs. It should be noted that from
our STM measurements it is not possible to distinguish the antiferromagnetic from
the paramagnetic coupling between Mn atoms. STM experiments using magnetic
field and a magnetic STM tip are necessary to further confirm experimentally the
prediction of the tight binding simulation regarding these two different magnetic
coupling.

Our results show discrepancies with the result of TB calculation for Mn pairs
in bulk GaAs [126, 119], which are also shown in Fig.6.9. The deviation between
the result of the bulk TB simulations and the simulation taking into account
the surface can be explained considering the influence of the surface on the Mn
properties. The lower coordination of Mn atoms in the surface layer has the effect
to localize the bound hole wavefunction and to increase the hole’s binding energy
[43, 119]. As a result of the enhanced hole localization the overlap between holes
bound to neighbouring Mn will be in general smaller, causing a weaker magnetic
coupling between Mn with respect to the bulk case (except for the [110] nearest
neighbour pair).

Our experimental results show significant deviations from the results reported
in the work from Kitchen et al. [70], especially concerning the splitting for the
[112] pair and the second nearest neighbour [110] pair. The discrepancies in the
splitting measured for the 2NN Mn pair along the [110] direction can be due to
a different interpretation of the levels introduced by Mn dopants in the bandgap.
In our CITS measurements a very small splitting is observed, around the position
of the Mn1 peak. In the identification of the two states the spatial information
plays a crucial role, since it shows that the two states have a different spatial sym-
metry, confirming that they are different states. In the \(\frac{dI}{dV}\) point spectrum the
two states cannot be resolved, due to the broadening of the states typical of STM
spectroscopy measurements [41]. Both for the single Mn and the Mn pair shown
in Fig.6.7 a second peak can be observed in the \(\frac{dI}{dV}\) spectra, which corresponds
to the Mn2 peak discussed in the single Mn spectroscopy measurements (Fig.6.2).
As discussed in the previous section this peak is due to a different tunneling mech-
anism, and not to a splitted Mn-related electronic state. The difference in energy
between these two peaks (about 490 meV) is comparable with the energy split-
ting reported by Kitchen et al.[70]. In conclusion we argue that the Mn2 peak
has been considered in the work from Kitchen et al. for the estimation of the
energy splitting in a 2NN [110] Mn pair, which explains the discrepancy between
the experimental data.

We argue that the discrepancy between the results for the [112] pair can be
explained considering the role of instabilities in a \(\frac{dI}{dV}\) spectrum. An instability
is a feature which is not reproducible in two measurements performed under the
same conditions. In a \(\frac{dI}{dV}\) spectrum this feature can give rise to a sharp peaks,
which has been interpreted as the signature of the bonding state of the [112]
Mn pair. During the CITS measurements performed in our experimental work the
non-reproducibility of this feature can be assessed comparing \(\frac{dI}{dV}\) spectra which
have been acquired close to each other. In this spectroscopy technique a \(\frac{dI}{dV}\)
spectrum is recorded for each point of the STM image, which has a resolution
equal to 0.1 nm. This length scale is shorter than the atomic radius and sharp variations of the LDOS are not expected. Therefore the fluctuations observed in our measurements cannot originate from a real electronic state, and no real splitting in energy for the states of the [112] Mn pair is observed.

It is interesting to notice that these instabilities are observed at the same position in voltage, suggesting that these features have a real physical origin, which will be discussed further in the next section. An interesting observation regarding the instabilities observed in our spectroscopy measurements is the fact that they seem to occur more often for Mn atoms in the nearest neighbour position along the [110] direction. Also the number of [110] nearest neighbour Mn pairs created by pulse manipulation (8) is much lower than the number of pairs created in the [001] direction (56). Whether the instability of this pair is due to the electronic structure of the pair or it is related to a structural instability of the Mn pair remains an open question. Most probably the instability is a consequence of the excitation of an inelastic transition, which can destabilize the (110) Mn pair.

6.3.3 Larger Mn complexes

During our atom manipulation experiments more extended structures are formed. We found a total of 11 trimers and one tetramer. The electronic properties of these structures are investigated with the same approach as the Mn pairs. The concentration of Mn adatoms on the surface is probably the most crucial aspect to control, in order to create trimers and large assemblies with the Pulse Mode manipulation. However, if the Mn concentration is too high, many Mn clusters will be introduced and the mutual interaction between these structures will affect their electronic properties.

In Fig. 6.1a one of the trimers obtained in our experiments is shown. During the spectroscopy measurements on these structures the same instability reported for some Mn pairs is again observed. This phenomenon has been exploited to study three different configurations of Mn atoms: a trimer with three Mn atoms aligned along the [001] direction, a triangular configuration, in which the central Mn is displaced by one atomic position along the [110] direction, and a kinked configuration, where the last Mn is displaced along the [110] direction. The three configurations and the analysis of their electronic properties are illustrated in Fig. 6.10, Fig. 6.11 and Fig. 6.12. The trimer reported in Fig. 6.10, where three surface Mn are aligned along the [001] direction, shows electronic properties similar to the Mn pair along the [001] direction and to a single Mn. In Fig. 6.10b,c,d two states are observed for each Mn and, especially for the mid gap state, it is possible to spatially distinguish the states of the three Mn atoms. As discussed for the case of Mn pair, this observation could indicate that in this configuration the holes bound to the Mn atoms do not interact, or that the trimer has a degenerate electronic state, as is expected in the case of antiferromagnetic coupling [119]. The feature observed in c) and d) around 0.9 V, in between the states of the second and the third Mn atom, is a sign of the instability responsible for the switching to the next different Mn configuration. The inset of panel d) shows a close up of the feature. During this measurements the central Mn atom is moved. The spectra
Figure 6.10: STM measurements on a trimer of Mn atoms in the GaAs surface layer, aligned along the [001] direction. In a) the STM image of the trimer is shown, taken at $V = -2.5\, V$, $I = 50\, \text{pA}$. In b) the $dI/dV$ spectra taken in the centre of the trimer is shown, and in c) and d) two cuts of the CITS measurement are reported.

reported in Fig.6.10b are taken before the spectroscopy map and confirm that the level of the three Mn atoms have the same position in energy.

The second configuration of the trimer we discuss is a triangular structure, in which the central atom is displaced by one surface cell along the [110] direction with respect to the other two, see Fig.6.11. Also in this case the point spectroscopy does not show any substantial shift in the energy of the peaks. In the cut along the [001] direction the states associated to the first and the third Mn atom are observed, and in between an unstable behaviour around $0.9\, V$ is observed. The cut along the [110] direction shows that the first Mn state is located around $0.75\, V$, and the instabilities observed in the [001] cut occur in proximity of this atom, which has been moved in the previous CITS measurement. During this spectroscopic analysis no complete switching of an atom occurred.

The third configuration has been obtained after a displacement of the first Mn atom along the [110] direction. Two adjacent Mn atoms are aligned and the third is shifted by one surface cell in the [110] direction. Also in this case instabilities are observed, in particular for the central atom. A detail of the instabilities is
Figure 6.11: STM measurements on a trimer of Mn atoms in the GaAs surface layer, arranged in a triangle with two Mn atoms aligned along the [001] direction and the central Mn atom displaced by one surface unit cell in the [110] direction. In a) the STM image of the trimer is shown, taken at $V = 2.5 \, V$, $I = 50 \, pA$. In b) the $dI/dV$ spectra taken on the last Mn of the trimer is shown, and in c) and d) two cuts of the CITS measurement are reported. The states of the three Mn atoms have the same energy as the state for a single Mn, but fluctuation of the tunneling current are observed in proximity of the central Mn atom.
shown in the inset of panel d), which clearly shows how the spectroscopic feature is composed of irregular spikes. Regarding the position in energy of the Mn levels there seems to be a very small shift (below 50\,meV) for the energy level of the third Mn. This shift close to the STM energy resolution limit [43] and is much lower than the splitting reported in the study of Kitchen et al [70].

The largest assembly of Mn atoms that has been built is composed of 4 atoms aligned in the [001] direction. Also for this structure no sign of Mn-Mn interaction is detected in our measurements. It should be noticed how the tetramer is relatively isolated from other Mn features, showing that with a careful optimization of the Mn coverage isolated large structures of Mn can be created by Pulse Mode manipulation.

From this measurements it can be concluded that the instability in the electronic properties can trigger the movement of Mn atoms in the surface of GaAs. The movement, which consists of an exchange in position of a Mn with another neighbouring surface Ga, is not always triggered. This exchange process has been observed along the [110] rows in Fig.6.12,6.11 but it has been observed also along the (001) and the (112) directions. This process seems to be triggered under high current conditions (during a CITS experiments the current can be higher that 1-2 nA) and for voltages where a Negative Differential Conductivity is observed. The origin and the mechanism behind the movement of a surface atom require further investigation.

The lack of energy splitting in trimers where two or more Mn atoms are aligned along a (112) direction are in agreement with our experimental result for the [112] Mn pairs, where no splitting is observed and the two surface Mn are predicted to have an antiferromagnetic coupling. The same lack of interaction is observed for the trimer and the tetramer composed of Mn atoms aligned along the [001] direction. From an intuitive molecular orbital picture, assuming antiferromagnetic coupling and only a nearest neighbour interaction, 3 degenerate states are expected for the trimers in Fig.6.12,6.11. No phenomena of spin frustration is expected since the magnetic coupling is dominated by the closest Mn neighbour. It is still an open question, from the experimental perspective, whether the Mn pairs along the [001] or the [111] direction are interacting antiferromagnetically or simply do not interact, due to a low overlap of the hole wavefunctions. No Mn assemblies larger than a pair are formed by Pulse Mode manipulation along the [110] direction. In fact, only 8 pairs were created along this crystallographic direction, over the total of 87 pairs created. We argue that this difference is related to a lower stability of the [110] pair. This hypothesis is supported by several CITS measurements, during which we observe that these pairs are likely to show an unstable behaviour, which can result in the rearrangement of the Mn configuration into a more stable pair, aligned in another direction.
Figure 6.12: STM measurements on a trimer of Mn atoms in the GaAs surface layer, where two Mn atoms are aligned along the [001] direction, while the last Mn is displaced by one atomic position along the [110] direction. In a) the STM image of the trimer is shown, taken at $V = -2.5 \text{ V}$, $I = 50 \text{ pA}$. In b) the $dI/dV$ spectra taken on the last Mn of the trimer is shown, and in c) and d) two cuts of the CITS measurement are reported. The states of the three Mn atoms also in this case appear to have a slightly different energy as the states for a single Mn, and also in this trimer instabilities of the tunneling current are reported in the CITS map.
Figure 6.13: STM measurements on a tetramer of Mn atoms in the GaAs surface layer, where four atoms are aligned along the [001] direction. In panel a) the filled state image is shown ($V = -2.5\,V$, $I = 50\,pA$) and in c) the empty state image ($V = 1.5\,V$, $I = 30\,pA$). In panel b) and d) two cuts of the CITS measurements are shown. The states introduced by the four Mn atoms have all the same energy as the state introduced by a single Mn atom.
6.4 Conclusions

In this chapter we investigated the properties of Mn pairs, trimers and one tetramer by STM spectroscopy. Our analysis shows that the Mn-Mn coupling is ferromagnetic only for [110] pairs and it decreases rapidly with the Mn-Mn distance. Our results are in good agreement with Tight Binding simulations which include the effect of the surface on the Mn electronic states. The discrepancy with previously reported results [70] has been explained linking the sharp peak features in the $dI/dV$ spectra to the structural instability observed for several Mn assemblies. This structural instability is observed during spectroscopy measurements and can lead to the movement of surface Mn. CITS measurements played an important role in the identification of these features, providing a combination of electronic and structural information which revealed the irregular behaviour of these features.

The demonstration that large, isolated Mn assemblies can be built by STM is an important step forward towards the creation of structures where interesting spintronic phenomena can be investigated. For example large Mn assemblies in the [001] or the [112] direction would allow the confinement of holes in an atomically defined QDs, as in the work from Pan et al.[103]. The chains created are still too small to observe a QD-like behaviour, but we believe that a simple optimization of the Mn coverage could lead to the creation of these structures. Moreover if Mn atoms aligned along these directions show an antiferromagnetic coupling, chains with an odd number of Mn would have a net magnetic moment. These structures would be a valuable model system for new spintronic phenomena in semiconductors.
Chapter 7

Segregation and diffusion of Mn in a modulation doped InGaAs QW structure.

In this chapter we investigate the Mn distribution originating from a Mn δ-layer, grown in the proximity of an InGaAs Quantum Well, by Cross-Section Scanning Tunnel Microscopy (X-STM). Heterostructures with Mn modulation doping show interesting magnetic properties, but to understand their behaviour the distribution of Mn atoms should be determined. In this work back diffusion and segregation of Mn atoms from a nominal δ layer are observed and quantified; this information is useful to gain a deeper insight in the magnetic and the optical properties of this semiconductor heterostructure.

7.1 Introduction

Diluted Magnetic Semiconductors (DMS) are materials where the optoelectronic properties of semiconductors are combined with magnetic properties, introduced by doping the material with magnetic impurities [101, 25]. The combination of these properties makes this class of materials interesting due to a connection between the rising field of spintronics and the conventional electronics [2].

In the last decades many different ferromagnetic semiconductors are investigated, including III-V [16, 104], II-VI semiconductors [73] but also more exotic semiconductors systems [143, 40]. One of the most studied and best understood DMS is GaAs doped with Mn; in the first decade of 2000’s a great effort has been made in order to raise the Curie temperature of this systems above room temperature [16] and a model to explain the ferromagnetism in this semiconductor system was developed [23]. In this model the magnetic interaction between the Mn magnetic electronic core (half filled 3d shell, total spin $S = 5/2$) is mediated by the holes introduced in the semiconductor.

A Mn atom is an acceptor in GaAs and it introduces one hole in the valence
band. Therefore the first approach followed in order to raise the Curie temperature of the magnetic semiconductor is to increase the Mn concentration, which is expected to increase the hole concentration and the ferromagnetic coupling. However there are some intrinsic limitations to the doping level that can be achieved in these materials. When the Mn concentration is very high, Mn can be incorporated not only in the Ga substitutional position, where it behaves as an acceptor, but also in an interstitial position, where is expected to behave as a double donor \cite{33,16}. A second limitation is given by the limited solubility limit for Mn in GaAs, which can induce the formation of MnAs clusters for high temperatures and high Mn concentration\cite{102,96}. These issues limited the achievable Curie temperature for bulk GaMnAs to around 185 K \cite{137}, while the optoelectronic properties of the system are degraded by the presence of many defects and magnetic clusters.

A recently developed approach circumvents some of these limitations: it entails the introduction of a Mn δ-layer close a region where a 2D Hole Gas (2DHG) is present \cite{97}. This design where dopants are concentrated in an area separated from the region where the carriers are confined is called modulation doping. This structure is used in order to introduce a separation between carriers and dopants, with the aim to enhance the carrier mobility. In this case the magnetic coupling between Mn atoms is mediated by the holes present in the semiconductor, therefore an increase of the hole mobility can enhance the magnetic properties of the system. In this structure a relatively high Curie temperature was achieved ($T_C = 250$ K), thanks to the combination of an high density of magnetic ions in the delta layer and of the high hole concentration in the semiconductor 2DHG.

A similar structure has been realized in the work by Dorokhin et al. \cite{27}, where the Mn δ-layer is placed in proximity of a InGaAs QW. The Curie temperature for this structures is low (around 40 K), but the QW retains excellent optical properties \cite{27}, thanks to the separation from the δ-layer by a tunneling barrier a few nanometers thick. Interestingly the carriers confined in the QW show new magnetic properties, due to the coupling with the Mn in the δ-layer. The optical properties of these structures are investigated in several studies \cite{19,4,28,3} and the magnetic coupling between the carriers in the QW and the Mn dopants is explained by theoretical models \cite{112,110,111}. The theoretical model explains the magnetic coupling as the result of a resonant exchange between the holes confined in the QW and the holes localized on the Mn atoms in the δ-layer \cite{112}. The distance between the QW and the Mn atoms represents a tunneling barrier which will control the magnetic interactions in the system. It is known from previous studies on different δ layers that their ideal shape is not preserved during growth \cite{63}. Given the importance of the distance between the Mn atoms and the QW for the properties of this system, a more detailed study of the Mn distribution is required.

In this work we use Cross Sectional Scanning Tunnel Microscopy (X-STM) to investigate the structural properties of this system, in particular regarding the real Mn distribution. With the insight gained in this study some phenomena previously observed in this system can be explained.
CHAPTER 7. MN PROFILE IN A MODULATION DOPED INGAAS QW STRUCTURE

7.2 Experimental method

X-STM measurements are performed on a sample composed of a n-doped GaAs substrate on which a buffer layer of undoped GaAs (~200 nm) is grown, followed by an $In_{x}Ga_{1-x}As$ QW 10 nm thick with an In concentration of $x = 0.01$ and a GaAs spacer of 2.5 nm. The layers have been grown by MOCVD at high temperature (600$^\circ$C). Subsequently the Mn δ layer and a GaAs cap layer are grown by laser ablation, using a Q-switched YAG:Nd laser and targets of Mn and GaAs and keeping the sample in the same growth chamber [27]. The temperature was kept at 400$^\circ$C during this growth. The delta layer contains 0.25 ML of Mn and the GaAs cap layer is 70 nm thick. The X-STM measurements are performed with an Omicron Low Temperature STM, operated at a temperature of 77 K and with the pressure in the STM chamber around $2 \cdot 10^{-11}$ mbar. The STM tips are obtained by electrochemical etching of a polycrystalline W wire and are further prepared in-situ by baking and Ar sputtering. The samples is cleaved in-situ, obtaining a clean and atomically flat {110} surface suitable for STM analysis.

7.3 Results

The spatial distribution of Mn dopants, intentionally deposited as a δ-layer, is investigated over a region 1.5$\mu$m along the InGaAs QW. In Fig. 7.1 an image of the epilayer’s cross section is shown. The image is taken with a low positive voltage applied to the sample ($V = 1.35V$), since under these conditions the acceptor level introduced by Mn are empty and give rise to a bright feature, which can be easily identified in the STM image [141]. The shape of the feature depends on the depth below the cleaved surface of the Mn atom: it evolves from a crab-like feature for the surface Mn to an asymmetric bow-tie feature for Mn below the surface [41].

The QW appears in the STM image as a bright region, approximately 10 nm wide. The bright contrast of the QW originates from two contributions: one part stems from the fact that InGaAs has a lower bandgap with respect to the surrounding GaAs, which increase the number of states available for tunneling in this region. The other component stems from the outward relaxation of the QW, which minimizes the elastic energy accumulated in the QW as a consequence of the lattice mismatch between GaAs and InGaAs [100]. The sample has been grown on a (001) substrate with a miscut angle of 3$^\circ$, which is also observed in our measurements between the QW edge and the atomic rows in the [110] direction. On top of the QW the intrinsic GaAs spacer layer is observed. The layer is approximately 3 nm thick, which is in agreement with the thickness expected from the MOCVD growth. The Mn delta layer and the GaAs cap layer are instead grown by Laser Ablation. Our STM images show that the interface between the spacer layer and the δ-layer is surprisingly free of defects. This is, to our knowledge, the first STM study of GaAs grown by Laser Ablation and it confirms the possibility to achieve good quality epitaxial growth with this deposition technique [148]. The Mn distribution deviates substantially from the expected δ-layer profile: there is a well defined and relatively sharp interface between the spacer and the Mn delta layer, but an Mn concentration above $2 \cdot 10^{19}$ at/cm$^3$ is detected in the GaAs cap
layer. It should be noticed that this value represent an lower bound limit of the Mn concentration, since some of the Mn subsurface features could not be clearly resolved in our images. A lower concentration of Mn atoms is also found inside the GaAs spacer layer and the InGaAs QW, respectively around and $5 \times 10^{16} \text{at/cm}^3$.

In the following sections the Mn distribution is described by dividing it into two components: one is the slow decay of Mn concentration along the growth direction, where the segregation has played a prominent role. The other is the presence of Mn in the region underneath the initial Mn position, which is attributed to a back-diffusion process.

### 7.3.1 Segregation profile

The concentration profile for Mn in the GaAs cap layer is extracted from our STM measurements and is shown in Fig. 7.2. For this analysis four $80 \times 30 \text{nm}^2$ images are considered and the images are combined aligning the δ-layer position at $x = 0$. The bin size for the distribution is chosen to be equal to 3 atomic rows, since the high Mn concentration sometimes prevents a clear identification of the dopant’s position.

The distribution shows that the Mn concentration decrease slowly with the distance from the δ-layer position: the number of Mn atoms observed 25 nm away from the intended δ-layer position is about half the amount of Mn detected at the δ-layer position. It was not possible to estimate precisely the segregation length in our system, since in proximity of the epilayer’s edge no STM measurements could be performed due to a reduced conductivity of the sample. Moreover the Mn distribution is not well described with a Muraki profile, which is typically used to model segregation phenomena [95]. These observations suggest that there are two contribution to the Mn profile: the first is that the segregation length in
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Figure 7.2: Mn distribution in the GaAs cap layer, originated from a Mn δ-layer positioned at \( x = 0 \) in the plot. Long range Mn segregation occurs and the Mn concentration appears to be only halved 20 nm away from the expected δ-layer position.

This system is large, longer than the width of the area analyzed by STM (more than 25 nm); similar observations have been reported for other Mn-doped layers, grown by MBE [50]. The second contribution which could explain the large Mn concentration and the deviation from a simple segregation profile is that a complex growth process take place, where not all the Mn becomes absorbed on the surface when the delta layer is grown, but it remains in the gas phase or it is adsorbed on the growth chamber walls and is incorporated in a later stage of the capping layer’s growth. This mechanism is supported by the seemingly constant Mn concentration over the first 10 nm after the δ-layer position, where the Mn concentration appears to have reached saturation.

Our measurements show that the GaAs cap layer can be effectively considered as a GaMnAs layer, with a Mn concentration in the order of \( 2 \cdot 10^{19} \text{at/cm}^3 \). The bulk-like character of the GaMnAs could explain the low \( T_C \) for this system (\( T_C = 50 \text{ K} \) [27]) with respect to a previous report of samples with Mn modulation doping \( T_C = 250 \text{ K} \) [97]). Interestingly the unintentionally created GaMnAs layer shows a good crystalline quality. It should be noticed that this work is the first STM study performed on a GaAs layer grown by laser ablation. The high crystalline quality observed in our measurements is a proof of the high level of control recently achieved on this growth technique. Only a few feature could be associated to clusters of Mn atoms in our STM images, as shown in Fig.7.3a. The estimated
Figure 7.3: STM images of the GaAs cap layer. In panel a) two Mn clusters can be detected. They appear as bright features where the single Mn features cannot be resolved. In panel b) some of the Mn features are identified by comparison with previous studies; new features are also observed which can be related to Mn interstitials. In panel c) and d) previous report of this feature for Mn in GaAs are shown, from the studies of Garleff et al. and Richardella et al. In panel d) the feature is marked as 1st, which stands for Mn in the first subsurface layer. In the study from Garleff the feature has been associated to a Mn pair in the [001] direction.

The concentration of these clusters is around $10^{17} / cm^3$. The presence of the clusters might affect the magnetic properties of the GaMnAs layer (by raising its Curie temperature), but the low concentration of these features indicates that the main contribution to the magnetization of the QW comes from the coupling with substitutional Mn in the $\delta$-layer.

From a detail of our measurements on the GaMnAs cap layer, shown in Fig.7.3b, many features related to substitutional Mn dopants can be identified. The hole wavefunction, which is imaged under empty state conditions, changes according to the depth of the Mn below the cleavage surface. It evolves from a crab-like feature, extended along the [001] direction, for surface Mn to an asymmetric bowtie feature, with the lobe in the [001] which is brighter and more extended for subsurface Mn dopants.
In our measurements another feature is observed, marked in green in Fig. 7.3b. This feature consists of a bright point-like protrusion (comparable in height with the surface Mn feature), with a bright tail in the [001] direction. A similar feature has been also reported in another study \[108\] where a sample with a high Mn concentration (about \(10^{20}\) atoms/cm\(^3\)) was examined by STM. In this study the feature has been interpreted as a substitutional Mn in the first subsurface layer. Since there are no reports of this feature in GaAs samples with low Mn concentration \[41, 13, 87\], we suggest that this feature is associated to Mn interstitials in the surface layer of GaAs. It is well known that during the growth of GaMnAs part of the Mn atoms can be incorporated in the substrate as interstitials, when the Mn concentration is sufficiently high \[105\]. Mn in the interstitial position behaves as a double donor, compensating the holes introduced by substitutional Mn, which behaves as an acceptor. Further support to our identification is given by the DFT simulation performed by Stroppa et al. for Mn interstitials \[121\]: the LDOS calculated for this feature is in good agreement with the feature observed in our measurements. The number of interstitial Mn observed seems to be comparable with the number of surface Mn atoms which would suggest a high interstitial concentration, as high as the substitutional Mn concentration. However, Mn interstitials in subsurface layers have not been clearly detected by STM. This is probably due to the weak coupling between the Mn interstitial and the surrounding environment, which lead to a small change in the electronic and topographic contrast obtained by STM. As a result any measurement of the interstitial concentration would be only based on the data for interstitial in the surface layer. However a very large energy is developed during the cleaving process, which could cause the migration of the interstitial Mn in the GaAs. In conclusion our measurements prove that interstitial Mn are present in the GaAs layer, but it is not possible to extract a reliable data about their concentration.

### 7.3.2 Mn back-diffusion

In this section the distribution profile of Mn dopants in the spacer layer and in the QW is investigated. The results, which are shown in Fig. 7.4, have been obtained investigating an area \(1.5\) \(\mu\)m long, in order to gain sufficient statistical information on the tail of the Mn distribution. Our results show that Mn atoms can be found in the GaAs spacer layer \((-3 \geq x \geq 0)\) and, in low concentration, in the InGaAs QW \((-10 \geq x \geq -3)\).

The shape of the Mn concentration profile can be explained by the diffusion of Mn atoms in the heterostructure. The initial distribution is expected to be a \(\delta\)-layer, but since the segregation process has a smaller time scale with respect to diffusion phenomena, it has to be taken into account in the initial Mn distribution. Therefore the initial Mn concentration profile is described by a step function with an enhanced, \(\delta\)-like Mn concentration at the expected \(\delta\)-layer position \((x = 0)\). The outcome of the diffusion process is the convolution of a Gaussian distribution with the initial Mn profile. In Fig. 7.4 the Gaussian broadening is applied separately to the two components of the initial Mn distribution, a delta layer (blue) and a step function (green) both centred in \(x = 0\), which is the position of the Mn \(\delta\)-layer.
Figure 7.4: Mn distribution in the GaAs spacer layer and in the InGaAs QW. The final Mn concentration profile is the result of a diffusion phenomenon, which can be modelled applying a gaussian broadening of the initial Mn distribution. The Mn diffusion length estimated from our fit is \( \lambda = 1.5 \pm 0.2 \text{nm} \).

The result is a Gaussian distribution and a profile which can described with an error function, respectively. The sum of these two contributions is used to fit the Mn profile extracted from our STM measurements. From the best fit the diffusion length for Mn in the system is estimated to be \( \lambda = 1.5 \pm 0.2 \text{nm} \).

The fit reproduces reasonably well several features of the Mn distribution, such as the maximum of Mn concentration corresponding with the Mn \( \delta \)-layer position and the decay of Mn concentration around this point. However some discrepancies can be observed in the tail of the distribution extending in the direction opposite to the growth \( (x \leq 0) \): the concentration of Mn detected is higher than the concentration predicted by our simple diffusion model. This deviation could arise from the fact that Mn atoms in the spacer layer are more isolated and easier to count than the atoms in the delta layer and the GaAs capping, introducing a overestimation of the Mn present in the tail respect to the Mn considered in the cap layer. Another possible explanation of the pronounced tail is that there could be a contribution to the diffusion from Mn interstitials, which have a longer diffusion length. The Mn distribution obtained from our STM measurements also shows that some Mn atoms are located inside the InGaAs QW. These Mn atoms will be detuned from the energy level of Mn dopants in GaAs, and they will not directly contribute to the magnetic properties of the system.

The presence of Mn atoms in the GaAs spacer layer has important consequences on the magnetic properties of the heterostructure. As discussed in the work from Rozhansky et al. [112], the magnetic properties of the GaMnAs region are en-
enhanced by the holes confined in the QW. The origin of the enhancement is attributed to a resonant exchange interaction, where holes in the QW and holes in the Mn δ-layer are coupled by tunneling through the GaAs spacer layer. From this theory an exponential dependence of the Curie temperature from the spacer layer thickness would be expected. However, in previous experimental studies the dependence of the Curie temperature from the distance between QW and δ-layer was found to be linear \[1\]. We argue that this discrepancy could be explained by the long Mn tail observed in the GaAs spacer layer in our experiments: even if the distance between the broadened Mn δ-layer and the QW is relatively large, some Mn atoms are found quite close to the QW, giving rise to an efficient coupling. If the broadened δ-layer is grown closer to the QW interface more Mn atoms will couple efficiently, but the dependence of the Curie temperature from the distance between QW and delta layer will not be exponential.

The presence of Mn in proximity of the QW can also explain other observations concerning the optical properties of this system, reported in the work from Balanta et al.\[3\]. In this work the magneto-optical properties of the system were explained with the presence in the QW of bound magnetic polarons \[114\] and by claiming that the QW states efficiently couples to a small number of Mn atoms. In our measurements the tail of the Mn distribution introduces a few atoms which are the closest to the QW, thus it could be argued that these atoms dominate the magnetic coupling between Mn and QW holes. The presence of bound magnetic polarons requires a localization of the exciton close to the surface, which could be provided by the interface roughness, by irregularity in the Mn distribution or by the presence of Mn in the QW which could bind the exciton. The existence of potential fluctuation which can induce this effect will be demonstrated in the next section.

### 7.3.3 Spectroscopy analysis

The contrast obtained in an STM image is not only related to the topography of the surface, but also contains a contribution from the electronic properties of the sample. The combination of these two factors in an STM image can be clearly observed in Fig.7.5a. In this image of the heterostructure, taken at high negative voltage, an apparent step is observed, which is not related to a real topographic feature. The contrast can be explained considering the effect of the electric field applied by the tip on the semiconductor bands, illustrated in Fig.7.5c. When a negative voltage is applied to the sample, a triangular potential well is formed close to the surface. If the well is sufficiently deep a confined state associated to a 2DEG is formed. This state is an additional tunneling path for the electron which will increase the tunneling current detected. The increase of tunneling current will be compensated by the feedback loop (since we are measuring in constant current mode) and the onset for the 2DEG’s formation will appear as a step in the STM image. The spectroscopy measurements reported in Fig.7.5d support this interpretation: the plot shows the dI/dV information along the growth direction and the different region of the sample can be identified. The position of the step feature, which in the dI/dV spectrum appears as a peak, varies within the
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Figure 7.5: Study of the electronic properties across the heterostructure by STM spectroscopy. In a) the STM topography measurement is shown, taken at $V = 3V$ and $I = 40pA$. The feature with a long range modulation observed in this image is the onset for tunneling in the 2DEG layer induced by the tip band banding, shown in panel b). In panel c) a scheme of the electrostatic potential across the sample in the growth direction is shown. In panel d) a colorplot of the $dI/dV$ across the heterostructure is shown. Several electronic feature can be observed in this measurement: the onset for the 2DEG in the GaAs, the presence of a band offset for the InGaAs QW and the presence of states in the gap in the Mn:GaAs layer, related to the presence of Mn acceptors.

heterostructure, as a consequence of the band bending in a $p-i-n$ junction which shifts the conduction band and the 2DEG offset at higher voltages (Fig.7.5b).

From Fig.7.5a we can observe that the position of the step-like feature is not constant over the length of the QW, but shows a long range modulation and local dips, such as the one emphasized by the red dashed line in the figure. This feature can be regarded as a contour line for the local electrostatic landscape; the line appears to be smooth, confirming the good quality of the QW, but the presence of dips in the electrostatic potential could give rise to the confinement of the exciton in the QW, which is necessary for the observation of the magneto-polaron effect. The low Mn concentration in and nearby the QW suggest that the magneto-polaron effect observed in this system could have similar properties to the magneto-polaron effect observed in QDs coupled to a single Mn dopant [106], as suggested in the work from Balanta et al. [3]. The dip in the electrostatic landscape could arise from inhomogeneity in the GaMnAs layer, such as a small cluster of Mn atoms or the presence of a single Mn in the QW.
7.3.4 Conclusion

In this Chapter we used STM to investigate the structural and electronic properties of a semiconductor heterostructure, consisting in a QW coupled to a $\delta$-doped Mn layer. Our analysis showed that a long range segregation phenomena takes place during growth, and the Mn is incorporated in a large area of the GaAs cap layer above the expected $\delta$-layer position. Moreover the Mn distribution is broadened by a diffusion process, which turns the $\delta$-layer in a gaussian profile. As a result Mn is found into the GaAs barrier between the InGaAs QW and the original $\delta$-layer. This observation could explain the linear dependence of the system’s Curie temperature on the distance between QD and the broadened $\delta$-layer.
Chapter 8

Summary

Atomically precise formation of Mn doped semiconductor nanostructures

In this work Cross-sectional Scanning Tunnelling Microscopy (X-STM) has been used to analyse the formation process of different semiconductor nanostructures. Their morphology, which is crucial to understand their electronic properties, is investigated with an atomic resolution. Furthermore it has been shown that the STM allows us to move and incorporate in a semiconductor dopant atoms adsorbed on the surface. With this method it is possible to create nanostructures on the semiconductor surface with atomic precision. These capabilities of the STM technique have been employed to develop new methods for the controlled creation of nanostructures in semiconductors.

In the first part of this thesis we focus on the morphology of semiconductor Quantum Dots (QDs) after their formation and capping. The effect of the overgrowth process on the QDs height has been studied, comparing the X-STM experimental results with growth simulations performed using a Kinetic Monte Carlo model. The InAs QDs have been grown on a GaAs substrate and subsequently overgrown with different InGa(1-x)As capping layer. The In concentration varies between x = 0 and x = 0.2. In this system an higher In concentration reduce the lattice mismatch between the capping layer and the QDs, reducing the strain in the system. A linear dependence between the QDs height and the In concentration in the capping layer is found, which shows that QDs overgrown by a capping layer with higher In concentration preserve better their height. This observation proves that the strain between capping and QDs control the erosion of the dot during the overgrowth.

The second nanostructure which has been investigated is based on a GaAs/InGaAs/GaAs Quantum Well (QW) in proximity of a layer of Mn dopants. Mn is a magnetic dopant and the interaction between the carriers confined in the QW and the Mn delta layer confers the structure interesting magneto-optical properties. The crucial aspects in this nanostructure are the distance between the QW
and the Mn-layer and the real Mn distribution. By X-STM we have determined the position of the Mn-layer, the segregation and the back diffusion profile. This information provides a complete picture of the Mn distribution and gives an understanding of the origin of the nanostructures electronic, optical and magnetic properties.

The third system studied consists of a few Mn atoms, which have been deposited on a clean [110] GaAs surface. It has been previously demonstrated that Mn adatoms, under the influence of the STM tip, can be moved across the surface or exchange their position with a Ga atom in the surface. The problem is that the lack of control on the outcome prevents the creation of complex Mn structures. In order to address this issue new manipulation processes have been designed and the influence of several parameters on the manipulation result has been investigated by STM. It has been found that the outcome probability depends on the tunnelling current and the bias voltage applied during the manipulation. The new manipulation techniques, together with the deeper understanding of the manipulation process, have been exploited to create pairs and trimers of Mn dopants. The electronic properties of these nanostructures are analysed by STM. These measurements are a step forward towards the creation and the study of larger and more complex dopant structures.
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Curriculum Vitæ

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List of Publications


- D. F. Grossi, P. M. Koenraad. "Characterization and manipulation of Mn adatoms on the GaAs (110) surface”. In preparation

- D. F. Grossi, I. V. Krainov, N. S. Averkiev and P. M. Koenraad. "Segregation and diffusion of Mn in a modulation doped InGaAs QW structure”. In preparation


- D. F. Grossi, P. M. Koenraad. "Mn manipulation and characterization on ZnTe (110) surface by STM”. In preparation
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