Atomic-scale study of Mn- and Sb-containing III-V semiconductor nanostructures

PROEFSCHRIFT

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Chapter 1

Introduction

From the first transistor radios to present day computers or light emitting diodes (LEDs) for illumination, electronic products have become part of our daily life. The last mobile phones on the market even manage to fit all the main electronic products of the 20th century (like radio, audio/video player, GPS, telecommunication, and internet access) in one small handset that fits in your pocket. Since the fabrication of the first semiconductor transistor in 1947 which is the key element in electronics, technology has progressed so quickly that humanity is now capable to produce each year more transistors than grains of rice.\[1\] This staggering comparison resulted from the downscaling of the transistor size that allows us in the meantime to have more powerful and less expensive products. A continued trend of miniaturization of the transistors has been predicted already in 1965 by Gordon Moore who stated that the number of transistors per integrated circuit will double every 18 months.\[2\] This remarkable prediction, known as Moore Law’s, has been kept since its first suggestion (see Fig 1.1). The increased speed and processing power of integrated circuits has consequences in terms of data storage and transmission where more bits need to be stored on the same area, accessed and exchanged at a higher speed. Moreover energy efficiency has become increasingly important since more transistors need to be driven in the same device, and more electronic products have to function on a single battery. Furthermore energy conservation is an important challenge for society and industry. As devices are miniaturized, controlling their operation becomes more complicated. In 1970, the channel length of a transistor was about 1 micrometer whereas Intel has recently announced the beginning of the production of a 22 nm channel length transistor. At this length scale, quantum effects begin to have an impact on the behavior of the device. The interface thickness and roughness lead for instance to uncontrollable leakage due to tunneling and atomic scale composition fluctuations can be of major importance in novel functional devices that are based on quantum effects. For example, the opto-electronic properties of self-assembled quantum dots where excitons are confined
to a tiny portion of semiconductor material, strongly depend on the structural properties at the atomic scale. Quantum dot materials are promising candidates for efficient LEDs, semiconductor optical amplifiers, solar cells, and even quantum computing.

Nanostructured magnetic semiconductors comprise another class of promising materials for novel applications. Because these materials exhibit ferromagnetism, the optoelectronic control of the spin of the carriers becomes available in a semiconductor device. Due to their easy compatibility with the present semiconductor technology, magnetic semiconductors could also improve the speed and lower the energy consumption of devices by adding new functionalities based on spin manipulation. Nowadays, the information processing performed by an integrated circuit is still based on the charge of carriers. Interestingly, the storage of information is mostly carried out elsewhere by magnetic recordings such as on hard drives which are based on the control of the electronic and nuclear spins. Controlling both the charge and the spin of the electrons at the same time in a single circuit could potentially enhance device performance strongly. In this thesis we will present a number of studies which we have performed to unravel the relation between atomic scale details of the semiconductor material and its magnetic or optical properties by exploring them with cross-sectional scanning tunneling microscopy (X-STM). We will focus on magnetic semiconductor materials that are doped with Mn and nanostructured semiconductor materials for optical devices where Sb has been used to control their optoelectronic properties.
Ferromagnetism can be implemented in semiconductors by doping the semiconductor host with transition metals. (Ga,Mn)As has been the most studied dilute magnetic semiconductor (DMS) since the breakthrough of Hideo Ohno’s group in 1996 that demonstrated a Curie temperature ($T_C$) of 110 K for this material.\cite{4,5} By improving further the growth conditions, a Curie temperature of 190 K has even been reached for (Ga,Mn)As.\cite{6} Mn in GaAs acts as an acceptor in the semiconductor creating holes in the semiconductors and introduces a magnetic moment. Although the main properties of GaMnAs are well understood, the origin and the control of ferromagnetism is still debated especially at high doping levels where ordering of Mn atoms in the crystal starts to play an important role.\cite{7} The quest for DMS’s with a higher Curie temperature is an important area of research in material science since potential applications in electronics require a $T_C$ well above room temperature. Despite a Curie temperature record that holds since 2008, (Ga,Mn)As is still extensively studied as a system model for understanding the concept of ferromagnetism in DMS and applying these mechanisms to other DMS’s. The presented work developed in this thesis focuses on Mn-doped semiconductors where enhanced Curie temperature has been predicted or observed. We will pay attention at the atomic composition of ordered (Ga,Mn)As multilayers, the structural properties of a hybrid material composed of metallic MnAs nanoclusters embedded in a GaAs, and the ordering of Mn atoms in (In,Mn)Sb.

Electroluminescence from a semiconductor was reported already 8 years after the invention of the transistor. Since then, applications that are derived from this phenomena are present in our every-day life as for example LEDs lighting, laser diodes, or terahertz emitters. The emission wavelength is directly related to the band gap of the semiconductors defined by the energy difference between the top of the valence band and the bottom of the conduction band. Figure 1.2 shows the band gap energy of the semiconductor as function of the lattice constant for different semiconductors. By deposing compounds with different lattice constants one can tune the emission wavelength of the engineered nanostructures. Present day research focuses on getting lasers emitting in the mid-infrared spectral regions (25 $\mu$m) for applications such as laser radar, biomedical sensing, pollution monitoring, and molecular spectroscopy.\cite{8,9,10} Intense research is spent on devices emitting near 1.55 $\mu$m since at this wavelength the losses are minimized for the optical fiber communication systems. Quantum dots have been intensively studied in the last decades because of their potential application in opto-electronic devices such as high efficiency laser\cite{11} or in quantum computing.\cite{12} It has been previously shown that the electro-optical properties of self-assembled quantum dots are affected when the size, shape and composition is modified. A study of the incorporation of Sb during the growth of self-assembled quantum dots is very interesting because of the surfactant role of Sb that can reduce the mobility of ad-atoms on the surface or modify the surface energy and therefore impact the structural properties at the atomic scale of the quantum dots. The thesis focuses also on quantum cascade laser devices that consist of alternating thin III-V semiconductor multilayers of only few nanometers. Quantum cascade lasers containing
AlAsSb or GaAsSb layers are candidates for ultra-fast emission in the 1.55 μm range. Therefore a fine control of the atomic composition and layer thickness and uniformity is essential to achieve the desired emission wavelength. The presence of Sb in the quantum cascade laser can be problematic due to the curious role of this atom.

A wide variety of techniques exists to study the structural and electro-optical properties of engineered semiconductor nanostructures and doped semiconductors at the nanoscale. Photoluminescence is an excellent tool to study the optical properties of emitting nanostructures such as quantum dots or quantum wells but the limited resolution (~1 μm) puts constraints when atomic resolution is needed. The structural properties of quantum dots are often probed with atomic force microscopy because of the ease and speed of these experiments. However, only uncapped quantum dots can be measured with a lateral resolution of around 30 nm and a vertical resolution of about 1 nm. More importantly, it has been shown that the capping of quantum dots has a strong influence on their final shape and composition. Transmission electron microscopy is widely used for studying semiconductor nanostructures. Although atomic resolution is commonly achieved with
Figure 1.3: (a) X-STM image of a single neutral Mn dopant in bulk InSb. (b) X-STM image of a GaAsSb alloy taken at a voltage where the group V elements are imaged. Dark blue atomic-like features correspond to Sb atoms whereas white atomic-like features correspond to As atoms (c) X-STM image of an InGaAs/GaP quantum dot.
this technique, the thickness of the sample is typically around 50 nm and gives only an average measurement of the parameters probed. Scanning tunneling microscope (STM) on semiconductors is a good compromise of the scanning probe techniques previously mentioned. It can reveal the structural properties of nanostructures with an outstanding resolution down to 0.1 nm in the lateral direction and 10 pm in the vertical direction. In STM, the quantum tunneling effect of electrons is used to image nanostructures and therefore the electronic properties of atoms can be probed. Because semiconductor devices are manufactured by a multi-planar process, the complete structure needs to be analyzed and not only the top surface. Similar to AFM, cross-sectional STM is also a 2D technique. Thus in order to image the full-layer structure, X-STM can be used. By cleaving the wafer along one of the easy cleavage planes and scanning the STM tip over the cleaved surface, the multi-layer structure is available from the substrate to the top surface. With X-STM, the electronic contrast of the atoms and the topographic contrast caused by strain relaxation of nanostructures can be probed at the same time. Figure 1.3 illustrates how X-STM can image dopants in semiconductors, the size and shape of a nanostructure, or the atomic composition of an alloy. Besides cross-sectional STM, new scanning probe techniques are emerging which combine the advantages of the above-mentioned experiments with other experimental approaches. Such as for instance scanning tunneling luminescence that probes the optical properties of semiconductors at the atomic scale by inducing luminescence with a STM tip, and spin-polarized STM that uses magnetic STM tips to reveal the magnetic contrast. These techniques are still difficult to implement in an X-STM unit. One likes to combine these techniques to open a wide range of new experiments since the electronic, optical and magnetic properties are often intimately linked. Finally more and more semiconductors materials are investigated by means of atom probe tomography. The main advantage of this technique is the fact that the obtained data are three dimensional, however due to the difficulty of the data reconstructing process of atom probe tomography the spatial resolution of this technique is very close to but often not as good as that from X-STM.

The scope of the thesis covers a cross-sectional STM study of ferromagnetic semiconductors nanostructures doped with Mn and light-emitting nanostructures containing Sb. The thesis can be divided into three main parts. Firstly, in chapter 2, the experimental procedure and the theory behind cross-sectional STM are discussed in order to give a deeper insight to the reader into the X-STM technique. Then the second part describes the X-STM analysis performed on ferromagnetic semiconductors. Chapter 3 depicts the X-STM study on thin (Ga,Mn)As/(Al,Ga)As multilayer structures where an enhanced Curie temperature has been predicted. Chapter 4 focuses on Mn:InSb where room-temperature ferromagnetism has been measured. Chapter 5 is dedicated to the study of a hybrid material where metallic MnAs nanoclusters are embedded in a zincblende GaAs host. Finally, in the third part the X-STM analysis on Sb containing light emitting devices is discussed. Chapter 6 describes the influence of surface termination and growth techniques for In-
GaAs/AlAsSb quantum wells. In chapter 7 the influence of the substrate orientation on InAs quantum dots grown on GaAsSb is investigated. Chapter 8 brings into focus the role of Sb in a InGaAs/GaAsSb quantum cascade laser where an asymmetric behavior of the optical signal depending on the carrier flow direction has been observed.
Chapter 2

Experimental procedures and background for cross-sectional STM measurements

In this chapter, the experimental techniques for cross-sectional STM measurements are described which includes the preparation of the samples and the fabrication of the tips. Moreover, the underlying principle of scanning tunneling microscopy on semiconductors is explained in order to give a good understanding of the interpretation of the X-STM measurements.

2.1 Sample preparation, mounting, and cleavage

Rectangular pieces of about 3.5 mm × 10 mm are cut along the <110> direction from the III-V semiconductor wafer containing the heterostructures. These are the natural cleavage directions for most of the III/V semiconductors with a zinc-blende structure. The semiconductor materials are in general conductive. Contacts are evaporated on the top surface of the sample in order to improve the conductivity. For an n-type semiconductor, a Zn/Ni/Au layer (5/20/150 nm) is deposited whereas a Ge/Ni/Au layer (20/10/150 nm) is deposited for a p-type semiconductor. The thickness of a wafer varies typically between 340 μm and 400 μm. In order to maximize the chances of obtaining an atomically flat surface after cleaving of the sample, the backside of the samples is mechanically thinned by polishing with Al₂O₃ powder and water until a sample thickness of about 100 μm is reached. Before mounting and clamping the sample into its holder, a small scratch of about 0.5 mm is made with a diamond pen on the top side of the sample as shown in Fig.
2.1(a). This scratch will act as the starting point of the propagation of the cleavage plane later on when the sample is cleaved in the UHV chamber. The sample is mounted in its holder as displayed in Fig. 2.1(b) and only one corner of the sample is clamped between the two metal blocks of the sample holder. Before clamping, two small discs of In are inserted between the sample and the metal blocks. These two discs are then melted to prevent applying too much pressure on the sample when tightening the screws. The samples are loaded in the UHV system where they are degassed at around 200°C during 20 minutes.

The cleavage is then realized by pushing gently the sample until this one breaks. Figure 2.2 shows a typical cleaved surface with the characteristic pattern of induced steps due the relaxation of the strain accumulation after cleavage. The tip approach is realized on the area indicated by the white rectangle in Fig. 2.2(b). The STM tip approach is monitored by a CCD camera until the mirror reflection of the tip becomes visible on the cleaved surface. The final approach is then realized via the STM controller unit until a tunneling current of about 100 pA is obtained.

2.2 Tip preparation

The tips are made from a 99.97% pure tungsten wire (Ø= 0.25 mm). A piece of about 1 cm long is cut and then spot welded on a so-called tip carrier. For use in ultra-high vacuum, the ensemble is cleaned in an ultrasonic bath before etching. The tips are then electro-chemically etched using a 2 molar potassium hydroxide solution and applying a voltage of about 6.2 V between the anode and the cathode. Only 2-3 mm of the tungsten wire is immersed in the solution and serves as the anode, whereas a Pt-Ir spiral serves as
Figure 2.2: (a) Optical microscope image of the (110) surface of a GaAs sample after cleavage showing the cleavage induced steps due to the relaxation of the strain accumulation in the sample. The white square represents the area where the tip approach is achieved. (b) Close-up of the area represented by the white rectangle in Fig. 2.2(a). (c) AFM image (20 × 20 μm²) of the area represented by the white rectangle in Fig. 2.2(a) showing large areas where the surface is monoatomically flat. (d) Height profile taken along the white line showed in (c).
the cathode as displayed in Fig. 2.6(a). The following reactions take then place\[13]\:

\[
\text{Cathode: } 6H_2O(l) + 6e^- \rightarrow 3H_2(g) + 6OH^- \\
\text{Anode: } W(s) + 8OH^- \rightarrow WO_2^{2-} + 4H_2O(l) + 6e^- \tag{2.1}
\]

Because the chemical reaction rate at the anode is higher at the meniscus due to $WO_2^{2-}$ ions sinking along the wire and bringing a fresh stream of $OH^-$ ions, the tip is etched faster at the air-liquid interface than deeper in the fluid as shown in Fig. 2.6(b). Due to gravity the tip will eventually break by itself at its thinnest point leaving an atomically sharp tip, see Fig. 2.6(c). The tips are then loaded in the UHV chamber where they are first degassed 20 minutes at 200 °C. Before the measurements, the tips are bombarded with Ar ions for about 20 minutes in order to remove the oxide layer.

### 2.3 The UHV unit

Measurements are performed using a commercial room temperature Omicron scanning tunneling microscope (STM). The setup consists of three compartments: the STM chamber, the preparation chamber and the load lock. The load lock where the base pressure is $1 \times 10^{-6}$ mbar is used to transfer the tips and the samples from the outside world to the UHV unit. This chamber is pumped by a Varian V-70 turbomolecular pump and prepumped by a BOC Edwards XDS10 scroll pump. These two pumps pump in series with a larger Varian V-250 turbomolecular pump also the preparation chamber where the samples and the tips are degassed and where the Ar bombardment takes place. Typically the pressure in the preparation chamber is around $1 \times 10^{-9}$ mbar. Finally when the samples and the tips are ready for measurement, they are transferred into the STM chamber which is pumped by an ion getter pump in combination with a titanium sublimation element. The samples are cleaved in the STM chamber where the pressure is typically lower than $4 \times 10^{-11}$ mbar. This allows us to measure for about 24 hours at room temperature without suffering from surface contamination. During measurement, only the ion getter pump stays on, the other pumps are switched off to avoid any vibrations due to moving mechanical parts moving. Furthermore, in order to reduce vibration the whole setup is positioned on an active damping system and the STM scanner on an internal eddy current damping stage.
Figure 2.3: (a) Photography of the tungsten etching setup. (b) Schematic view representing the tip etching process. (c) SEM image of the tip apex. Image was taken from\textsuperscript{14}.
2.4 Tunneling theory

If a very sharp metallic tip is brought close to a semiconductor surface within an atomic distance where electrons can tunnel from the tip to the semiconductor or from the semiconductor to the tip through vacuum, the tunneling current $I$ given by Bardeen’s formalism\cite{15} is defined as follows:

$$I = \frac{4\pi e}{\hbar} \int_{0}^{eV} \rho_s(E_{Fs} + \epsilon)\rho_t(E_{Ft} - eV + \epsilon)|M|^2 d\epsilon$$  \hspace{1cm} (2.2)

where $V$ is the applied bias voltage between the sample and the tip, $\rho_{s,t}$ the local density of states (LDOS) and $E_{Fs,t}$ the energy of the Fermi level of the sample and the tip. $M$ represents the tunneling matrix element between the tip states and the sample states.

By assuming that the tip is a point-like probe with an s-wave function for the tip state,\cite{16,17} the tunneling matrix element can be reduced to:

$$|M|^2 = \exp(-2\kappa d)$$  \hspace{1cm} (2.3)

with $d$ the distance between the tip and the surface, and $\kappa$ the inverse decay length in vacuum defined by:

$$\kappa = \sqrt{\frac{2m_0\phi}{\hbar}}$$  \hspace{1cm} (2.4)

where $m_0$ is the electron rest mass, and $\phi$ the effective barrier height.

If we assume that $\phi$ is constant regardless of the applied voltage and that the Local Density of States (LDOS) of the STM tip is constant then the equation simplifies to:

$$I \propto \int_{0}^{eV} \rho_s(E_{Fs} + \epsilon)\exp(-2\kappa d)d\epsilon$$  \hspace{1cm} (2.5)

Furthermore, if a fixed applied voltage is applied between the tip and the sample, the integrated sample LDOS is constant and the equation 2.5 becomes:

$$I \propto \exp(-2\kappa d)$$  \hspace{1cm} (2.6)

Typically, the decay length has a value of 10 nm$^{-1}$, thus a variation of only 0.1 nm of the tip-sample distance leads to variation of one order of magnitude of the tunneling current. This exponential dependence of the tunneling current on the tip-sample distance is at the origin of the high-resolution of the STM at the atomic scale.

Besides imaging the topography profile of a surface, STM is also used as a probe for the sample LDOS. If the tip-sample distance is fixed then by taking the derivative of an $I(V)$ spectrum, equation 2.5 becomes:

$$\frac{dI}{dV} \propto \rho_s(E_{Fs} + \epsilon)\exp(-2\kappa d)$$  \hspace{1cm} (2.7)
The $dI/dV$ spectrum is thus directly proportional to the sample LDOS. The LDOS mapping of the sample surface is usually obtained by taking several I(V) curves on the sample surface and by differentiating numerically the signal.

One has to remind that a lot of assumptions have been made to simplify the expression for the tunnel current. The tunneling process on semiconductors surfaces can be more delicate as for example in the case of tip induced band bending effects which will be further described. However, this coarse model approach is usually sufficient to give a good interpretation of the STM images.

2.5 The (110) surface of a III-V zinc blende crystal semiconductor

This thesis focuses on Mn- and Sb-containing III-V semiconductors with nanostructures grown on (100) or (311)B substrates. Therefore the cross-sectional view of the nanostructures is obtained by scanning one of the {110} planes which are the easy cleavage planes for a zinc blende crystal. After the cleavage, the {110} planes show a 1 × 1 surface unit cell reconstruction with zig-zag rows of alternating cations and anions as displayed in Fig. 2.4(a). Figure 2.4(b) and (c) show that the anions move outward and the cations move into the surface due to this relaxation. The consequence of this buckling effect is a charge transfer and an energy shift where the half-filled dangling bonds of the atoms become filled for the anions and empty for the cations.\[18,19\] Therefore by applying a different polarity between the sample and the STM tip, either the filled states of the anions are imaged ($V_{\text{sample}} < 0$) or the empty states of the cations ($V_{\text{sample}} > 0$). Figure 2.5 shows a typical X-STM image of the (110) GaAs surface taken at negative voltage where the As atoms are imaged. The distance between the atomic rows observed in this picture is equal to the lattice constant because the sub-surface is not imaged. The atomic rows imaged on the (110) surface are thus separated by a bilayer distance.

2.6 Tip induced band bending

An important property of the (110) surface of the III-V zinc blende semiconductors is the unpinning of the Fermi level due to the absence of surface states in the band gap. Therefore when a tip is brought close to the semiconductor surface, the Fermi levels of the tip and the sample align themselves. Figure 2.6 shows the three possible cases for a p-type semiconductor. If a voltage ($V_{FB}$) is applied that compensates exactly the difference between the workfunction of the tip and the electron affinity of the semiconductors, the bands inside the semiconductor are flat i.e. no internal electric fields are present. This is known as the flat band condition ($V = V_{FB}$). If a voltage smaller than $V_{FB}$ is applied then the bands will bend downwards, and if a voltage larger than $V_{FB}$ is applied the bands will
Figure 2.4: Schematic view of a (110) surface of a zinc blende semiconductor (a) top view, (b) side view of the unrelaxed surface, (c) side view of the cleaved surface.

bend upwards. The magnitude of this tip induced band bending (TIBB) effect depends on different parameters such as the doping level, the tip sample-distance, the tip shape, and the flat band voltage. A model has been developed by Feenstra[20] to calculate the TIBB. Typically the TIBB extends over few nanometers in the vertical direction as well as in the lateral direction.

The TIBB effect has a consequence on the imaging of doped regions with the appearance of contrast height between two different doped regions. Moreover, due to the shifting of the bands, the charge state of single dopants below the cleaved surface can be manipulated. Figure 2.6 displays how the charge state of an acceptor in a p-type semiconductor is changed when the bands are bent. When tunneling at negative voltage, the acceptor is ionized and the impurity will appear as a bright isotropic circular feature due to the extra current from the Coulomb field. At positive voltage, the acceptor is in its neutral state and an anisotropic contrast will appear.

2.7 Topography analysis in constant current mode

While the size and the shape of the nanostructures are directly imaged by X-STM, the determination of the material composition is not always straightforward. Semiconductor heterostructures grown by the Stranski-Krastanov method consist of alternated layers of semiconductors materials with different lattice constants. Because of this difference of
Figure 2.5: (a) X-STM image ($20 \times 20 \text{nm}^2$) of the (110) GaAs cleaved surface where filled states are imaged ($V_{\text{sample}} = -3 \text{ V}$ and $I = 40 \text{ pA}$). A missing atom in the As lattice is observed in the center of the image. (b) 3D-view of the same area as (a). (c) Topographic profile taken on the white line as displayed in (a).
Figure 2.6: Energy diagram of the band alignment for a p-type semiconductor with an acceptor close to the cleaved surface. (a) Bands are bent upwards. The acceptor charge state is neutral ($A^0$). (b) Flat-band condition. (c) Bands are banded downwards. The acceptor is ionized ($A^-$).

Figure 2.7: Strain relaxation at the cleaved surface of a strained quantum well.

Figure 2.7: Strain relaxation at the cleaved surface of a strained quantum well.
lattice constant, the strain in the nanostructure builds up. When a sample is cleaved, the strained materials relax and a height displacement is observed as shown in Figure 2.7. This strain relaxation can be measured at the subatomic level with X-STM due the exponential dependence of the tunneling current on the tip-sample distance as demonstrated in section 2.4. The amplitude of this strain relaxation depends on the lattice mismatch and therefore on the composition. The composition is deduced by comparing the experimental data with the finite element calculations using the continuum elasticity theory.\textsuperscript{[21,22]} For a correct measurement of the topographic profiles, the electronic contrasts that can appear in the constant-current images must be minimized. Therefore, in order to reduce those electronic contrasts, the X-STM images are acquired at high positive or negative voltages as shown by Bruls et al.\textsuperscript{[22]}
Chapter 3

Abruptness of (Ga,Mn)As/(Al,Ga)As interfaces

This chapter presents a cross-sectional scanning tunneling microscopy study of (Ga$_{1-x}$Mn$_x$)As/GaAs and (Ga$_{1-x}$Mn$_x$)As/(Al$_{0.2}$Ga$_{0.8}$)As multilayer structures grown by molecular beam epitaxy. These dilute magnetic semiconductor multilayer structures have been predicted to have a strong giant magnetoresistance effect and enhanced Curie temperature. However, a sharp and short-period digital doping profile of the Mn acceptors is essential to achieve this and therefore the studied samples were grown at a low growth temperature (250°C). Cross-sectional scanning tunneling microscopy measurements show that the overall quality of the structure is good but many As antisites are present due to the low growth temperature. The observed Mn profile showed that, despite the low growth temperature, about 20% of the Mn acceptors from the doped layers (8 monolayers thick) end up in the nominally undoped spacer layers (4 monolayers thick) i.e. in the region which should be undoped the concentration of Mn is half that in the deliberately doped region. This segregation puts serious constraints on the creation and application of short-period dilute magnetic superlattices because of the magnetic shortcut caused by the Mn acceptors in the spacer layer.

3.1 Motivation

Dilute magnetic semiconductors (DMSs) have attracted a strong scientific interest in recent years. Such materials can combine electrical, optical and magnetic properties that can be applied, for instance, in information processing.\cite{23} Due to the ready compatibility with current state of the art of semiconductor technology and its potential for room tempera-
ture ferromagnetism,\(^5,^{24,25}\) (Ga,Mn)As has become the model system in the DMS field. Theory, based on a \(k \cdot p\) approach, has predicted that short-period (Ga,Mn)As/(Al,Ga)As superlattices with low Mn concentration allow for an anti-ferromagnetic interlayer exchange coupling (AFM IEC) which can give rise to giant magnetoresistance effects or spin polarized devices.\(^{26}\) Additionally, it has been predicted that these structures may exhibit enhanced Curie temperatures over that of bulk (Ga,Mn)As, potentially making short-period superlattices a route towards creating a room temperature DMS.\(^{27}\)

But, in spite of good structural properties shown by X-ray diffraction measurements, only ferromagnetic interlayer exchange coupling has been found in similar (Ga,Mn)As/GaAs multilayer structures with undoped barriers.\(^{28,29}\) The presence of Mn in the non-magnetic layers may be the reason for the absence of an anti-parallel ferromagnetic alignment across the magnetic layers. Mn can redistribute due to diffusion and segregation which could result in a migration into the spacer layers. Particularly, segregation was shown to occur in both Mn doped III/V materials and in Mn doped II/VI materials.\(^{30,31,32,33}\) To verify this hypothesis for the (Ga,Mn)As/GaAs multilayer structures, we imaged individual Mn atoms in the cross-sectional cleavage (110) surface of the short-period superlattice in order to determine the distribution profile of Mn atoms in the growth direction.

### 3.2 Experiment details

The superlattices were grown by low temperature molecular beam epitaxy (LT-MBE) techniques at 250°C, according the design proposed by Giddings et al.\(^{34}\) The periodic structure, deposited on a (001) semi-insulating GaAs substrate, consists of 50 times repeated sequence of 8 MLs (MLs) (2.2 nm) of (Ga\(_{1-x}\),Mn\(_x\))As and 4 MLs (1.1 nm) of either GaAs or (Al\(_{0.2}\),Ga\(_{0.8}\))As. The intended Mn concentration, \(x\), in the doped layers was 2.26 %; this low concentration was planned to minimize interstitial Mn and to reduce the diffusion of Mn into the barriers.\(^{35}\) Samples were cleaved \textit{in situ} under ultra-high vacuum (<\(6 \times 10^{-11}\) mbar) and measurements were performed using a commercial room temperature Omicron STM.

### 3.3 Results

Figures 3.1 and 3.2 show part of the multilayer structure and the GaAs substrate as measured by X-STM. The tunnel conditions were chosen at sample voltage \(V_{\text{Sample}} = -2\) V and a tunneling current \(I = 0.04\) nA in order to achieve atomic resolution. Under these conditions, only Mn atoms in the uppermost monolayer of the (110) cross-sectional surface are imaged. Because the substrate is undoped and the multilayer structure has a \(p\)-type conductivity, due to the Mn doping, fewer states are available for tunneling out of
Figure 3.1: X-STM image (100 × 100 nm$^2$) of the (110) cleavage plane through the (Ga$_{0.98}$Mn$_{0.02}$)As/GaAs superlattice structure. Top inset is a close-up (8 × 7 nm$^2$) on a single Mn$_{Ga}$ impurity.
Figure 3.2: X-STM image (100 × 100 nm$^2$) of the (110) cleavage plane through the (Ga$_{0.98}$Mn$_{0.02}$)As/(Al$_{0.2}$Ga$_{0.8}$)As superlattice structure. Top inset is a close-up (8 × 7 nm$^2$) on an As$_{Ga}$ defect.
the valence band in the GaAs substrate compared to the superlattice for the chosen tunnel conditions. Therefore, the substrate appears darker than the multilayer area. Atomic-like bright features correspond to substitutional Mn atoms whereas interstitial Mn are not visible. Dark atomic-like features are interpreted as \( \text{As}_{\text{Ga}} \) anti-site defects localized in the uppermost monolayer. A high concentration of \( \text{As}_{\text{Ga}} \) (0.3%) is observed, which is not surprising for the low growth temperature of 250 °C.

Adsorbates are also seen, especially in Fig. 3.2. These adsorbates are present only in the multilayer part of the structure and their concentration is higher for the sample containing Al, which is known to be very reactive and to easily bind adsorbates. Due to the electronic contribution of ionized acceptors at negative voltage, Mn atoms appear as elevations on topographical images in constant current mode, as we can see in Fig. 3.3(a).

At first sight, no periodic arrangement of the Mn atoms can be distinguished from either picture. In order to better determine if the grown structure contains a modulation in the doping distribution the Mn distribution profile is plotted along the growth direction. Counting of Mn atoms was realized by image analysis and Fig. 3.3 shows the results of this automated selection procedure. The atomic row positions, determined by automatic selection, of Mn atoms are sorted along the [001] growth direction. Counting Mn atoms in each atomic row was performed over a length of about 100 nm perpendicular to the growth direction.

The distribution profiles obtained from the X-STM measurements of Figs. 3.1 and 3.2 are shown in Figs. 3.4(a) and (b). From these distributions, the estimation of the average Mn concentration in the multilayer is equal to \( x = 1.1\% \) and \( x = 1.2\% \) for respectively the \((\text{Ga}_{0.98}\text{Mn}_{0.02})\text{As/GaAs}\) and the \((\text{Ga}_{0.98}\text{Mn}_{0.02})\text{As/(Al}_{0.2}\text{Ga}_{0.8})\text{As}\) sample. The growth conditions were chosen with the intention of achieving a Mn doping of 2.26% in the 8 ML thick magnetic layers. Taking into account of the periodic structure, which also includes spacer layers with a thickness of 4 ML, the bulk concentration averaged over all the layers is expected to be 1.5%. This value is close to the experimentally observed concentration. The small difference between the intended and the measured concentration might be related to the calibration of the Mn flux during the growth or the difficulties in identifying all Mn atoms via our automated image analysis. From the histograms shown in Figs. 3.4(a) and (b), it is still difficult to distinguish a periodicity. Figure 3.4(c) shows the frequency distribution \( f(k) \) for the number of rows perpendicular to the growth direction which contain \( k \) Mn atoms obtained from the data of Figs. 3.4(a) and (b). Both distributions are centered on \( k = 2 \) and have the same width. This suggests that Al has no effect on the Mn distribution. Figure 3.5 shows a comparison between \( f(k) \) obtained from the data of Fig. 3.4(a) (yellow histogram) and simulations (green histogram) for various degrees of Mn redistribution.

Figure 3.5(a) shows a comparison with an ideal superlattice in which Mn atoms are only found in the magnetic layers and not in the spacer layers. Figure 3.5(f) shows a comparison with an homogeneous Mn concentration in the growth direction. Figures
Figure 3.3: (a) Topographical X-STM image (29.3 × 18.8 nm²) of the multilayer structure showing surface Mn atoms (brightest features) and As anti-sites (darkest features). (b) Same area as (a); black boxes show where the algorithm identified only Mn atoms. From such a picture, the position and the number of Mn atoms along each atomic row in the [001] direction is determined.
Figure 3.4: (a) and (b) represent the number of Mn atoms present in each atomic row along the [001] growth direction for respectively the $(\text{Ga}_{0.98}\text{Mn}_{0.02})\text{As}/\text{GaAs}$ superlattice structure and the $(\text{Ga}_{0.98}\text{Mn}_{0.02})\text{As}/(\text{Al}_{0.2}\text{Ga}_{0.8})\text{As}$ superlattice structure. (c) shows the frequency distribution $f(k)$ for the number of rows, of length 100 nm, perpendicular to the growth direction which contain $k$ Mn atoms obtained from the data of Fig. 3.4(a) (yellow histogram) and 3.4(b) (green histogram).
3.5(b)–(e) are intermediate cases in which a fraction $d$ of respectively 5%, 10%, 15%, 20% of Mn atoms has diffused or segregated into the non-magnetic layers. For a homogeneous distribution along the growth direction, the probability, $f$, of finding exactly $k$ Mn atoms in one atomic row corresponds to a binomial distribution, where $n$, the number of observations, corresponds to the total number of atoms in one atomic row, and $p$, the probability of finding a Mn atom per atomic row, corresponds to the Mn concentration. In our case, the Mn concentration was chosen to be equal to the concentration measured from Fig. 3.4(a), namely $p = 1.1\%$, and $n = 178$.

$$f(k, n, p) = \frac{n!}{k!(n-k)!} p^k (1-p)^{n-k}, k = 0,1,2,\ldots, n$$

(3.1)

Furthermore, in order to simulate the same distribution for a superlattice, the previous expression is modified to take into consideration a heterogeneous Mn concentration. Following the design of the multilayer structure, the ratio between the thickness of magnetic layers and non-magnetic layers, is taken as 2 to 1, with $p_M$ the Mn concentration in the magnetic layers and $p_N$ the Mn concentration in the spacer layers.

$$f(k, n, p_M, p_N) = \frac{2}{3} \frac{n!}{k!(n-k)!} p_M^k (1-p_M)^{n-k} + \frac{1}{3} \frac{n!}{k!(n-k)!} p_N^k (1-p_N)^{n-k},$$

$$k = 0,1,2,\ldots,n$$

$$p_M = \frac{3}{2} (1-d)p$$

$$p_N = 3dp$$

(3.2)

(3.3)

Equation (3.3) shows the definition of the concentrations $p_M$ and $p_N$. The parameter $d$, representing the fraction of Mn in the spacer layer, can be altered in order to simulate different levels of Mn redistribution. $d = 0$ represents the case of an ideal superlattice with no Mn in the spacer while $d = 0.33$ represents the case with a uniform Mn doping in all layers.

The simulations show that for an ideal superlattice (cf. Fig. 3.5(a)) there are two peaks in the distribution appearing at $k = 0$ and $k = 3$, which means that, in the case of an ideal superlattice with a Mn concentration about $x = 2.3\%$, it is most probable to find atomic rows with either no Mn atoms or 3 Mn atoms in the length of 100 nm that we analyzed. When simulating an increase of Mn segregation in the spacer layers, the two peaks of the distribution tend to merge and center around $k = 2$. For a bulk (Ga,Mn)As sample with an homogeneous distribution of Mn, approximately 2 Mn atoms are expected in the length of 100 nm. Both measured samples have their distribution centered around $k = 2$ and the frequency of atomic rows without Mn atoms is rather low. From careful comparison between the measured distribution and the range of simulated distributions representing either an ideal doped superlattice, bulk doped (Ga,Mn)As or the several intermediate cases, it appears that the shape of the measured distribution is closest to the shape of the simulated
Figure 3.5: The histograms represent the probability of finding atomic rows which contain either 0, 1, 2, 3 ... Mn atoms over a length of 100 nm. The filled histogram is the experimentally obtained distribution also shown in Fig. 3.4(a) (x = 0%) whereas the open histograms are simulated distributions of multilayer structures where a fraction $d$ of Mn atoms of the magnetic layers has ended up in the spacer layer. (a) $d = 0$ corresponds to an ideal superlattice, (b) $d = 0.05$, (c) $d = 0.10$, (d) $d = 0.15$, (e) $d = 0.20$, (f) $d = 0.33$ corresponds to bulk (Ga,Mn)As where Mn atoms are uniformly distributed.
distribution for \( d = 0.20 \). Therefore, we conclude that a periodic distribution is observed but a fraction of about 20% of the Mn deposited in the doped layers has ended up in the non-magnetic layers.

In the theoretical predictions for anti-ferromagnetic interlayer exchange coupling (IEC) in short-period DMS superlattices, it has always been assumed that no magnetic impurities are present in the spacer layers.\(^{[34,39]}\) Experimental work on (Ga,Mn)As based multilayers and superlattices with spacer layers greater than 3 nm has found evidence of both ferromagnetic\(^{[28]}\) and antiferromagnetic\(^{[29,40]}\) IEC. Polarized neutron reflectivity measurements of multilayers consisting of two (Ga,Mn)As layers separated by a GaAs spacer showed evidence of strong coupling between the two layers when the spacer is 6 nm thick, with the IEC increasing in strength for a 3 nm spacer. Mn diffusion is expected to be 1.5 nm or less\(^{[31]}\) and thus the thick spacer layer will contain little Mn. This means the coupling will not be the result of a ferromagnetic short between the two layers. Instead this suggests that the IEC is mediated by carriers through a mechanism such as RKKY-like ferromagnetic exchange or an overlap of the wavefunctions of holes in the two layers.\(^{[28]}\) Although in RKKY theory one of the terms describing the coupling strength becomes greater as the spacer thickness is reduced, there is also an oscillatory term which can change the sign of the coupling between ferromagnetic and antiferromagnetic. In that study there was no indication of this oscillatory behavior as only ferromagnetic coupling was reported.

However, AFM coupling has been found in GaMnAs based superlattices\(^{[29]}\) and trilayers\(^{[40]}\) where the non-magnetic spacer was doped with Be, increasing the hole concentration in the spacer. In this case the AFM coupling was observed when the spacers were doped with Be whilst when the spacer was undoped the magnetic layers were either ferromagnetically coupled or not magnetically coupled. In these studies the width of the spacer is again greater than 3 nm, although for larger spacers the AFM coupling disappears. This again suggests that the interlayer coupling is being mediated by carriers in the non-magnetic spacer.

In order to analyze the magnetic properties of our short-period superlattices, superconducting quantum interference device (SQUID) magnetometry was used to measure a series of samples with different concentrations of Al in the 1.1 nm spacer layer. As can be seen from the \( M(H) \) loops in Fig. 3.6, there is no evidence of any AFM IEC: the square hysteresis shapes with fast magnetization reversal at the coercive field is typical for a ferromagnetic material. If there was a strong AFM coupling then, as the magnetic field is reduced, the measured net magnetic moment would be expected to decrease as the magnetization of adjacent layers rotate in to antiparallel alignments. It is possible that all the magnetic layers are uncoupled, rather than being ferromagnetically coupled. However, in such a case, it might be expected that the magnetization reversal would not occur simultaneously as individual layers may have different coercive fields due to inhomogeneities in the layers. As a result, the switching would be ragged, occurring over a
Figure 3.6: $M(H)$ hysteresis loops at $T = 2$ K for (Al$_z$Ga$_{1-z}$)As superlattices with the magnetic field aligned along the cubic easy magnetic axis. The Al concentration, $z$, is varied between 0% and 40%. The inset shows the temperature dependent remnant magnetization after cooling in a 1 T field has been applied along the principal crystalline axes of the (Al$_{0.2}$Ga$_{0.8}$)As superlattice. The calculated spontaneous magnetization, $M_S$, is plotted alongside.
range of applied fields. This is not observed; the magnetization reversal seems to occur cohesively, indicating that the material is behaving as a single ferromagnet rather than an ensemble of many ferromagnetic layers.

Further evidence that these short-period superlattices are acting as a single ferromagnetic is given by the remnant magnetization data in the inset of Fig. 3.6. The good agreement between the calculated spontaneous magnetization $M_0 = M_{[110]}^2 + M_{[110]}^2$ and the easy cubic remanent magnetization $M_{[100]}$ suggests the sample is acting as a single domain with a Curie temperature of 25 K. Moreover, the average magnetic moment for the Ga$_{0.98}$Mn$_{0.02}$/Al$_{0.2}$Ga$_{0.8}$As sample calculated from the SQUID measurements and the average Mn concentration in the multilayer observed by X-STM (1.2%) is 6 $\mu$B. It has been previously mentioned in this chapter that the concentration observed by X-STM is underestimated. Hence, the magnetic moment is overestimated. However, the magnetic moment calculated with the bulk expected Mn concentration (1.5%) is 4.3 $\mu$B which is close to the value of 4.5 $\mu$B the average magnetic moment found for a well prepared GaMnAs film. Therefore, we suggest that the Mn present in the spacer layers also contributes to the ferromagnetic behavior and we believe that the magnetic layers are ferromagnetically shorted by the Mn and thus the sample behaves like a single ferromagnetic material rather than a multilayer.

Although previous studies have claimed that Mn does not diffuse or segregate within 2-3 MLs in GaAs below a growth temperature of 400°C, our data clearly show that Mn can move out of the magnetic layers into the spacer layer even for structures grown at a temperature as low as 250°C. Classical diffusion can be excluded as the mechanism responsible for the redistribution of Mn because of the low growth temperature. Moreover, measurements performed by Bozkurt et al. have shown that Mn segregation occurs in GaAs for structures grown at 350°C. Due to the high Mn concentration in the magnetic layers leading to a high 2D carrier concentration $N_{2D} \approx 1 \times 10^{15}$ cm$^{-2}$, another possible mechanism for the redistribution of Mn could be drift resulting from the Coulomb repulsion between the ionized dopant.

### 3.4 Conclusions

In conclusion, from the X-STM measurements a periodic Mn distribution in our short-period 2.2 nm/1.1 nm (Ga$_{1-x}$Mn$_x$)As/(Al,Ga)As superlattices was observed with a reduced amplitude due to segregation of Mn from the doped layers into the undoped layers. These magnetic impurities within the spacer layers may be the reason for the absence of IEC in the superlattices. The high concentrations of Mn in the spacer layers act as magnetic shorts, mediating ferromagnetism between the ferromagnetic layers. We suggest that the concept of a short-period superlattice may not be valid considering the atomistic and discrete nature of Mn atoms in these thin and low density (Ga,Mn)As layers.
Chapter 4

Disorder in Mn doped InSb studied at the atomic scale

This chapter presents an atomically resolved study of metalorganic vapor epitaxy grown Mn doped InSb where ferromagnetism at room-temperature has been observed. Both topographic and spectroscopic measurements have been performed by cross-sectional scanning tunneling microscopy. The measurements show a perfect crystal structure without any precipitates and reveal that Mn acts as a shallow acceptor. The Mn concentration obtained from the cross-sectional STM data compares well with the intended doping concentration. While the pair correlation function of the Mn atoms showed that their local distribution is uncorrelated beyond the STM resolution for observing individual dopants, disorder in the Mn ion location is noted. This inhomogeneous distribution is proposed to play an important role in the magnetic behavior that mean field theory fails to explain.

4.1 Motivation

DMS have attracted a strong scientific interest in recent years. Such materials can combine electrical, optical and magnetic properties that can be applied, for instance, in information processing.\textsuperscript{[5,24]} On the road to achieve room temperature applications, the highest Curie temperatures (T\textsubscript{C}) for DMS have been predicted for transition metal dopants in wide gap semiconductors. However, transition metal dopants in wide gap semiconductors form deep levels in the band gap. Additionally, the formation of defects in the host material, such as for example As antisites and Mn interstitials in (Ga,Mn)As reduce the carrier concentration and lower the carrier mediated ferromagnetism.\textsuperscript{[45]} Interestingly, high Curie temperatures have recently been achieved for narrow gap (III,Mn)V semicon-
Figure 4.1: $M(H)$ hysteresis loops at $T = 2\, \text{K}$, $20\, \text{K}$, and $300\, \text{K}$ of a Mn:InSb sample with a similar doping level as the sample measured with X-STM. The magnetic field is aligned along the [001] direction. The inset shows the temperature dependent remnant magnetization after a 100 Oe field has been applied.

Dilute magnetic semiconductors grown by metalorganic vapour phase epitaxy (MOVPE) with respectively a $T_C$ of $330\, \text{K}$ for (In,Mn)As$^{[46,47]}$ and larger than $400\, \text{K}$ for (In,Mn)Sb,$^{[48]}$ despite the prediction of a low $T_C$ by mean field theory for molecular beam epitaxy grown DMS.$^{[45]}$ The position of the Mn acceptor level in narrow gap III-V semiconductors is believed to be either shallow or resonant in the valence band and narrow gap III-V semiconductors have the advantage to remain highly conductive even for a high Mn concentration and therefore should allow for interesting magnetic properties.$^{[49]}$

Theoretical calculations have shown that disorder in the distribution of the magnetic dopant atoms in dilute magnetic semiconductors such as atomic scale clusters or pairs can lead to an increase of the Curie temperature.$^{[50]}$ As an additional source of disorder Kennett et al.$^{[51]}$ have developed a two-component model whereby disorder in the Mn ion locations can lead to spatially inhomogeneous local magnetizations that are strongly correlated with the local charge density. Thus the transition metal dopant distribution can play a central role in determining the magnetic properties of the DMS. The question arises as to the nature of the dopant disorder at concentrations of the order of $10^{20}\, \text{cm}^{-3}$. X-STM is well-suited to reveal the dopant distribution at high resolution$^{[52,42]}$ since to the knowledge of the authors no spatial study at the atomic scale has been reported. Here we show that the dopant distribution is uncorrelated for pair distances beyond $3\, \text{nm}$. However, local disorder in the form of well-resolved percolation pathways is observed in the
X-STM images of ionized Mn acceptors in (In,Mn)Sb. This inhomogeneous distribution can potentially lead to a higher Tc than observed for an ordered lattice of Mn spins.\(^{[53,54]}\)

### 4.2 Experiment details

The InSb films doped with Mn were grown by MOVPE on an InSb substrate at a temperature of 400°C. The film thickness of our samples is 500 nm and the Mn concentration measured by Energy Dispersive X-Ray Spectroscopy is \(9 \times 10^{19}\) cm\(^{-3}\). Temperature dependent resistivity measurements show that the samples exhibit a metallic-like conduction which is consistent with the Mott limit indicating a critical hole composition of \(2.4 \times 10^{17}\) cm\(^{-3}\). At a similar doping level, SQUID magnetometry has revealed a clear magnetic hysteresis at room-temperature and a magnetic moment of 0.44 \(\mu_B\) assuming a homogeneous distribution of Mn atoms. For the X-STM measurements, the samples were cleaved \textit{in situ} along their natural (110) cleavage plane under ultra high vacuum conditions (< \(4 \times 10^{-11}\) mbars) and the measurements were performed at 77 K using a commercial Omicron STM.

### 4.3 Results

A typical large scale atomically resolved X-STM image of the (In,Mn)Sb (110) cleavage surface obtained at constant current and positive sample voltage is shown in Fig. 4.2. The bright features correspond with substitutional Mn acceptors at different depths below the cleavage surface. Depending on the polarity of the applied voltage, either the neutral or ionized charge state of the Mn atom is imaged.\(^{[36]}\) This is due to tip-induced band bending which can pull the Mn acceptor level below the Fermi level at a negative voltage bringing the Mn acceptor in a ionized state, whereas at positive sample voltage, the acceptor level of the Mn dopant can be pulled above the Fermi level bringing the acceptor in a neutral state (see Fig. 2.6). In Fig. 4.2 we observe the Mn acceptors in their neutral state and the STM contrast of a single Mn acceptor reflects the charge distribution of the hole bound to the Mn acceptor. Previous STM studies on various acceptors with a different binding energy in III-V semiconductors have shown that the charge distribution of the hole bound to the acceptor is related to the binding energy of the acceptor.\(^{[55]}\) At a fixed depth, the charge distribution of a deep acceptor (binding energy of the order of 100 meV or more) is characterized by a bow-tie shape whereas the shape of the charge distribution of a shallow acceptor is triangular (binding energy 30 meV or less). Our X-STM measurements clearly show a triangular contrast for the Mn dopants which agrees with Obukhov et al.\(^{[56]}\) where it is predicted that Mn acts as a shallow acceptor in InSb. The differences in the shape and intensity of the Mn contrast observed in Fig. 4.2 is related to the depth of Mn
Figure 4.2: $100 \times 85$ nm$^2$ constant current X-STM image of the (110) Mn:InSb surface. The indices correspond with the depth of the Mn acceptor below the (110) surface ($V_{\text{sample}} = +0.5$ V and $I = 50$ pA).
atoms below the (110) surface.\cite{57}

Figure 4.3(b) shows the different classes of contrast of Mn acceptors that can be found in Fig. 4.2. The highly localized feature of class A in Fig. 4.3(b) corresponds to a Mn acceptor localized in the uppermost monolayer of InSb. The contrasts B-E all have an almost triangular shape but the intensity of the contrast varies strongly as shown by the profile lines taken in the 110 direction and shown in Fig. 4.3(a). The Mn impurities with a less intense contrast are located deeper below the (110) cleavage plane than the impurities with a more intense contrast. Thus we conclude that the acceptors of class B-C-D-E are located respectively in the 2nd, 3rd, 4th and 5th monolayer below the (110) surface. Because Mn acceptors deeper below the cleavage surface are not resolved as clearly and distinctively as those in layer 1 to 5 they are not categorized. Figure fig:Fig2InMnSb(b) shows the frequency distribution of the different classes of Mn contrast. The frequency of appearance is homogeneous for every class of Mn contrast except for the Mn in the uppermost layer which appears less than the other classes. The frequency of the Mn acceptors in the top five layers was used to determine the Mn doping concentration. The estimated Mn concentration based on the X-STM measurement shown in Fig. 4.2 is $3 \times 10^{19}$ cm$^{-3}$ which is somewhat lower than obtained form EDX measurements ($9 \times 10^{19}$ cm$^{-3}$) on this sample.

The sample was also analyzed by X-STM spectroscopy. In these measurements the feedback loop of the piezo-scanner is deactivated and at each point in the studied area the current is measured while the voltage is scanned. Figure 4.4 shows the $dI/dV$ spectrum taken on a free InSb (110) surface (blue line) and on a Mn impurity (red line). The current at negative sample voltage is due to the electrons tunneling from the filled states of the sample (i.e. valence band) to the tip whereas at positive sample voltage, the current is due to the electrons tunneling from the tip into the empty states (i.e. conduction band). The band gap of InSb, at the measurement temperature of 77 K, can be determined from the range of low tunnel current and is about 0.3 eV. This is a good agreement with the value of 0.23 eV at 80 K that is reported in the literature. Although during the spectroscopy measurements the set point is chosen to keep the tip-sample distance constant as much as possible during the STS scan ($V_{sample} = +1$ V and $I = 200$ pA), the Mn atoms are still visible in the constant current images and appear as dark contrasts. Because the tunneling current exhibits an exponential dependency on the tip-sample separation, a small change of the tip-sample induces a dramatic change in the tunneling current and thus in the differential conductivity. When no voltage is applied between the semiconductor sample and the STM tip, the Fermi levels of the tip and the semiconductor are aligned. We can thus conclude from the spectroscopy measurements that the semiconductor Fermi level is located close to the top of the valence band, which is to be expected for p-type material. The spectroscopy measurements on a Mn atom show an extra current channel at about 0.4 V which is due to the electrons tunneling from the STM tip into the neutral acceptor state. At these tunnel conditions the appearance of the triangular contrast is best observed. The
Figure 4.3: (a) Topographic profile lines along the $[\bar{1}10]$ direction for the various classes of Mn acceptors in InSb observed in Fig. 4.2 which are all in their neutral charge state configuration. (b) $10 \times 7$ nm$^2$ constant current X-STM images of the same classes of Mn acceptors. (c) Histogram of the number of Mn acceptors of each class observed in Fig. 4.2.
Figure 4.4: Local tunneling spectroscopy spectra measured on Mn:InSb obtained with the set point at $V_{\text{sample}} = +1$ V and $I = 200$ pA. The red line represents the $dI/dV$ spectrum on the free InSb (110) surface whereas the blue line represents the $dI/dV$ spectrum taken on a Mn acceptor. The inset shows an empty state X-STM image of a Mn acceptor in InSb obtained at $V_{\text{sample}} = +0.5$ V and $I = 50$ pA.

Because we cleave the sample along the growth direction we get a cross-section through the grown epilayers and the substrate and thus can assess various regions of the epilayer and the substrate. From a large number of scans taken at different positions in the epilayer and the substrate we always find a perfect single zinc blende phase with no evidence for clusters. While scanning the (110) plane in the [00\bar{1}] direction from the epilayer towards the substrate no clear (In,Mn)Sb/InSb interface was found. Instead, we observe a monotonous decrease of the Mn concentration extending from the epilayer into the substrate. Mn atoms have been found at a distance of up to 1.5 $\mu$m from the top of the film. Because the Mn:InSb epilayer thickness is 500 nm Mn atoms must have diffused by 1.0 $\mu$m into the substrate. The small difference between the melting point of InSb (527°C) and the growth temperature (400°C) might be related to this long range diffusion.

In order to analyze the spatial correlation of Mn impurities in InSb, the radial distribution function (RDF) has been computed from the X-STM measurements. The position of each Mn acceptor in Fig. 4.5(a) is determined by an automated procedure to find the maximum in the contrast of each Mn acceptor. For each Mn impurity, the distance between a chosen impurity and all the other Mn dopants is measured. Then the number of Mn impurities which are located inside a ring of a thickness $\delta r$ at a distance $r - \delta r/2$ to
Figure 4.5: (a) $100 \times 100 \text{nm}^2$ filled state X-STM image of the ionized Mn acceptors (black stars) below the (110) InSb surface. ($V_{\text{sample}} = -0.8 \text{ V}$ and $I = 200 \text{ pA}$) (b) Radial distribution function of the Mn acceptors observed in (a). Inset: Topographic profile line along the $[\bar{1}10]$ direction of a Mn acceptor in InSb observed in Fig. 4.5(a) in its ionized charge state.
$r + \delta r/2$ from the chosen impurity is obtained. This distribution is then normalized by taking into account the size of the scanned area. This process is repeated for each Mn impurity in the scanned area. The average of all distributions is used to plot the RDF. Figure 4.5(b) shows the RDF obtained from the X-STM measurements. At a radius greater than 3 nm the RDF is constant and equal to 1. This means that the distribution of Mn is random beyond this range. At a radius smaller than 3 nm the RDF decreases smoothly from 1 to 0. This is due to the resolution limit of the X-STM for observing separated ionized impurities. For Mn-Mn separations smaller than 3 nm we cannot always determine the positions of the individual impurities because at the tunnel conditions used in Fig. 4.5(a) the ionized Mn impurities appear as round isotropic elevations with a radius of a few nanometers as shown in the inset in Fig. 4.5(b). Even when the tunnel conditions are chosen such that the Mn impurities are observed in their neutral charge state and the Mn pairs can be split down to a distance of 0.8 nm, no Mn pairs in this range of distances were observed. Note, that near-neighbor cation pairs that are 0.5 nm apart can probably not be resolved by this technique, but such pairs should not be present in the sample for a Mn concentration less than $10^{20}$ cm$^{-3}$ unless there is a strong pair chemical interaction. It has been suggested that the Curie temperature in MOVPE grown (In,Mn)As and (In,Mn)Sb is strongly increased compared to MBE-grown materials due to local correlations effects i.e. near-neighbor clustering and pair formation of the Mn dopant atoms. In this MOVPE sample we have looked for these correlation effects but could not identify a non-random distribution down to 0.8 nm.

The image in Fig. 4.5(a) shows in addition to Mn atoms (dark spots), dark blue regions which are attributed to regions of enhanced tunneling current. The dark blue regions are attributed to the presence of Mn. Away from these regions are light blue regions which is attributed to areas with low tunneling current and lower carrier concentration. It appears that the dark blue regions are forming interconnected networks or percolation pathways through the InSb matrix. Those experimental X-STM image of (In,Mn)Sb supports a theoretical model for DMS by Kennett et al. of an inhomogeneous DMS material. The model views the magnetism in DMS in terms of Mn spins coupling either to a large or small local charge density. In the light of this model the dark blue regions in the X-STM image are attributed to strongly coupled Mn species, whereas the light blue regions are weakly coupled regions of Mn spins. Kennett et al. indicate that an inhomogeneous magnetic state can lead to a higher $T_C$ than is found for an ordered lattice of Mn spins. Thus the model of two species of Mn spins suggests that the magnetization versus temperature curves of a moderately doped DMS should show the presence of both weakly and strongly coupled magnetic species at low temperature and only strongly coupled species at higher temperature. We suggest that high Curie temperature observed in (In,Mn)As and (In,Mn)Sb is associated with the presence of these strongly coupled species. The low average magnetic moment of about 0.44 $\mu_B$ with a similar doping concentration also suggests that only a part of the Mn dopants, those in the percolative paths, contribute to the
ferromagnetic behavior.

4.4 Conclusions

In conclusion disorder in diluted, magnetic semiconductor (In,Mn)Sb was investigated by X-STM. The impurities are randomly distributed for pair distances greater than the 3 nm resolution limit of the STM technique. Well-resolved percolation pathways associated with the Mn acceptor are observed in the X-STM images. These percolation pathways are presumably responsible for the observed ferromagnetism in DMS and supports a previously proposed phenomenological two-component model for ferromagnetism in these materials. We suggest that the magnetic coupling between Mn impurities in the InSb material is strongest for those Mn acceptors that are closest to each other due to a strong overlap of their wavefunctions. The percolation paths correspond to areas with a high LDOS and thus represent the pathways for strong Mn-Mn interactions for nearby Mn pairs.

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Chapter 5

Atomic-scale structure of MnAs nanoclusters embedded in a Be-doped GaAs matrix

This chapter presents a cross-sectional scanning tunneling microscopy study of nanostructured hybrid semiconductor material composed of MnAs nanoclusters embedded in a GaAs matrix. These nanoclusters are formed in situ by annealing a Be-doped GaMnAs layer which was grown by molecular beam epitaxy. The X-STM data reveal that the MnAs nanoclusters have an hexagonal shape and that the Mn content of the initial GaMnAs epilayer has a strong influence on the size of the nanoclusters. X-STM measurements show that the GaAs matrix surrounding the nanoclusters is strain-free and exhibits a homogeneous perfect zinc blende structure. Furthermore, the Mn concentration in the semiconductor host is much smaller than the initial concentration incorporated during growth thus revealing that Mn atoms migrate very efficiently during the annealing step to create the nanoclusters.

5.1 Motivation

On the road to implement ferromagnetic functionalities in semiconductors\cite{61}, GaMnAs has been widely studied as a model to understand and control the ferromagnetic properties of dilute magnetic semiconductors\cite{25,7}. Although recent advances in epitaxial growth have shown that a Curie temperature of 185 K for GaMnAs can be reached,\cite{6} the potential applications in industry still remain uncertain because this is still far below room temperature. A possible solution can be created by incorporating metallic ferromagnetic
nanoclusters of MnAs in a semiconductor host. Such nanostructured materials can have a Curie temperature well above room temperature and still profit from the opto-electronic properties of the semiconductor host.\textsuperscript{[62,63]}

One method to obtain MnAs nanoclusters embedded in a semiconductor matrix consists in annealing \textit{in situ} a (Ga,Mn)As thin film grown by MBE.\textsuperscript{[64]} Rench et al.\textsuperscript{[65]} have shown that the size of the nanoclusters and their magnetic and structural properties depend on the Mn content. For an initial Mn concentration in the range 5-7.5 \%, a homogeneous distribution of small superparamagnetic clusters (diameter \(\approx 6\) nm) with a low blocking temperature (10 K) is obtained whereas for a higher Mn concentration (\(\geq 8\) \%) a distribution of small and much larger clusters (>25 nm) is observed. These larger clusters exhibit a NiAs-phase and superparamagnetism with a much higher blocking temperature well above room-temperature. Moreover, another study on similar materials has demonstrated the metallic character of MnAs nanoclusters in a GaAs matrix.\textsuperscript{[66]} Although most of the structural, electronic and magnetic properties of the nanoclusters in the semiconductor host are known, the composition and the structural properties of the semiconductor host around the nanoclusters still remain uncertain. In this study, we used X-STM to image large areas of the (110) cleavage plane of thin films composed of MnAs nanoclusters embedded in Be-doped GaAs at the atomic level. We focus in this chapter on the composition and the crystal phase of the semiconductor host as well as on the size distribution and the shape of the nanoclusters.

\section{5.2 Experimental details}

The samples were grown by MBE on a \(p\)-doped [001] GaAs substrate. A 100 nm Be-doped buffer layer is grown on top of the substrate followed by a low-temperature 100 nm Be:Ga\(_{1-x}\)Mn\(_x\)As layer grown at 245 \(^\circ\)C with a Mn content \(x\) varying from 5 \% to 8 \% and then covered by a 2 nm high temperature Be:GaAs capping layer. The growth of this capping layer acts also as an annealing step in order to form the nanoclusters and to reduce the amount of As antisites. The Be concentration after annealing in the sample was estimated from transport measurements to be about \(10^{18}\) cm\(^{-3}\). Samples with a low Mn content (\(x<7.5\) \%) and small clusters will be referred as type I whereas samples with a higher Mn content (\(x>7.5\) \%) and larger NiAs-phase clusters will be referred as type II. For the X-STM measurements, the samples are cleaved along their natural (110) cleavage plane under ultra high vacuum conditions (< \(4 \times 10^{-11}\) mbars). The acquisition of the X-STM images is performed at room-temperature using a commercial Omicron STM.
Figure 5.1: 100 × 74.4 nm² constant current X-STM images of (110) plane of the hybrid MnAs:GaMnAs layer of a type I sample taken at $V_{\text{sample}} = -2.7$ V and $I = 40$ pA. The inset shows a close-up of a single Mn atom.
5.3 Experimental results

Figures 5.1 and 5.2 show large atomically resolved X-STM images of the Be:GaMnAs epilayer for respectively the type I and the type II samples. In both figures large hexagonal features are easily distinguished. Bright hexagonal features are indicated by the letter A as shown in Fig. 5.3(a) and dark hexagonal features are indicated by the letter B as shown in Fig. 5.3(b). Figure 5.3(c) shows a comparison between typical topographic profile lines taken on the bright and the dark features. The profile line for the bright feature of Fig. 5.3(a) has a trapezoidal shape and shows an elevation of about 1 nm and a diameter of 6 nm whereas the profile line for the dark features of Fig. 5.3(b) reveals a diameter somewhat equal to the bright feature, but a depression of about 1 nm instead of an elevation is observed. Furthermore, the area of the surface corresponding to the holes (3.2 % of the total area for the type II sample) is comparable to the area defined by the nanoclusters (3.2 % of the total area for the type II sample). We suggest then that the bright features correspond to the MnAs clusters that are still present on the (110) surface whereas the black features corresponds to holes in the (110) surface created by pulling out of the sample nanoclusters during the cleaving process. This latter effect has been observed for every cleaved sample with a probability of having about half of the clusters removed and leaving holes on the scanned surface and the other half of the clusters remain locked into the surface. The hexagonal shape of the clusters is consistent with the fact that the largest clusters exhibit a NiAs phase\(^{65}\). Moreover, the clusters exhibit a two dimensional hexagonal shape on a \{110\} plane and the profile line taken on the clusters along the [001] direction has a trapezoidal shape. Therefore, we suggest that the three dimensional shape of the MnAs nanoclusters is comparable to a hexagonal truncated bipyramid (see Fig. 5.4).

The X-STM images show no discontinuity of the crystal phase at the interface between the buffer layer and the Be:GaMnAs epilayer as well as inside the epilayer. Moreover, no deformation or bending of the atomic rows around the nanoclusters due to strain field has been observed. The GaAs matrix around the clusters exhibits thus a perfect zinc blende structure without strain or appearance of a second crystal structure. Small atomic bright features in the epilayer are observed as shown in the insets in Fig. 5.1 and 5.2. These features correspond to single Mn atoms that are present in the GaAs matrix.\(^{67}\) The Mn concentration is estimated by counting all the single Mn atoms that appear in the X-STM pictures. The Mn content in the Be:GaMnAs epilayer is found to be 0.7 % for the type I and 0.9 % for the type II. This much lower Mn concentration compared to the initial Mn concentration indicates that Mn atoms migrate efficiently during the annealing step in order to form the MnAs nanoclusters. This is corroborated by the presence of very few As antisites compared to GaMnAs layers grown at the same growth temperature.\(^{68}\) If we consider that the number of atoms per area inside the clusters is equal to the number of atoms per area in the GaAs matrix and that the nanoclusters are purely MnAs, the con-
Figure 5.2: 100 × 74.4 nm² constant current X-STM images of (110) plane of the hybrid MnAs:GaMnAs layer of a type II sample taken at \( V_{\text{sample}} = -2.7 \) V and \( I = 40 \) pA. The inset shows a close-up of a single Mn atom.
Figure 5.3: (a) Close-up of a bright feature indicated by the blue cross in Fig. 5.2 corresponding to a MnAs nanocluster locked into the surface. The blue line represents the line where the topographic contrast has been taken. (b) Close-up of a dark feature indicated by the blue cross in Fig. 5.2 corresponding to a hole created by pulling-out a nanocluster during the cleaving process. The red line represents the line where the topographic contrast has been taken. (c) Topographic profile lines taken on the bright and the dark features in (a) and (b). The curves have been zeroed.
centration of Mn that formed nanoclusters can be deducted from the measured areas of the clusters and the holes. Thus a Mn concentration in the nanoclusters of 6.3 % is found for the type I and 7.2 % for the type II. If these concentrations are added to the concentration of single Mn atoms present in the GaAs matrix, the total Mn concentration in the type I sample is 6.2 % and 8.0 % in the type II sample. This agrees with the fact that for a Mn concentration between 5.0 % and 7.5 % a type I sample is obtained and for concentrations higher than 7.5 % a type II sample is obtained.

Figure 5.5 shows histograms of the diameter distribution for both samples. The distributions have been calculated from several X-STM images and then fitted using the following relation\cite{69}:

\[
p(D) = \frac{A}{\sigma D \sqrt{2\pi}} \exp \left[ -\frac{3\ln(D/D_0)}{\sigma^2} \right]^{2}
\]

where \( D \) is the cluster diameter, \( D_0 \) is the median diameter of a cluster in the material, \( \sigma \) the variance of the distribution, and \( A \) a constant that normalizes the probability density function, \( p(D) \).

The coefficients calculated from the fitting gives a median diameter of 3.4 nm and 4.6 nm for the type I and type II, respectively, and a variance of 1.1 nm and 0.9 nm for the type I and type II, respectively. These values agree with the previous work of Rench et al.\cite{65} where the size of the clusters for similar samples have been measured from TEM measurements. Moreover, the size distribution is also found to be log-normal. The histograms show also that the size of the nanoclusters for the type I is smaller than 8 nm whereas in the type II sample clusters with a diameter larger than 20 nm have been found. This confirms the appearance of a second class of much larger clusters when the Mn content in the initial Be:GaMnAs layer is increased.
In summary, MnAs nanoclusters have been formed in a semiconductor host and X-STM measurements have shown that the MnAs clusters in GaAs have a hexagonal shape and that the Mn content has a strong influence on the size of the nanoclusters. The GaAs matrix exhibits a perfect strain-free zinc blende crystal phase around the clusters while the Mn concentration around the clusters is much smaller than the intended concentration indicating that Mn migrates efficiently during the last annealing step to form the clusters.

Figure 5.5: Log-normal-fitted cluster size distributions for the type I and type II samples.
Chapter 6

An atomic scale study of surface termination and digital alloy growth in InGaAs/AlAsSb multi-quantum wells

6.1 Introduction

An atomic scale study has been performed to understand the influence of the (As,Sb) shutter sequences during interface formation on the optical properties of InGaAs/AlAsSb quantum wells. Our X-STM results show that the onset of the Sb profile is steep in the Sb-containing layers whereas an appreciable segregation of Sb in the subsequently grown Sb free layers is observed. The steep rise of the Sb profile is due to extra Sb that is supplied to the surface prior to the growth of the Sb-containing layers. No relation is found between the (As,Sb) termination conditions of the Sb-containing layers and the resulting Sb profiles in the capping layers. Correspondingly, we see that the optical properties of these quantum wells are also nearly independent on the (As,Sb) shutter sequences at the interface. The digital alloy growth in comparison to conventional MBE growth was also explored. X-ray results suggest that the structural properties of the quantum well structures grown by conventional MBE techniques are slightly better that those formed by digital alloy growth. However, photoluminescence studies indicate that the digital alloy samples give rise to a more intense and broader PL emission. X-STM measurements reveal that lateral composition modulations present in the digital alloys are responsible for the enhancement of the photoluminescence intensity and inhomogeneous broadening.
6.2 Motivation

Intersubband (ISB) transitions in semiconductor quantum wells (QWs) have found several device applications in the mid- and far-infrared spectral regions, including QW infrared photodetectors and quantum cascade lasers. Due to their fast carrier relaxation\cite{70} and large optical non-linearities, these transitions are also promising for the development of ultrafast all-optical modulators and switches.\cite{71} These devices are expected to play an important role in long-haul optical fiber communication systems for which wavelengths near 1.55 $\mu$m are required.\cite{72} Material systems with sufficiently large conduction-band offsets to allows ISB transitions at these short wavelengths are (CdS/ZnSe)/BeTe,\cite{73} GaN/Al(Ga)N,\cite{74} and InGaAs/AlAsSb QWs.\cite{75}

$\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{AlAs}_{0.44}\text{Sb}_{0.56}$ QWs present a band offset at $\Gamma$-points as large as 1.6 eV.\cite{76} Strong ISB absorption at 1.93 $\mu$m was reported\cite{77} and shorter wavelengths can be reached using indium-rich strained InGaAs/Al(As,Sb) single wells\cite{78} and coupled-double wells.\cite{75} Strain inside the QWs and strain symmetrization by adding AlAs strain compensating layers place a stringent demand on the growth control.\cite{79} An efficient way for molecular beam epitaxy (MBE) growth of ternary compounds of various compositions without additional source cells or laborious cell temperature changes during growth interruptions consists of the growth of binary alloys with periods of a few MLs. This technique for growing short period superlattices (SPS) or digital-alloy has been employed to approximate various ternary alloys: GaAs/AlAs for (Al,Ga)As or GaAs/InAs for InGaAs. It has been employed to make complex nanostructures and devices with structural and optoelectronic properties comparable or even better than those grown using standard procedures, though nanoscale chemical analyses have revealed lateral modulation of the composition in InAs/GaAs\cite{80} and InAs/AlAs SPS.\cite{81}

In order to obtain a 1.55 $\mu$m ISB absorption, 5-7 MLs thick InGaAs/Al(As,Sb) QWs should be grown. For such a thickness an excellent control of the interface formation is required. However, the change of anions (As, Sb) and cations (Al, Ga, In) at the interfaces poses special challenges for MBE since interfacial abruptness may be compromised by intermixing, due to As/Sb exchange at the surfaces or Sb and In segregation. It has been shown that optimized shutter sequences at the interfaces leads to dramatic improvement on the homogeneity and abruptness of the composition profile.\cite{82} Although a longer growth interruption can smoothen the growth front, a too long soaking time or too strong flux can lead to strong exchange and eventually cause unintentional incorporation and intermixing into the subsequent capping layer. It has been shown that the quality of interfaces terminated with As are generally superior to the ones terminated with Sb, but due to the nature of the weak Sb bond and subsequent floating layer, an excess of Sb is needed at the beginning to ensure a less graded Sb profile in the barrier.\cite{83} In this paper, GaAs/InAs SPS between (Al,As)Sb barriers, lattice matched on InP, are investigated. Optical and structural properties are compared with conventional InGaAs alloys.
6.3 Experimental details

Two sets of samples were grown for this study. One set (T1) was used for the optical and X-ray diffraction (XRD) measurements whereas the second set (T2) was only dedicated to the X-STM measurements. Samples were grown by solid source MBE on InP:S (001) substrates. The substrate temperature was set at 450°C during the entire run. Valved cracker cells were used to produce As₂ and Sb₂ fluxes. A low III/V beam equivalent pressure ratio was used during growth in order to accurately control the (Al,As)Sb composition. Lattice matched conditions were verified by high resolution XRD on thick layer test samples. After oxide protective layer desorption, a 0.2 μm thick InP buffer layer was grown, followed by a 0.15 μm thick lattice matched Al(As,Sb) layer.

The samples of the first set (T1) consist of 10 periods of 7 nm thick In₀.₅₃Ga₀.₄₇As layers or the corresponding GaAs/InAs SPS, surrounded by 15 nm AlAs₀.₄₄Sb₀.₅₆ barriers. To protect the Al(As,Sb) layers against oxidation, a 5 nm thick Ga(As,Sb) layer, lattice matched on InP, was grown on the top of the sample. For the SPS samples, the number of MLs of the individual GaAs and InAs layers was set at 0.43 and 0.48, respectively. A growth interruption under As₂ of 5 seconds was performed between each layer. Thick SPS samples were grown to confirm the SPS lattice matched condition with InP. For interface formation of InGaAs on AlAsSb (Interface I) and AlAsSb on InGaAs (Interface II) various shutter sequences have been employed for interface formation and these are presented in table 6.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>InGaAs</th>
<th>Interface I</th>
<th>Interface II</th>
</tr>
</thead>
<tbody>
<tr>
<td>S726</td>
<td>SPS</td>
<td>As 5s</td>
<td>As &amp; Sb 5s</td>
</tr>
<tr>
<td>S829</td>
<td>Normal</td>
<td>As 5s</td>
<td>As &amp; Sb 5s</td>
</tr>
<tr>
<td>S727</td>
<td>SPS</td>
<td>Sb 20s then As 5s</td>
<td>As 5s then As &amp; Sb 5s</td>
</tr>
<tr>
<td>S830</td>
<td>Normal</td>
<td>Sb 20s then As 5s</td>
<td>As 5s then As &amp; Sb 5s</td>
</tr>
<tr>
<td>S728</td>
<td>SPS</td>
<td>As 25s</td>
<td>As 5s then Sb 20s</td>
</tr>
<tr>
<td>S831</td>
<td>Normal</td>
<td>As 25s</td>
<td>As 5s then Sb 20s</td>
</tr>
</tbody>
</table>

For the set T2, the same interfaces as in the set T1 are reproduced but in a single sample. This was realized in order to minimize the number of cleavage operations for X-STM and to measure all layers and interfaces with the same STM tip and tunnel conditions. Each InGaAs/AlAsSb interface is separated by a 10 nm InP layer in order to reset the surface flatness. The first three interfaces consist of a 7.5 nm thick In₀.₅₃Ga₀.₄₇As
layer grown on the top of a 10 nm thick AlAs_{0.44}Sb_{0.56} layer and will be named hereafter as 1, 2 and 3. The last three interfaces correspond to the inverted interfaces where a 10 nm AlAs_{0.44}Sb_{0.56} layer is grown on the top of a 7.5 nm In_{0.53}Ga_{0.47}As and will be named in this article A, B and C. The different conditions during growth interruptions between each interface are summarized in Table 6.2. In this set (T2), two samples were grown. One sample (S680) where the InGaAs layers were grown by the SPS method, whereas in the other sample (S844) the InGaAs layers were grown by a conventional MBE method.

<table>
<thead>
<tr>
<th>Interfaces</th>
<th>Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlAsSb/InGaAs</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>As 5s</td>
</tr>
<tr>
<td>2</td>
<td>Sb 20s then As 5s</td>
</tr>
<tr>
<td>3</td>
<td>As 25s</td>
</tr>
<tr>
<td>InGaAs/AlAsSb</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>As &amp; Sb 5s</td>
</tr>
<tr>
<td>B</td>
<td>As 5s then As &amp; Sb 5s</td>
</tr>
<tr>
<td>C</td>
<td>As 5s then Sb 20s</td>
</tr>
</tbody>
</table>

6.4 Experimental Results

6.4.1 XRD results

The set T1 was analyzed first by high resolution XRD around the InP(004) reflection. For all samples similar XRD patterns are observed. A thickness fluctuation of less than 3% was determined by comparing the relative positions of the substrate peak and its satellites. For all samples similar XRD patterns are observed with thickness fluctuation as small as 3%. Only the experimental XRD rocking curves of samples S727 and S830 are shown in Fig. 6.1, together with a simulation based on the dynamical diffraction theory. The XRD scan of sample S830 exhibits a number of additional Pendellosung fringes. This indicates that the multiple interfaces within the structure are smooth and alloy layers are of high crystalline quality. The thicknesses of QW layers are obtained by the best fit of the simulated XRD pattern to the experimental data, and are found to agree with nominal values. Less satellite peaks are detected for the sample S727 compared with the sample S830. The disappearance of the satellite peaks can be interpreted as a reduced repeatability of the periods.
6.4.2 Photoluminescence results

During Photoluminescence (PL) experiments, samples are excited by a frequency doubled YAG laser emitting at 532 nm and detected by a Peltier cooled extended InGaAs array detector. The maximum power density on samples was around 4 kW/cm\textsuperscript{2}. The measurements were performed at 10 K in a closed cryostat.

The PL spectra recorded of the set T1 are shown in Fig. 6.2. The E\textsubscript{1}-HH\textsubscript{1} ground-state exciton transition energy calculated using envelope function approximation for 25 ML thick InGaAs/AlAsSb QWs is 0.93 eV. So we assign the main peak around 0.9 eV to the carrier recombination inside QWs. Additional much weaker peaks around 1.05 eV are related to a type II transition at the interface between AlAsSb and InP buffer layer.\textsuperscript{[84]}

The PL peak energy of the samples grown conventionally are all virtually at the same energy (0.85 eV) and thus are not influenced by the interface termination as opposed to the SPS samples that show a shift as large as 20 meV and where it has been suggested that the shutter sequence used at the interfaces is important. The PL linewidth of SPS samples are around 60 meV while for the conventionally grown InGaAs alloy samples PL linewidth of 50 meV are measured. Due to the huge electron confinement system, one ML fluctuation leads to a PL energy shift of 75 meV. However the main difference between samples grown with both methods, concerns the PL intensity. The PL intensities of samples for which InGaAs layers were grown conventionally are 10 times lower than those of SPS samples. More insight can be obtained from combined structural (XRD and X-STM) and optical characterization.
6.4.3 X-STM results

Only the set T2 was used for X-STM measurements. The samples were cleaved \textit{in situ} along their natural (110) cleavage plane under ultra high vacuum conditions ($< 4 \times 10^{-11}$ mbar) and the measurements were performed at room-temperature using a commercial Omicron STM.

Figure 6.3 shows two large scale atomically resolved X-STM images of samples S680 and S844 at constant current and negative voltage where filled states are imaged. Figure 6.3(a) shows the interfaces 2, 3, A and B of the S680 sample with the InGaAs digital alloy barrier whereas Fig. 6.3(b) shows the interfaces 3, A, B and C of the S844 sample with the InGaAs conventional alloy barrier. By comparing the two X-STM images, contrast fluctuations along the $\overline{[110]}$ direction (i.e. perpendicular to the growth direction) are observed for the InGaAs digital-alloy layers. Figure 6.4(a) and (b) show a close-up of those contrast fluctuations of the InGaAs layers 3 and A of both the S680 sample and the S844 sample. At negative voltage the filled states are probed and thus the In and Ga atoms are not directly imaged but rather the the electronic effects these two atomic species have on the As surface atoms. GaAs has a wider band gap than InAs, thus when scanning across the InGaAs layers on Ga-rich region at constant current, the tip-sample distance is reduced to keep the tunneling current at the same value whereas on In-rich region the tip-sample distance is increased. Therefore, in the X-STM images of the InGaAs region, the Ga-rich regions appear darker than the In-rich regions. The contrast fluctuations can be better observed by taking an averaged height profile on the InGaAs barrier. Figure 6.4(c) shows height profiles on a length of 50 nm taken along the $\overline{[110]}$ direction on the
InGaAs barrier number 3 of the digital-alloy and the conventional-alloy sample. The amplitude of the height profiles are clearly higher for the sample S680 than for the sample S844 indicating that the InGaAs layer is less homogeneous for the sample where InGaAs was grown using the digital-alloy method. Moreover, the Ga-rich region and the In-rich region seem to alternate periodically. In order to confirm this periodicity and to compare the amplitude of the height profiles taken on every InGaAs layer of both samples, Fourier transforms of the height profiles have been computed from the measurements.

Figure 6.5 shows the Fourier transforms of the height profiles taken on the six InGaAs barriers of both samples. Peaks at wavenumber around 0.1 nm\(^{-1}\) are only observed for the InGaAs digital-alloy sample. Thus the Ga-rich region and the In-rich region alternate with a periodicity of about 10 nm. This confirms also the results obtained by XRD showing a slight degradation of the structural quality of the SPS sample. The InGaAs layers are grown by alternating the opening of the Ga and the In shutters. Thus if the first monolayers of the InGaAs barriers are not homogeneous, GaAs and InAs will preferably grow on the lattice matched region enhancing the inhomogeneity of the capping layers. We suggest then that the surface diffusion in the SPS samples is directly linked to the homogeneity of the first monolayers grown. Moreover, this lateral modulation in the [\(\bar{1}10\)] direction for the InGaAs digital-alloy sample explains the difference of intensity observed in the PL spectra for the SPS GaAs/InAs samples. We suggest that the increased strength of the PL spectra in the digital alloy is due to the localization of the carriers in the Ga-rich or the In-rich region reducing the non-radiative transitions.

Another important parameter affecting the PL emission is the sharpness of the interfaces InGaAs barriers grown on top of the AlAsSb barriers and AlAsSb barriers on top of the InGaAs barriers. In order to study the quality of those interfaces, the Sb concentration is analyzed along the growth direction for every interface of both samples. Counting of Sb atoms was realized by image analysis of the X-STM measurements obtained at negative voltage where only the group V elements are imaged. Because Sb states in (Al,As)Sb have a higher energy than As states, the Sb atoms appear as brighter atoms than the As atoms. By detecting the maximum extrema and applying a carefully chosen threshold value, the position of Sb atoms can be determined. Counting Sb atoms in each atomic row was performed over a length of about 50 nm perpendicular to the growth direction in order to obtain the Sb composition profiles in the [001] direction. All the six interfaces for both samples have been studied. Figure 6.6 shows the results of this automated selection procedure for the interface 2 (InGaAs on AlAsSb) and the interface B (AlAsSb on InGaAs) of both the S680 sample and the S844 sample where the Sb composition profile exhibits a sharp onset whereas segregation occurs in the capping layers. The profile is then fitted using the following equation:\(^{[85]}\)

\[
S(x) = K \times [H(x - x_1) - H(x - x_2) \times (1 - e^{(x_2-x)/b})]
\]  

(6.1)
Figure 6.3: 100 × 100 nm² constant current X-STM images of the InGaAs/AlAsSb interfaces. The arrows indicate the growth direction. (a) SPS GaAs/InAs sample (S680) $V_{sample} = -3.0$ V and $I = 43$ pA. (b) Conventional InGaAs alloy sample (S844) $V_{sample} = -3.5$ V and $I = 40$ pA.
Figure 6.4: (a) $51 \times 35 \text{ nm}^2$ constant-current STM image of the SPS sample illustrating the contrast between Ga-rich and In-rich regions ($V_{\text{sample}} = -3.0 \text{ V}$ and $I = 43 \text{ pA}$). The arrow indicates the growth direction. (b) $51 \times 35 \text{ nm}^2$ constant-current STM image of the conventional alloy sample illustrating the homogeneity of the InGaAs region ($V_{\text{sample}} = -3.5 \text{ V}$ and $I = 40 \text{ pA}$). The arrow indicates the growth direction. (c) Topographic profile lines taken along the $\bar{[110]}$ direction on the InGaAs region number 3 for the SPS sample (red line) and the InGaAs conventional alloy sample (blue line). The curves are vertically shifted.
Figure 6.5: Fourier transform of the topographic line profiles taken along the $[\bar{1}10]$ direction on the InGaAs region. A Hann filter was used before applying the Fourier transformation.
Figure 6.6: Sb concentration along the growth direction for the two interfaces InGaAs on top of AlAsSb (layer 2) and AlAsSb on top of InGaAs (layer B) for both the SPS GaAs/InAs sample (S680) and the conventional InGaAs alloy sample (S844). The growth interruption conditions for the interfaces are summarized in Table 6.1.

$K$ represents the Sb ratio in the AlAsSb layer, $x_1$ the position of the first bilayer of the AlAsSb barrier and $x_2$ the position of the last bilayer of the AlAsSb barrier, $b$ the exponential decay length, and $H(x)$ is a Heaviside function. The fitting coefficients calculated for the distributions shown in Fig. 6.6 are summarized in Table 6.3.

The Sb concentration found in the AlAsSb layers is constant and varies from 24% to 36%. This is lower than the intended concentration (56%). This is due to the high Sb concentration in the AlAsSb barrier which makes it difficult to distinguish each Sb atom individually, despite the fact that atomic resolution is achieved. The average thickness of the AlAsSb barriers is found to vary from 14 bilayers (8.2 nm) to 16 bilayers (9.4 nm) which is close to the intended 10 nm thickness of the AlAsSb barrier. The sharpness of
the interface InGaAs grown on AlAsSb, which corresponds to the interfaces (1-2-3), and all Sb distribution profiles show that segregation of Sb occurs into the InGaAs barrier. By comparing the fitting coefficients of all the interfaces (1-2-3) for both samples, the decay length varies from 2 to 4 bilayers but no clear trend can be extracted depending of the surface termination or the growth method of the InGaAs barrier. As for the inverted interface AlAsSb grown on InGaAs, the interface is much sharper due to the supply of additional Sb at the formation of this interface step. Within one ML the Sb concentration is already at about 30% which is the Sb ratio observed by X-STM inside the barrier. Once again no clear differences can be found in the sharpness of the interface depending of the surface termination or the growth method of the InGaAs barrier. Because an InP layer is also grown between each interface (1-2-3-A-B-C) the sharpness of the InP/AlAsSb and AlAsSb/InP interfaces can be observed. Interestingly, a similar behavior is observed. The interface AlAsSb on InP is sharp whereas a segregation profile is observed for the interface InP on AlAsSb. Moreover, the decay length is comparable to the one observed for the interface InGaAs on AlAsSb. It seems that the sharpness of interfaces of AlAsSb layers grown between the InGaAs layers is not correlated to the growth method of the InGaAs barriers or the surface termination at the interface. This is confirmed by the PL study showing almost no change in the broadening of the PL spectra as a function of the surface termination or the growth method of the InGaAs barriers.

Figure 6.7 shows two typical comparisons between the number of Sb-Sb pairs in an AlAsSb layer in the [-110] lateral direction measured by X-STM and the number of Sb-Sb pairs calculated if the Sb distribution inside the AlAsSb layers is random. In this chapter, only comparisons for the AlAsSb layers A of the samples S680 and S844 are displayed but the same behavior is observed for the other layers where the measured number of pairs matches the calculated number of pairs for a random Sb distribution. Thus the Sb distribution inside all the AlAsSb layers is homogeneous despite the fact that the growth of AlAsSb lattice-matched on InP has been reported to be problematic due the wide miscibility gap of this compound[86] and the strong dependence of the group V flux ratio on the alloy composition.[87]
6.5 Summary

In conclusion, the influence of the InGaAs alloy growth method on the structural and optical properties of InGaAs/AlAsSb QWs on InP was investigated as well as the interface surface terminations. XRD suggests that QWs with InGaAs barriers grown with a conventional MBE growth method have slightly better structural properties than QWs with InGaAs barriers grown with the SPS method. However, PL studies show that QWs grown by the SPS method have better quality in terms of emission intensity. X-STM has revealed that a lateral modulation of about 10 nm with alternating Ga-rich and In-rich regions is present in the GaAs/InAs SPS sample. This leads to a better confinement of the carriers and therefore an increased PL emission but unfortunately also an increase of the inhomogeneous broadening resulting in an increased PL-width for such samples. X-STM study has also shown that the sharpness of the interfaces is uncorrelated with the surface termination treatment and the growth method of the InGaAs barrier. A sharp interface is observed when AlAsSb is grown on top of InGaAs due to the supply of additional Sb during the formation of the interface. In contrast, Sb segregation into the InGaAs capping barrier is observed when InGaAs is grown on top AlAsSb. The decay length of this Sb segregation is estimated to be between 4 and 8 MLs.
Chapter 7

The surfactant role of Sb on the growth of InAs/GaAsSb quantum dots studied at the atomic scale.

In this chapter, the dependence of the InP substrate orientation on the growth of InAs/GaAsSb quantum dots by molecular beam epitaxy is analyzed. AFM and cross-sectional STM measurements have been performed in order to understand the structural properties of the deposition of InAs on GaAsSb. This chapter presents also a photoluminescence study that has been realized on those nanostructures.

7.1 Motivation

Epitaxial growth of InAs quantum dots (QDs) has been extensively studied during the last decade with InAs/GaAs quantum dots being the most studied system. However, the emission wavelength of those nanostructures around 1.2 μm is not interesting for telecommunication oriented applications. Therefore, a strong interest has been focused on obtaining quantum dots emitting in the 1.55 μm range and above. One method to redshift the emission wavelength consists of growing InAs quantum dots on a different substrate such as InP for example. The small lattice mismatch between those two materials (3.2%) allows the nanostructures to emit at longer wavelengths. But the nature of the nanostructures formed on the (100) substrate by the Stranski-Krastanov growth mode depends largely on the growth system and growth conditions and leads to the formation of quantum wells like structures, quantum wires, quantum dots or dashes. The difficulty of growing InAs/InP quantum dots can be overcome by using a different oriented surface substrate due to dif-
ferent surface energy. In this manner, InAs/InP quantum dots emitting at 1.55 μm have been obtained by using a (311B) substrate. One solution to further increase the emission wavelength is the encapsulation of InAs quantum dots in Sb-containing layers grown on InP substrates which allows type II band alignments and therefore an emission energy smaller than the band gap. In this chapter, the growth of InAs quantum dots embedded in lattice-matched GaAs$_{0.51}$Sb$_{0.49}$ ternary alloy on a (100) and a (311B) InP substrate is presented. The structural properties of uncapped QD’s are studied by AFM whereas the structural properties of capped QD’s are studied by cross-sectional STM. The optical properties are characterized by photoluminescence and compared with calculations using a Poisson-Schrödinger solver.

7.2 Experiment details

Three sets of samples have been grown, one for each characterization method. Each set of samples is grown by molecular beam epitaxy on a n-doped (100) and (311B) InP oriented substrate at a temperature of 450 °C. As$_2$ and Sb$_2$ fluxes are produced by valved cracker cells, with the beam equivalent pressure ratio between group V and III elements kept as low as possible during the growth of GaAsSb so the composition of the GaAsSb layers are lattice matched with InP. The indium growth rate is fixed at 0.1 ML/s and is calibrated on InP (001) surface.

The first series of samples is grown for the AFM measurements and consists of uncapped quantum dots. First a GaAsSb buffer layer is deposited on the substrate followed by a 2 s growth interruption under an As$_2$ flux. Then an InAs layer is grown. The quantity of InAs varies from 2.0 to 6 MLs. Finally, the substrate is cooled down under an As$_2$ flux.

The second set of embedded QD is dedicated to the PL characterization. The samples are grown in a similar way as the first set. But before the growth of the GaAsSb buffer layer, an AlAs$_{0.56}$Sb$_{0.44}$ with a thickness of 10 nm is grown. Then an InAs layer is grown. The quantity of InAs varies from 2.0 to 6 MLs. Finally, the substrate is cooled down under an As$_2$ flux.

The second set of embedded QD is dedicated to the PL characterization. The samples are grown in a similar way as the first set. But before the growth of the GaAsSb buffer layer, an AlAs$_{0.56}$Sb$_{0.44}$ with a thickness of 10 nm is grown. Then the InAs layer is deposited on top of the buffer layer. The thickness of the InAs layer in this case is 3, 4, or 5 MLs. The InAs deposition is followed by a 30 s growth interruption. Then the InAs layer is capped with a GaAsSb layer followed by a second AlAs$_{0.56}$Sb$_{0.44}$ layer. The purpose of the first AlAs$_{0.56}$Sb$_{0.44}$ layer is to suppress the type-II transition across the GaAsSb/InP interface, whereas the purpose of the last AlAs$_{0.56}$Sb$_{0.44}$ layer is to suppress surface recombination.

The set of samples used for the X-STM measurements is different from the two previous sets. Instead of having only one InAs layer per sample, one sample contains 4 layers of embedded QD. This is realized in order to reduce the number of cleavage operations and tip preparations. Moreover, the whole structure is imaged under the same conditions. Therefore, only two samples are grown: one sample on a (100) InP substrate and the other on a (311B) substrate. Both samples are grown with the same conditions. First a 40 nm GaAsSb layer is grown then an InAs layer is deposited. The same operation is repeated
four times, each time with a different InAs thickness. The thickness of the InAs layer is in the order of the growth: 3, 4, 5 and 6 MLs. After the deposition of each InAs layer, the growth is interrupted during 30 s under an As flux. On top of the last InAs layer, a 40 nm GaAsSb capping layer is grown. In order to improve the conductivity for the X-STM measurements of the sample the GaAsSb layers are doped with Si.

7.3 Results and Discussion

7.3.1 Structural properties

The samples were cleaved in situ along their natural (110) cleavage plane under ultra high vacuum conditions (< $4 \times 10^{-11}$ mbars) and the measurements were performed at room-temperature using a commercial Omicron STM. Figure 7.1 shows two large atomically resolved X-STM images of the samples grown on a (311B) and (100) substrate at constant current and negative voltage where filled states are imaged. In Figure 7.1(a), InAs quantum dots are clearly observed for the layers where 3 and 4 MLs of InAs have been deposited whereas no quantum dots are found in Figure 7.1(b) where the same amount of InAs has been deposited on the (100) GaAsSb surface. The layers with a larger amount of InAs are more difficult to image by X-STM. Instead of having an atomically flat surface across those layers, a step edge as shown in Fig. 7.1(a) and indicated by the black arrow occurs during the cleavage operation at the exact position where the InAs layers have been deposited. In Stranski-Krastanov growth mode, the strain builds up with the amount of the lattice mismatched material deposited. We suggest that the amount of strain present for the 5 MLs and 6 MLs InAs layers becomes significant and makes it difficult to obtain a flat cleaved surface at those positions.

Figure 7.2 shows images of the (311B) sample treated with a high-pass Fourier filter where the outward displacement due to strain relaxation is suppressed. Images were taken at negative voltage samples where the group V-elements are imaged. The GaAsSb layers show different atomic-like contrasts due to alloy fluctuations. Because the top of the valence band is higher for GaSb energy than GaAs, the brightest atomic-like features correspond to Sb atoms and the darkest atomic-like features correspond to As atoms. The quantum dots show no internal contrast and therefore we suggest that no alloying is present in the quantum dots and thus the quantum dots are composed of a binary III/V compound. The magnitude of the contrast of the atoms inside the quantum dots is intermediate compared to the fluctuations in the contrast observed in GaAsSb. Figure 7.3 shows the band alignment between InAs, GaAs and GaSb. It appears that the top of the valence band of InAs is situated between the top of the valence band of GaAs and GaSb. Therefore we suggest that the quantum dots are purely composed of InAs with no Ga or Sb atoms in the dots.

The high-pass Fourier filtered images reveal also the absence of a wetting layer be-
Figure 7.1: (a) 100 × 83 nm² constant-current X-STM of the InAs quantum dots capped with Ga(As,Sb) grown on a (311B) substrate. The black arrow indicates a step edge. $V_{\text{sample}} = -3.1$ V and $I = 40$ pA. (b) 100 × 83 nm² constant-current X-STM of the InAs layers deposited on Ga(As,Sb) grown on a (100) substrate. $V_{\text{sample}} = -3.1$ V and $I = 40$ pA.
Figure 7.2: 81 $\times$ 24 nm$^2$ constant-current X-STM images of the InAs quantum dots in GaAsSb grown on a (311B) InP substrate where 3 MLs (a) and 4 MLs of InAs have been deposited (c). The arrow indicates the growth direction. $V_{\text{sample}} = -3.2$ V and $I = 40$ pA. (b) and (d) High-pass Fourier filtered images of (a) and (c), respectively.
between the quantum dots. This wetting layer is usually present in Stranski-Krastanov growth mode but absent in droplet epitaxy.

Figure 7.4 shows the InAs/GaAsSb quantum dot height distribution measured by X-STM for the layers where 3 MLs and 4 MLs of InAs were deposited. These results can be compared with the same distribution of uncapped dots measured by AFM. The height of the capped quantum dots measured by X-STM is lower than the uncapped dots measured by AFM. During the capping process, because the capping layer is not lattice mismatched with the quantum dots, dot decomposition occurs which decreases the size of the quantum dots. Both measurements show the same trend where quantum dot height increases monotonously with the amount of InAs deposited. AFM images show also that the dot density increases also monotonously with the quantity if InAs. This behavior differs from the growth of InAs/InP on (311B) substrate where the dot density increases with the amount of InAs deposited but the dot size stays constant.

X-STM measurements have shown that InAs/GaAsSb dot formation occurs on a (311B) plane without the formation of a wetting layer whereas no dot formation at all occurs on a (100) plane. We suggest that the absence of dot formation on (100) is due to the surfactant effect of Sb. The presence of Sb limits the surface diffusion of In ad-atoms,\textsuperscript{[89]} hence the In ad-atoms do not migrate to form InAs quantum dots and a 2D growth mode is observed.

As for the (311B) sample, the In ad-atoms can diffuse because dots are formed. Therefore, the surfactant effect of Sb that limits diffusion of ad-atoms appears to be suppressed. However, the absence of the wetting layer is unusual. It is difficult to consider that the InAs wetting layer has been formed and then has been destroyed during the GaAsSb capping process since an InAs wetting layer is observed for InAs/InP quantum dot grown on
Figure 7.4: Height distribution of the InAs quantum dots measured by cross-sectional STM for (a) 3 MLs and (b) 4 MLs of InAs deposited.

Figure 7.5: 1.1 $\times$ 0.8 $\mu$m$^2$ AFM images of surface QD produced by (a) 2 MLs, (b) 2.4 MLs, (c) 6 MLs of InAs deposition. The graphs in the lower part show the density, the height and the diameter of the quantum dots as a function of the amount of InAs deposited. Connecting lines between data markers are only guides for eyes only.
Figure 7.6: Various low-temperature (15 K) PL experimental results. (a) PL spectra of embedded InAs QD 4ML (b) Evolution of the PL peak on varying incident power. (c) Comparison of experimentally observed peak energy and calculations.

(311B) InP and subsequently capped with a thin GaAsSb layer.\textsuperscript{[90]} It has been previously shown than the presence of Sb modifies the surface energies.\textsuperscript{[91]} Thus, we consider that on the (311B) plane the GaAsSb surface energy is smaller than the InAs surface energy. This can explain the absence of a wetting layer and, as a consequence, the formation of InAs quantum dots.

### 7.3.2 Photoluminescence

The PL experiments were performed in a temperature range from 15 K up to room temperature. A 532 nm laser was used as an excitation source, and an InGaAs array detector for the detection. Figure 7.6(a) shows the spectra obtained for various excitation powers for the 4 ML InAs embedded QD’s. Two discernible peaks are visible at low temperature and low incident power with a stronger peak corresponding to the ground state exciton emission and a weaker peak corresponding to a higher energy exciton emission, respec-
tively, named peak 1 and 2. When increasing the excitation power, a blue shift is clearly observed. This excitation power dependence is expected for a type-II band alignment like the InAs/GaAsSb system. The electrons are confined in the InAs dot whereas the holes are located in the GaAsSb layer. Due to Coulomb interactions the carriers are attracted closer to the interfaces of the quantum dot and this results in the formation of triangular confinement barriers. This formation of a triangular well at the interface shifts the transition energy towards a higher energy which is expected to be proportional to the third root of the excitation power.\[92\] Figure 7.6(b) shows a good agreement between the experimental data and the model. The type-II band alignment is also responsible of the non-saturation of the ground state emission observed in Fig 7.6(a). The absence of saturation is due to the fact that although the number of photo-excited carriers increases this is compensated by the better overlap of the wave-function of the holes and the electrons which decreases the radiative lifetime.

Figure shows 7.6(c) the emission energy as a function of the quantity of InAs deposited. A red-shift is observed indicating a change of the confinement conditions. This observation agrees well with calculations that have taken into account the size and shape of the quantum dots measured by X-STM and AFM where the dot height increases with the amount of InAs deposited (see Fig. 7.4 and 7.5).

### 7.4 Summary

The X-STM results have confirmed the absence of quantum dot formation in a InAs/GaAsSb system grown on a InP (100) oriented substrate whereas dots are clearly observed on a (311B) oriented substrate. As for the (311B) sample the X-STM images show that the quantum dots are composed of pure InAs with no Ga or Sb inside the dot. The X-STM measurements reveal also the absence of a wetting layer in the InAs/GaAsSb system. To the knowledge of the authors the absence of a wetting layer in the formation of III-V quantum dots has already been reported in the case of droplet epitaxy but not yet in the Stranski-Krastanov growth mode. We attribute the absence of a wetting layer to the surfactant effect of Sb that modifies the surface energies. Finally, PL measurements on the 311B sample confirm the type II band alignment of the InAs/GaAsSb system.
Chapter 8

InGaAs/GaAsSb quantum cascade laser studied at the atomic scale by X-STM

8.1 Motivation

Quantum cascade lasers are promising candidates for emitters in the mid-infrared and Terahertz region \(^\text{[8]}\) that could be used for example in bio-medical sensing \(^\text{[9]}\) or gas phase spectroscopy \(^\text{[10]}\). The record operating temperatures for THz emitters designed on GaAs/AlGaAs systems and InGaAs/InAlAs systems are still below room temperature (186 K and 122 K, respectively) \(^\text{[93,94]}\) and therefore further optimizations are needed. The growth quality is still the main parameter that determines the performance of a QCL \(^\text{[95,96]}\) especially for the InGaAs/InAlAs quantum cascade lasers that requires InAlAs barriers as thin as 1.8 nm. Deutsch et al. \(^\text{[97]}\) have recently demonstrated high performance InGaAs/GaAsSb Terahertz quantum cascade lasers emitting in a range between 3.3 and 4 THz and operating up to 142 K. The replacement of InAlAs barriers by GaAsSb barriers allows to design thicker barriers for the active region and, therefore, put less demand on the growth thickness accuracy. However, an asymmetric behavior of the device performance is observed depending of the direction of the carrier flow. The mixing of group V atoms at the interfaces terminated by GaAsSb is suspected to play a role in this asymmetric behavior. This can be investigated by means of the cross-sectional STM technique which allows us to determine the alloy composition of the quantum cascade laser at the atomic scale. In this chapter, the results obtained by X-STM on a similar InGaAs/GaAsSb quantum cascade laser structure will be presented.
8.2 Experiment details

The sample was grown by MBE using a Riber 32 set-up, located at the Center for Micro-
and Nanostructures of the Vienna University of Technology. The solid-source MBE sys-
tem is composed of Ga, In, Al, Si single-filament cells with As and Sb valved cracker cells. The sample was grown on a 2-inch n$^{+}$ doped InP (100) substrate, with the native oxide thermally removed under an As$_4$ flux. The Ga and In fluxes are determined by the cell temperatures whereas the As$_4$ and Sb$_2$ fluxes are determined by the valve positions. The Ga/In flux ratio is chosen to achieve the InGaAs lattice-matched condition on InP (In$_{0.53}$Ga$_{0.47}$As) and a V/III ratio larger than 20. The Sb$_2$ flux is chosen to achieve the GaAsSb lattice-matched condition on InP (GaAs$_{0.49}$Sb$_{0.51}$) using the same Ga flux as for the InGaAs layer. The sample is grown continuously at a substrate temperature of 470°C, without growth interruptions for interface engineering. The Ga and As shutters remain open during the entire growth, while the InGaAs layers and GaAsSb layers are controlled only by In and Sb shutter operations. For example, the transition from InGaAs to GaAsSb is achieved by closing the In shutter and opening the Sb shutter. Therefore, time transients in the flux exist only for In and Sb.

Sample R404 is a symmetric 3-well THz quantum cascade laser (QCL) structure originally modified from an efficient asymmetric 3-well design. The active region consists of 170 periods of 1/13.3/3/22.8/3/13.3 nm, where the GaAsSb barriers are in bold font, In-
GaAs wells in normal font, and the doped InGaAs is underlined. There are highly doped (7.2 $\times$ 10$^{18}$ cm$^{-3}$) top 50 nm and bottom 100 nm InGaAs contact layers.

The samples were cleaved in situ along their natural (110) cleavage plane under ultra high vacuum conditions (< 4 $\times$ 10$^{-11}$ mbars) and the measurements were performed at room-temperature using a commercial Omicron STM.

8.3 Experiment results

Figure 8.1 shows a large atomically resolved X-STM image of the active region of the quantum cascade laser (QCL) at constant current and negative voltage where filled states are imaged. The bright thin layers correspond to the GaAsSb barriers whereas the darker thicker layers correspond to the InGaAs quantum wells. The bright atomic-like features observed in the GaAsSb layers correspond to Sb atoms due to the fact that GaSb has a higher valence energy than GaAs. In the InGaAs wells, inhomogeneity of the contrast is observed where the relative bright region corresponds to As-rich regions and the relative dark regions correspond to Ga-rich regions. The same atomic-like bright features are observed in the GaAsSb barriers which also correspond to Sb atoms indicating that Sb segregation occurs during the growth of the wells. In order to better resolve the position of Sb atoms across the QCL structure, a high-pass Fourier filter is applied to the X-STM images. Figures 8.2(a) and (b) show a comparison of the same X-STM image before (a)
Figure 8.1: $100 \times 100 \text{nm}^2$ constant current X-STM image of (110) plane of the QCL structure. The thin bright layers correspond to the GaAsSb barriers whereas the thick dark layers correspond to the InGaAs wells. The arrow indicates the [001] growth direction. $V_{\text{sample}} = -2.6 \text{ V}$ and $I = 40 \text{ pA}$.

and after (b) the application of the high-pass Fourier filter where the colors have been inverted to better highlight the position of Sb atoms. The Sb states in InGaAs and GaAsSb have a higher energy than the As states. Thus by detecting the maximum extrema and applying a carefully chosen threshold value, the position of Sb atoms can be determined. Counting Sb atoms in each atomic row was performed over a length of about 50 nm perpendicular to the growth direction in order to obtain the Sb composition profiles in the [001] direction. This operation is repeated for several GaAsSb layers and the number of Sb atoms detected are added depending on the thickness of the GaAsSb layers (1 nm or 3 nm). These profiles for the thin and the thick GaAsSb layers are shown in Fig. 8.3. The Sb profile is found to start abruptly, then mainly constant in the thick layers and finally followed by a decay of the Sb content in the growth direction. Therefore, the profiles have been fitted using the following equation:

$$S(x) = a[H(x) - H(x - x_0)(1 - e^{(x_0-x)/b})]$$

(8.1)
where \( a \) is a constant, \( x_0 \) the position of the last bilayer of the GaAsSb barrier, \( b \) the exponential decay length, and \( H(x) \) is a Heaviside function. The result of this fitting process is shown by the black lines in Fig. 8.3.

The total number of Sb atoms found in the thin layers is lower than the number of atoms in the thick layers due to the fact that less layers have been analyzed for determining the Sb profile. The fitting parameters give a thickness of 2 bilayers for the thin layers and 4 bilayers for the thick layers which correspond to 1.2 nm and 2.3 nm, respectively. This corresponds with the intended thickness of respectively 1 nm and 3 nm. The decay length is found to be 0.7 nm for the thin GaAsSb layers and 1.3 nm for the thick layers. We suggest that this difference in abruptness of the InGaAs/GaAsSb interfaces along the growth direction is related to the observation of the asymmetric behavior of the optical output upon reversal of the direction of the carrier flow.

When taking a topographic profile along the [100] direction as shown in Fig. 8.4, an inward relaxation is revealed indicating that the GaAsSb layers are not lattice matched with the InGaAs layers. This means that the composition of the GaAsSb layers do not correspond to the lattice match condition (GaAs\(_{0.44}\)Sb\(_{0.49}\)). Figure 8.4 shows also peaks indicated by the arrows in the topographic profile close to the GaAsSb layers. Those contrasts are not due to the topography of the surface but are related to electronic effects. Because the X-STM image was taken at a sample voltage of -2.6 V, the effect of the tip induced band bending is not minimized enough. Therefore, a light bias is introduced during the acquisition of the topological surface of the QCL structure at the GaAsSb layers. The inward relaxation after cleaving the sample can be related to a lack of Sb in the GaAsSb layers. Because a Sb segregation is observed, the relaxation of the sample after the cleavage for different Sb concentrations in the GaAsSb barriers has been calculated using finite elements. The Sb profile is modelled following the same equation as shown in Equation with an exponential decay length \( b \) varying from 0.5 nm to 1.5 nm. Yet the Sb content is kept constant for the different decay lengths which means that the Sb concentration in the GaAsSb layers decreases when the decay length increases as shown in Fig. 8.4. The thickness of the layers is chosen to be 1 nm for the thin layers and 3 nm for the thick layers. Fig. 8.4 shows the results of the finite elements calculation for the following decay lengths of \( b = 0.5 \) nm, \( b = 1.0 \) nm, and \( b = 1.5 \) nm.

By comparing the three different relaxation profiles calculated for the different decay lengths, the best fit is obtained for a decay length of 1 nm. This value agrees with the two other values obtained by fitting the Sb distribution in Fig. 8.3 (\( b = 0.7 \) nm and \( b = 1.3 \) nm). The finite element calculations show also that the more Sb segregates into the InGaAs wells the more asymmetric the relaxation profile becomes. We suggest that this asymmetry of the strain distribution at the interface where the InGaAs wells are grown on the top of the GaAsSb barriers is responsible for the polarity effect observed in the electric measurements.
Figure 8.2: (a) 70 × 40 nm² constant current X-STM of the (110) plane of the QCL structure. $V_{\text{sample}} = -2.6$ V and $I = 40$ pA. (b) High-pass Fourier filtered of the same X-STM image as (a) where the colors have been inverted. The blue atomic-like features represent the Sb atoms. The arrows indicate the growth direction.
Figure 8.3: Histograms of the Sb profile along the [001] growth direction for the 1 nm and the 3 nm thick layers. The histograms are fitted (black lines) using the equation shown in Equation. 8.3

8.4 Summary

Nominally symmetric GaAsSb/InGaAs quantum cascade lasers have been investigated by X-STM. The X-STM measurements show that the profile of the Sb distribution is steep at the onset of the GaAsSb layers but much less sharp with the capping layers. This segregation of Sb into the InGaAs wells lowers the Sb concentration in the GaAsSb layers. Also an asymmetric strain distribution is observed in the GaAsSb layers. Both effects break the symmetry of the layer structure and the band alignment and results in the observed current polarity effects in the PL spectra.
Figure 8.4: Profile of the relaxation of the QCL structure extracted from the X-STM images (black line) and the results of the finite elements calculations (red, orange and blue lines) for three different exponential decay lengths ($b = 0.5$ nm, $b = 1.0$ nm, and $b = 1.5$ nm). The oscillations represent the atomic corrugation. The bottom image shows the Sb profile along the [001] when Sb segregation occurs into the InGaAs layers with the three different decay lengths.
Bibliography


Summary

Cross-sectional Scanning Tunneling Microscopy (X-STM) is used to study Mn and Sb containing III-V semiconductor materials. In this technique the cleavage plane of a nanostructured semiconductor material is imaged with an STM tip at the atomic scale revealing the structural and the electronic properties of the embedded nanostructures. Mn doped III-V semiconductors have been extensively explored in the last decade because of their ferromagnetic properties. Sb is often used as a surfactant to assist in the formation of nanostructured materials or to open special wavelength areas in photonic applications. Both Mn and Sb show a complex behavior and often ill understood behavior during growth. In this study we have used XSTM to explore a number of issues related to the incorporation and behavior Mn and Sb during the growth of nanostructured materials.

Thin GaMnAs/(Al,Ga)As superlattices have been predicted to have an enhanced Curie temperature compared to bulk GaMnAs. However X-STM measurements on thin GaMnAs/(Al,Ga)As multilayers structures have shown that even if the nanostructures are grown at low-temperature (250 °C), about 20% of Mn atoms segregate into the (Al,Ga)As barriers putting a serious constraint in the realization of an enhanced Curie Temperature.

Recently InMnSb has been explored as a new semiconductor material with ferromagnetic properties at room temperature. This material exhibits ferromagnetism at room temperature and has a Curie temperature exceeding 500 °C but several material related questions such as phase purity have been raised. The X-STM study of InMnSb revealed that the crystal phase is purely zinc-blend with no evidence of a second phase or cluster formation. The Mn distribution inside the InSb is fully random beyond the X-STM resolution for observing individual impurities, which is about 3 nm. Well-resolved percolation pathways due to the random Mn distribution in InSb were revealed for the first time. The percolative pathways are suggested to be responsible for the observed ferromagnetism at room temperature.

In order to create spintronic semiconductor materials that show magnetic behavior at room temperature, MnAs nanoclusters have been embedded in a semiconductor host. X-STM measurements have shown that the MnAs clusters in GaAs have a hexagonal shape and that the Mn content has a strong influence on the size of the nanoclusters. The GaAs
matrix exhibits a perfect zincblende crystal phase around the clusters while Mn concentration around the clusters is much smaller than the intended concentration indicating that Mn efficiently migrates during the last annealing step to form the clusters.

The influence of Sb on the growth AlAsSb/InGaAs quantum wells has been investigated. The effect of surface termination of the interface layers has been studied. It was proven that the sharpness of the interface is uncorrelated with the conditions of the surface termination. Every AlAsSb barrier shows a steep onset but a gradual Sb profile into the capping layer. Furthermore a comparison has been made between InGaAs barriers grown by the so-called digital alloy method or by a conventional MBE method. The samples grown by the so-called digital alloy method show degraded structural properties but a more intense PL emission than the samples where the InGaAs barriers were grown with a conventional MBE method. X-STM measurements have shown that digital InGaAs alloy exhibit periodic composition modulation in the direction lateral to the growth with a periodicity of about 10nm. This lateral modulation leads to a better confinement of the carriers and this results in a higher recombination rate due to a better overlap of the electron-hole wavefunctions.

Nominally symmetric GaAsSb/InGaAs quantum cascade lasers were also investigated by X-STM. PL emission of these lasers showed different spectra depending on the direction of the current flow. X-STM measurements have shown that the profile of the Sb distribution is steep on the onset of the GaAsSb layers but less sharp at the interface with the capping layer. Also an asymmetric strain distribution is observed in the GaAsSb layers, which is due to segregation of Sb into the InGaAs layers that lowers the Sb concentration in the GaAsSb layers. Both effects break the symmetry of the structure of the layer structure and results in the observed current polarity effects in the PL spectra.

The effect of the substrate orientation on the growth of InAs in GaAsSb was explored. Quantum dot formation was observed when InAs was deposited on a 311B GaAsSb surface. However, the deposition of InAs on a 100 GaAsSb surface leads only to the formation of a wetting layer. This is due to the curious role of Sb in semiconductor growth.
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List of Publications


S. J. C. Mauger, J. Bocquel, P. M. Koenraad, C. Feeser, N. Parashar, and B. W. Wessels, *Disorder in Mn doped InSb studied at the atomic scale by cross-sectional STM*, submitted to PRL.

S. J. C. Mauger, Yu Zhao, M. Bozkurt, P. M. Koenraad, Hervé Folliot, and N. Bertru, *An atomic scale study of surface termination and digital alloy growth in InGaAs/AlAsSb multi-quantum wells*, submitted to PRB.

S. J. C. Mauger, P. M. Koenraad, D. Rench, N. Samarth, *Disorder in Mn doped InSb studied at the atomic scale by cross-sectional STM*, in preparation.
Curriculum Vitae

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