Atomic-scale probing of metallic and semiconductor nanostructures

PROEFSCHRIFT

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Joris Gerhard Keizer

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prof.dr. P.M. Koenraad

en

prof.dr. R. Feenstra

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chapter 1

Introduction

Fire, wheel, printing press... Although there is little consensus over what are the most life changing inventions of all time, these three are, not surprisingly, always listed in the top ten. What is surprising though, is that the microscope is almost never included in these lists. Like no other invention, the microscope has unveiled the secrets of nature and thereby has had a huge impact on daily life. Before its invention, the world could only be probed with the resolution of the human eye. With the advent of the compound microscope in the early 17th century this changed, and a whole new world opened up. In the beginning though, the great potential of the microscope was only realized by a select few and for a long time it was merely a toy in the homes of the rich. Still, the early days of the microscope saw the discovery of bacteria, germs, cells, and parasites. These discoveries raised the awareness of the importance of hygiene among the general public, and as such had a tremendous impact on the quality of live. Over the next 200 years, the resolving power and design of the microscope changed little and it was as late as the 19th century that, due to the availability of higher quality lenses, great strides forward were made. Within a century however, these advances came to a halt when the physical limit of the compound microscope, i.e. the diffraction limit of light, was reached. Soon however, this obstacle was overcome by the invention of the electron microscope in the early 1930s, and the quest for probing the micro-cosmos with ever higher resolution continued. Despite the fact that the electron microscope provided two orders of magnitude higher magnification, the at the time "Holy Grail" of microscopy, the imaging of individual atoms, remained out of reach. In the 1950s, a completely new microscopy concept was developed. Instead, of probing with an electron beam, the geometry of the electric field around a sharp, high voltage biased tip was exploited in the field ion microscope. Finally, atomic resolution could be achieved with this microscopy technique. In the following years, the technique was refined and ultimately gave birth to the technique of atom probe tomography. Although, capable of providing a fully three-dimensional chemical composition profile, this promising technique failed to catch on due to the technically challenging sample preparation and the limited field of view. Furthermore, at the time its application was limited to metals. Only recently, interest in the technique was rekindled by advances in pulsed laser technology which boosted
accuracy and opened up the possibility to study semiconductors. In the 1980s, another completely different microscopy concept was developed: the scanning of surfaces with nanoscale probes. The scanning tunneling microscope was the first within the family which later became known as the family of scanning probe microscopes where this concept was utilized. Soon, it was realized that the technique could be extended from merely topographic imaging to the probing of electronic, magnetic, optical, thermal, and chemical forces and many other interactions. This versatility in combination with the atomic-scale resolution made scanning probe microscopy a popular imaging technique almost overnight. Furthermore, the unique capabilities of scanning probe microscopes are, for a large part, responsible for the emergence of the field of nanotechnology, a field that has already started to change daily life once again.

In scanning tunneling microscopy (STM) an atomically sharp metallic tip is brought in close proximity to a (semi)conducting sample to probe the electronic and topographic features of the surface. Three extensions of this technique, namely cross-sectional scanning tunneling microscopy (X-STM), scanning tunneling luminescence microscopy (STL), and spin-polarized scanning tunneling microscopy (SP-STM), are presented in this thesis. In the first technique, X-STM, a sample is cleaved along the (110) natural cleavage plane of a zinc-blende crystal to allow the observation of single dopants and embedded nanostructures such as quantum wells and quantum dots in a plane parallel to the growth direction\(^1\). The second technique, STL, in which the STM-tip locally induces luminescence can be used to extend optical probing beyond the diffraction limit. In this respect, this technique has the potential to provide a wealth of information about light–matter interactions on the atomic-scale. Already demonstrated applications of STL include the investigation into the coupling of plasmons with metallic nanostructures\(^2,3\), luminescence emission from semiconductor nanostructures\(^4,5\) and single dopants in semiconductors\(^6\). The optical properties of a material system can be linked to its magnetic properties by studying the polarization of the STM-induced luminescence\(^7\). In this respect, STL and the technique of SP-STM are complementary. In the latter technique a magnetic sensitive STM-tip is used to probe the electromagnetic properties of a surface on the atomic-scale, a highly sought after capability in modern day development of spintronics. Examples of SP-STM included domain wall imaging\(^8,9\), characterization of single magnetic dopants\(^10\), and characterization of magnetic nanostructures\(^11,12\). Although the techniques of STL and SP-STM have great potential, the downside is that they are notoriously difficult to implement experimentally. This is reflected in the small number of groups that have succeeded in implementing one of the techniques, let alone both simultaneously. This is a pity since the complementary nature of these two techniques opens up a myriad of experiments with which the optical, electronic, and magnetic properties of materials can be simultaneously investigated with atomic-scale resolution. The ultimate goal of the current work is to combine the two techniques of STL and SP-STM, which are in their own respect already experimentally challenging, with the technique of X-STM to study the properties of single dopants and embedded nanostructures, such as quantum wells and quantum dots. In this thesis the successful implementation of the before mentioned techniques in a single scanning tunneling microscopy is reported.

In the second chapter of this thesis, the theoretical and experimental background of STM and the three extensions on the technique (X-STM, STL, SP-STM) are described. The last part of this chapter is devoted to the introduction of atom probe tomography
(APT), a conceptually completely different characterization technique. This technique allows the fully three-dimensional characterization of embedded nanostructures, carrying the geometrical and chemical analysis beyond the two-dimensional cleavage plane to which the technique of X-STM is restricted.

In the third chapter, a relatively simple and cost-effective STM-induced luminescence collection system that can rival the current existing collection systems is proposed. The chapter focuses on the technological aspects of STL-implementation. As proof-of-principle, the collection system is tested on metallic and semiconductor surfaces. More specifically, STL on an Au(110) surface is demonstrated. In the last part of this chapter, the technique of STL is combined with X-STM to investigate the STM-induced luminescence from a highly Zn-doped GaAs sample.

In the fourth chapter, a proof-of-principle of SP-STM is presented. An unambiguous demonstration of SP-STM requires a dedicated sample with a lateral variation in the direction of magnetization. In this thesis, the chosen material system consists of thin layers of iron that are deposited on a vicinal tungsten (110)-surface. The surface of this material system is known to exhibit an alternating in-plane and out-of-plane direction of magnetization, and is therefore well-suited for a demonstration of SP-STM.

In the fifth chapter, the composition profiling of semiconductor quantum dot (QD) layers by APT and X-STM is presented. As mentioned earlier, the application of APT to semiconductors is a recent development, made possible by advances in pulsed laser technology. Hence, only few studies involving semiconductor nanostructures have been reported so far and much remains unclear about APT performance on semiconductors. In terms of capabilities, APT seems to complement X-STM very well. Where X-STM gives only two-dimensional cross-sections, APT provides a three-dimensional tomographic reconstruction, and where X-STM has a limited capability to distinguish chemical species, the mass-spectral analysis of APT offers the ability to not only distinguish different elements but also different isotopes from each other. However, a particular weakness of APT comes from the necessity to reconstruct the data, a process that requires many assumptions about factors such as apex shape, radius, evaporation conditions and so forth. The result is that, whilst APT provides a very unique dataset, its reliability and spatial accuracy are inherently inferior to direct measurements with X-STM. In this chapter, APT is benchmarked against X-STM. The two techniques are linked by means of computational methods that model surface relaxation and their complementary behavior is shown.

In the sixth chapter, the analysis of buried self-assembled semiconductor QDs is continued. In the last decade the fabrication of QDs has been intensively studied. The interest has been, and still is, stimulated by applications of self-assembled QDs in optoelectronic devices. Nowadays, QDs are for instance applied or suggested in QD lasers, single electron transistors, and spin manipulation. From these, and other studies, it is well known that the optical and electronic properties of QDs are strongly affected by their size, shape, and chemical composition. More specifically, control over the height of QDs allows the tuning of their emission wavelength and g-factor. Nowadays, several methods are available to control the height of QDs grown in the Stranski-Krastanov mode, among which the use of surfactants, double-capping, indium flush, and strain engineering of the capping layer. In this chapter, the latter two techniques are investigated in detail by X-STM and Kinetic Monte-Carlo (KMC) simulations. X-STM studies have, and will continue, to provide wealth of information.
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giving a better understanding of the growth process, but the technique only provides a cross-sectional snapshot of the buried QDs after the completion of the growth. In this respect, techniques such as APT and KMC simulations can be of great complementary value and provide further insight into the details of the growth process. Although KMC simulations have been used in the past to study the growth of nanostructures\textsuperscript{37–39}, the work presented in this chapter is the first in which a realistic, fully three-dimensional KMC simulation is compared with experimental results.

In chapter seven, the details and possibilities of droplet epitaxy as an alternative technique to grow self-assembled QDs are investigated. Traditionally, QDs are grown in the strain driven Stranski-Krastanov mode\textsuperscript{40}. Defect free QDs can be grown with this technique, but the presence of strain in the material during the growth process is a major complicating factor. For one, strain can strongly modify the electronic structure and is the driving force behind QD decomposition and intermixing\textsuperscript{41,42}. The resulting structural imperfections can obscure the intrinsic properties of the QDs and hinder the linking of experiment, e.g. photoluminescence measurements, with a realistic QD model\textsuperscript{43}. In this respect, QDs grown by droplet epitaxy provide a much simpler approach. This technique involves the low temperature growth of unstrained liquid group III-elements droplets that are subsequently crystallized into QDs by the incorporation of group V-elements\textsuperscript{44,45}. In this chapter, the growth of GaAs/AlGaAs QDs by droplet epitaxy QDs is investigated by means of X-STM.

To summarize, it is shown in this thesis that the techniques of X-STM, STL, and SP-STM can all be implemented in a single commercial low temperature STM. The combination of the three techniques makes possible a myriad of experiments to further investigate the optical, electronic, and magnetic properties of embedded nanostructures and single dopants. The well-established technique of X-STM was used, in conjunction with computational methods and APT, to study various aspects of the growth of self-assembled QDs.
In this chapter, the nanoprobing techniques of scanning tunneling microscopy and atom probe tomography are introduced. These two techniques were used to obtain the experimental results presented in the current work. A theoretical and an experimental background of both techniques is given. While only a very basic introduction to atom probe tomography is given, the technique of scanning tunneling microscopy and several variations, namely spin-polarized scanning tunneling microscopy, scanning tunneling luminescence microscopy, and cross-sectional scanning tunneling microscopy are treated in-depth.

2.1 Scanning tunneling microscopy

The first technique under consideration is scanning tunneling microscopy. Invented by Binnig and Rohrer in 1981, the scanning tunneling microscope (STM) was the first of the scanning probe microscope family. This family of microscopes shares the use of a mechanical probe to scan a surface, and nowadays includes, among others, the atomic force microscope, the magnetic force microscope, the electrostatic force microscope, and the scanning tunneling microscope. In STM an atomically sharp metallic tip is brought in close proximity to a (semi) conducting sample. In the case that the distance between the tip and the surface is sufficiently small, typically on the order of a nanometer, electrons will “tunnel” through the classically forbidden vacuum barrier. The direction in which these electrons tunnel can be directed by the application of a small bias voltage. The result is a net tunnel current that is found to be extremely sensitive to the size of the tunnel gap. This sensitivity can be exploited in STM to obtain atomically resolved topographic maps in the so-called constant-current-mode. In this mode of operation the tip is scanned across the surface while the tunnel current is kept constant by means of a feedback loop that controls the $z$-piezo actuator, see figure 2.1. A typical result of such a scan is shown in figure 2.2. In the remainder of this section both the theoretical and experimental backgrounds of STM, tip preparation, and three extensions of conventional STM, namely spin-polarized STM, scanning tunneling luminescence, and cross-sectional STM are discussed.
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Figure 2.1: Schematic representation of the workings of a scanning tunneling microscope. In constant-current-mode the tunnel current is kept constant by means of a feedback loop that controls the z-piezo actuator.

Figure 2.2: 9 × 7.5 nm² topographic map of the GaAs (110)-surface. Individual As atoms can be observed, demonstrating the lateral and vertical resolving power of the scanning tunneling microscope.

2.1.1 Theoretical background

The extreme topographic sensitivity of STM is best explained in the theoretical framework of Bardeen. In this formalism the current through a tunneling junction is described by the wave function overlap of charge carriers at both sides of the tunneling junction. The tunnel current through the junction is given by:

\[ I = \frac{4\pi e}{\hbar} \int_0^{eV} \rho_s(E_{Fs} + \epsilon)\rho_t(E_{Ft} - eV + \epsilon)|M|^2 d\epsilon, \]  

(2.1)

where \( V \) is the applied bias voltage, \( \rho_{s,t} \) the local density of states (LDOS) of the sample and the tip, respectively, \( E_{Fs,t} \) the energy of the Fermi level of the sample and tip, respectively, and \( M \) the tunneling matrix element. The latter represents the wave function overlap of charge carriers at both sides of the tunneling junction.
function overlap of the charge carriers in the tip and the sample. Equation (2.1) is visualized in figure 2.3. Although this description of the tunnel current is already very insightful, it can be simplified to show the extreme sensitivity of the tunneling current on the gap size. Under the assumption of a point-like probe with an arbitrary localized s-state wave function the matrix element can be approximated by:}

\[ |M|^2 = \exp(-2\kappa d), \]  

where \( d \) is the distance between the tip and the surface, and \( \kappa \) the inverse decay length in vacuum given by:

\[ \kappa = \sqrt{\frac{2m_e\phi}{\hbar}}. \]  

Here, \( m_e \) is the electron mass and \( \phi \) the effective barrier height. The latter has a bias voltage dependence which is suppressed for reasons of simplicity. Two other simplifications can be made. First, in the limit of low temperature all the states above (below) the Fermi level can be considered empty (filled). Second, the LDOS of a metallic STM tip can be considered constant. Under these assumptions, equation (2.1) reduces to:

\[ I \propto \int_0^{eV} \rho_s(E_F, + \epsilon) \exp(-2\kappa d) d\epsilon. \]  

In case that the STM tip is fixed laterally above the surface with a fixed bias voltage, the sample’s integrated LDOS is constant and the above equation reduces further to:

\[ I \propto \exp(-2\kappa d). \]  

The decay constant \( k \) has a typical value of \( 1 \times 10^{10} \text{m}^{-1} \). Hence, a variation of 1 Å in the gap size will yield an order of magnitude change in the tunnel current. If we
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assume an atomically sharp tip, i.e. the end of the tip is made up of a single atom, and given that typical lattice constants are in the order of several angstroms, we find that the bulk of the tunnel current flows through the outermost atom. This sharp localization of the tunnel current to a single atom is the origin of the atomic resolution in STM.

Besides the topographic imaging of a surface, a STM can also be used to extract electronic information. For example, taking the derivative of equation (2.4) with respect to $V$:

$$
\frac{dI}{dV} \propto \rho_s(E_F + \epsilon) \exp(-2\kappa d),
$$

shows that the LDOS of the sample can be addressed. This electronic information can be extracted in two ways. First, indirectly by numerically differentiating the $I(V)$-spectrum that is recorded by sweeping the bias voltage. Second, directly by use of a lock-in amplifier. In the latter technique a small AC-signal is superimposed on the bias voltage. The tunnel current will react to the AC-modulation and will oscillate accordingly at the same frequency. The lock-in amplifier extracts the in-phase component of the tunneling current (after conversion to a voltage) at the frequency of the superimposed AC-signal. The resulting signal is directly proportional to $dI/dV$.

The equations presented above are, given all the simplifications, only a very coarse approximation to STM and we can expect reality to be more complicated. Nevertheless, the equations constitutes an elegant first-order model of STM that allows for a good understanding of the basics of STM. More elaborate extensions on this model can be found in literature, e.g. wave-vector-dependent tunneling calculations by Baratoff and inclusion of $p$- and $d$-wave functions by Chen. However, for the purpose of this thesis the above results suffice.

2.1.2 Spin-polarized STM

Besides addressing geometric and electronic properties, the technique of STM can be extended to probe magnetic properties as well. This technique is known as spin-polarized scanning tunneling microscopy (SP-STM) and its principle of operation is based on a fundamental property of (anti-)ferromagnets. In (anti)-ferromagnetic materials the magnetic moment is related to an imbalance in occupation of electrons of different spins. The exchange interaction between electrons splits up the DOS in majority and minority states that accommodate electrons of opposite spin. The imbalance between the two spin-bands can result in a net spin-polarization of the material, which has immediate consequence on the tunnel current. This was demonstrated by Julliere in his famous magnetic tunneling junction experiment. The essence of this experiment is illustrated (in an adapted form to represent the situation in an SP-STM) in figure 2.4. Integration of the LDOS up to the Fermi level for both spin-bands and subsequent subtraction shows that for example in the case of figure 2.4a both the tip and the sample have a net spin-down polarization, comprising a parallel configuration. If this configuration is compared with the anti-parallel configuration as shown in figure 2.4b, a difference in the total magnitude of the tunnel current, i.e. the spin-up and spin-down contributions summed, is observed. Note however, that the difference in the magnitude of the tunnel current between the two configurations strongly depends on the bias voltage and the shape of the DOS. This is illustrated in figure 2.4c–d. In this case the tunnel current is strongly polarized for both configurations, but in contrast to
Figure 2.4: Schematic representation of the process of spin-polarized tunneling in STM. In (anti)-ferromagnetic materials, the DOS splits into a spin-up and spin-down band. The net polarization is given by the integration of the LDOS up to the Fermi level and subtracting the result for both spin-bands. The magnitude and the polarization of the resulting tunnel current depends on the configuration, bias voltage, and shape of the DOS.

The previous situation a notable difference in the total tunnel current for the parallel and anti-parallel configuration is not observed.

To quantify the change in tunneling current and derive an expression for the spin-polarized tunneling current, the DOS of the tip is assumed constant in energy (just as in the previous section) but different in size for the spin-up and spin-down band. Under further assumption of low temperature and small bias voltage, the spin-polarized tunneling current is then given by:

$$I(V) \propto \rho_t \int_0^{eV} \rho_s(E_{Fs} + \epsilon) d\epsilon + m_t \cdot \tilde{m}_s = \rho_t \tilde{\rho}_s + m_t \cdot \tilde{m}_s,$$  \hspace{1cm} (2.7)

with $m_t$ and $m_s$ vectors representing the magnetization of tip and sample, and the tilde shorthand for the integration over the energy. Written in this form, equation (2.7) clearly shows that the tunnel current can be split into two terms: a non-polarized part and a polarized part. Since the non-polarized density of states of the sample, $\tilde{\rho}_s$, always...
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increases with bias voltage, while \( \hat{m}_s \) may stay constant, it is generally hard to resolve any magnetic contrast when operating the SP-STM in constant current mode. These difficulties can be overcome in spectroscopy mode. Taking the derivative of equation (2.7) with respect to \( V \) yields:

\[
\frac{dI}{dV}(V) \propto \rho_t \rho_s + \hat{m}_t \cdot \hat{m}_s.
\]  

In the spectroscopy mode, the voltage can now be chosen such as to maximize either the topographic or the magnetic contribution. As explained in section (2.1.1) the differential conductivity can be measured experimentally in two ways. In this thesis, only the method that employs a lock-in amplifier is used.

### 2.1.3 Scanning tunneling luminescence

Briefly after the invention of scanning tunneling microscopy it was realized that an STM-tip can induce the emission of photons. If one would be able to detect and analyze the emitted photons, the extreme spatial resolution of STM could potentially be extended into the optical domain, going far beyond the resolution of other optical probe techniques such as confocal microscopy (≈500 nm) and scanning near field optical microscopy (≈20 nm). In 1988, Gimzewski et al.\textsuperscript{54} published the first observation of light emission induced by an STM-tip. Since then, scanning tunneling luminescence (STL) has been observed on a variety of samples. Although, it is in principle possible to probe the light emission induced by direct dipole transitions in general materials\textsuperscript{55} and intramolecular transitions in organic molecules\textsuperscript{56}, most STL work focused on either the electron-hole recombination in direct gap semiconductors or the radiative decay of tip induced plasmons on metal surfaces due to higher quantum efficiencies.

In the former mechanism minority carriers injected into a doped semiconductor recombine across the band gap with the readily available majority carriers, emitting photons with an energy equal to that of the band gap energy, see figure 2.5a. The quantum efficiency of this process is \( \approx 1 \times 10^{-4} \) photons/injected electron\textsuperscript{57}. Note that the injected carriers have to be minority carriers, otherwise, the luminescence will be quench by the limited number of available carriers for recombination. The spatial resolution that can be achieved in the luminescence will be determined by the length scale over which the injected carriers diffuse before they recombine. In contrast to other injection approaches, such as cathodoluminescence microscopy, the low-injection energy of a tunneling electron beam (0–5 eV) miniaturizes the excitation region/volume. However, the diffusion length of eV electrons in intrinsic semiconductors can still be in the micrometer range. Fortunately, the diffusion length depends strongly on the material properties (e.g. defects and dopant level), the nature of the probed nanostructures, and the temperature. These factors can greatly reduce the diffusion length. It has been demonstrated that a spatial resolution of \( \approx 2 \) nm in the luminescence could be achieved on semiconductor quantum well structures\textsuperscript{58} and single Zn-dopants\textsuperscript{59}. Very recently, it has been demonstrated that the resolution can be pushed even further on a \( n \)-type GaAs (110)-surface were the local change in the tunneling probability of the holes is exploited to achieve atomic resolution in the luminescence\textsuperscript{60}.

In case of metal–metal junctions, the close proximity of the tip to the sample combined with the tunneling of charge carriers through the vacuum barrier excites a plasmon. This tip induced plasmon opens up an inelastic tunneling channel that gives rise to the
Figure 2.5: Schematic representation of the two common mechanisms of STM-induced light emission. (a) Recombination of minority carriers with majority carriers across the band gap in semiconductors. The emitted photons have an energy equal to that of the band gap. (b) Excitation and radiative decay of a tip-induced plasmon in a metal-metal junction. The emitted photons have an energy that corresponds roughly to the resonance frequency of the plasmon.

emission of photons, see figure 2.5b. The energy of the emitted photons corresponds roughly to the resonance frequency of the plasmon. The quantum efficiency of this process is \( \approx 1 \times 10^{-3} - 1 \times 10^{-4} \) photons/injected electron \(^{57}\). The dimension of the tip induced plasmon is typically in the order of 5 nm \(^{61}\). Surprisingly, this does not limit the spatial resolution of the luminescence. As it turns out, the dominant factors are the elastic and inelastic contributions to the tunneling current \(^{62}\). Since these are local properties of the sample and can be addressed with a spatial resolution that is only limited by the extend of the tunneling beam, see section (2.1.1), angstrom scale resolution is expected. Indeed, atomic-scale resolution of the luminescence has been achieved on metals \(^{62-64}\).

Besides probing optical properties with the extreme spatial resolution of STM, more can be achieved with STL. In the 1990s, it was reported that the photons emitted from a tunnel junction that includes a ferromagnetic material exhibit an unexpected circular polarization \(^{7}\). As it turns out, the degree of polarization of the emitted photons can be related to the direction of the magnetization of the sample. Thus, measurement of the polarization of the tip induced luminescence introduces the possibility, next to the application of spin-polarized tips as describe in the previous section, to potentially probe the magnetic properties of materials with atomic-scale resolution.

2.1.4 Cross-sectional STM

An extension of STM is the technique of cross-sectional scanning tunneling microscopy (X-STM). The term cross-sectional refers to the geometry in which the surface of the sample is investigated. In conventional STM the surface of the sample is studied in an in-plane geometry, whereas in X-STM the measurements are performed on the (110) natural cleavage plane of a zinc-blende crystal that presents a cross-sectional surface of the sample. The technique allows the observation of embedded nanostructures such as
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Figure 2.6: Cartoon of cross-sectional STM. (a) The sample with the embedded nanostructures is clamped vertically in a holder. The sample is mechanically cleaved under UHV conditions by the application of a force \((F)\). The cleavage is facilitated by a scratch (white line) that is applied on the surface prior to clamping. (b) The tip and the cleaved sample with the embedded nanostructures exposed.

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

quantum wells and quantum dots in a plane parallel to the growth direction. Practically, this means that the sample, which contains the embedded nanostructures of interest, is mounted vertically in a holder and mechanically cleaved, see figure 2.6a–b. Before mounting, the sample is first thinned down to \(\approx 100\mu m\) and a scratch of \(\approx 1\) mm is applied along the (110)-plane to its surface. The thinning and the scratch facilitate the cleavage and ensures the propagation of the cleave in the (110)-direction. After the sample is mounted, it is \(in situ\) heated to remove contaminants such as water and organic sediments. The sample is then mechanically cleaved under UHV conditions \((p < 5 \times 10^{-11}\) mbar\), exposing a contaminant free surface with large atomically flat terraces.

Shape determination

Embedded nanostructures are, per definition, made out of at least two different materials or crystallographic structures. The materials can be either lattice-matched, for example AlGaAs/GaAs, or non-lattice-matched, for example InAs/GaAs. In the latter
case the material will be strained in the vicinity of the nanostructures. Consequently, the surface will relax to minimize its elastic energy when the sample is cleaved. This is schematically illustrated in figure 2.7 for a compressively strained quantum well. Typically, the extend of the outward relaxation perpendicular of the surface is in the order of a few 100 pm and can be observed in careful X-STM measurements. When determining the shape of embedded nanostructures the outward relaxation can obscure the exact outline of the nanostructure, see for example the topographic image of the QD shown in figure 2.9a. This problem can be circumvented by using the current image, which is a recording of the tunnel current as the tip is scanned across the surface, instead. In the so-called constant current mode, in which the tunnel current is kept constant by means of a feedback loop that controls the z-piezo, the observed contrast in the current image can be thought of as the derivative of the local changes in topography. This is caused by the finite response time of the feedback loop that will result in an increase (decrease) of the current in case of an (under-) overshoot of the tip. As a result, long scale features in topography (outward relaxation) are filtered out while small scale features (individual atoms) are accentuated, making the current image ideally suited to determine the exact shape of a nanostructure, see figure 2.9b.

Composition profile

More than just being a nuisance in the size determination of strained nanostructures, the outward relaxation can be put to use to determine the chemical composition of a nanostructure. For this continuum elastic theory and finite element (FE) calculations are employed. Continuum elastic theory describes the mechanics of elastic solids by relating the stress forces acting on a material to the strain, i.e. the deformation of the solid. Given the stress vectors $\sigma_{ij}$ working on a volume element, continuum elastic theory allows the calculation of the deformation, see figure 2.8a. This is done by solving the stress-strain relation:

$$\sigma = D \varepsilon,$$

in which $\varepsilon$ the strain tensor and $D$ the elasticity matrix. The latter contains Young's Modulus and Poisson's ratios, both material constants. In FE calculations the solution of the stress-strain relation is evaluated numerically on a dense grid of nodes in the evaluated volume. By building a model of a nanostructure, see for example the model of a cleaved QD as shown in figure 2.8b, and using it as input for the FE calculations the outward relaxation of the cleaved surface can be calculated. The result is checked against the experimentally obtained outward relaxation, after which the model can be adjusted to gain a better match if needed. Note that, in order to obtain a pure topographic signal in X-STM, the imaging has to be done at high bias voltages to suppress the electronic contribution. Depending on the complexity of the nanostructure, typically 5 iterations in the case of wetting layers and up to 100 in the case of QDs, are needed to find a matching composition profile. The FE calculations presented throughout the current work are performed using the MEMS module of COMSOL Multiphysics.

2.1.5 Experimental background

Two types of setups are available to perform STM-measurements with, the main difference between the two being the operational temperature. The first STM is operated at
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Figure 2.8: (a) Volume element, in this case a cube, with the components of the stress shown as vectors. (b) Three-dimensional model of a cleaved QD. The model serves as input for the finite element calculations.

Figure 2.9: (a) $26 \times 26 \text{nm}^2$ topographic and (b) current image of an InAs/GaAs QD. Individual indium atoms are resolved in the current image. The range of the color scale in (a) is 0–300 pm.

room temperature (RT-STM), while the second one is cooled with liquid N$_2$ (77 K) or He (5 K) and operated at low temperature (LT-STM). Both setups are equipped with an internal eddy-current damping stage and are placed on active damping units to minimize vibrations. To further reduce unwanted vibrations both systems are in their entirety placed on structurally isolated platforms which physically decouples the STMs from the building. The RT-STM is partially home-build and is equipped with an Omicron STM-1, TS2 Scanner, which is used in conjunction with the Omicron SCALA control platform. This STM is operated under UHV conditions ($p < 6 \times 10^{-11} \text{ mbar}$). The LT-STM is a commercially available Omicron low temperature STM equipped with a SPM PRE4 current pre-amplifier that allows the amplification of tunneling currents up to 333 nA. The LT-STM is used in conjunction with the Omicron MATRIX control platform.
and is operated under UHV conditions \( p < 5 \times 10^{-12} \) mbar). Both STMs are equipped with a multitude of \textit{in situ} preparation facilities, i.e. an oven to heat tips and samples, an ion gun for argon sputtering, and a setup to measure the emission current of tips in an electric field. In addition to these facilities the LT-STM is further equipped with a home build high temperature oven that can heat samples up to \( \approx 2500 \text{ K} \), a home build tip oven for the melting/rounding of tip apices, and three FOCUS EFM-3 evaporators for the deposition of metallic films.

2.1.6 Tip preparation

Conventional STM requires the ability to generate stable tips in a reproducible way with which atomic resolution can be achieved. Typically non-magnetic materials such as W, Pt, Ir, and Au are used for this purpose. In addition to conventional STM, spin-polarized STM requires magnetic tips that are sensitive to the magnetic properties of a sample. The generation of both types of tip, non-magnetic and magnetic, is discussed in the next two sections.

Standard tips

High quality tips can be made by electrochemically etching pure poly-crystalline tungsten wires. This is done in the following manner. A short tungsten wire, \( \varnothing = 0.25 \text{ mm} \), is fixated in a tip-holder in such a way that \( \approx 6 \text{ mm} \) of the wire extends freely. Next, \( \approx 2 \text{ mm} \) is lowered into a 2.0 molar KOH solution. To drive the etching process, a positive voltage \( (\approx 6 \text{ V}) \) is applied between the W wire and a Pt/Ir counter electrode, see figure 2.10a. In the reaction that subsequently takes place:

\[
\text{W(s) + 2OH}^- (\text{aq}) + 2\text{H}_2\text{O(l)} \rightarrow \text{WO}_2^{2-} (\text{aq}) + 3\text{H}_2(g),
\]

the tungsten is dissolved. To ensure that the \( \text{H}_2(g) \) bubbles produced at the anode do not disturb the etching process, the beaker-glass is partially separated in two compartments by a vertical glass plate. The dissolved reaction products sink down along the wire, a process that can be observed due the local change of the solution's refractive index, and partially shield the wire from etching, see figure 2.10b. The shielding is lowest at the point where the wire penetrates the surface, resulting in the highest etching rate at this point. During the final stage of the etching process the wire abruptly breaks at its thinnest point leaving an atomically sharp tip. To ensure that the newly formed tip is not etched blunt after the breakage of the wire, a fast automatic switch outs the voltage at the moment the current drops below a preset threshold.

The newly formed tip and its holder are heated \textit{in situ} up to \( \approx 550 \text{ K} \) to evaporate contaminants such as water and organic sediments. Next, the tip is heated separately to remove its oxide layer. This is done by bringing the side of the tip in ohmic contact with a sharp-edged conducting plate. Driving a current through the contact locally heats the tip while the holder remains at a relatively low temperature. The tip will glow orange/yellow indicating that the temperature is about 1200–1400 K. At these temperatures the bulk of the oxide layer is removed. As a last preparation step, the tip is bombarded with argon ions for \( \approx 20 \text{ minutes} \). This sputtering further cleans and mechanically stabilizes the tip without changing its geometry to much.
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Figure 2.10: (a) Schematic representation of the electrochemical etching process. (b) Close up of the etching of the tungsten wire. The flow of the reaction products is indicated by the black arrows. (c) Close up of the etching of the chromium rod. The polymer tube is represented by the dark gray rectangles.

Figure 2.11: SEM image of rounded tungsten tips. Rounded by (a) electrochemical etching and (b) by e-beam.

Magnetic tips

Generally, magnetic tips can be divided in two classes. The first class is comprised of tips that are made by electrochemically etching bulk (anti-)ferromagnetic wires or rods. While this can result in very stable magnetic tips, bulk ferromagnetic tips have the disadvantage to exhibit a large magnetic stray field that can influence the magnetization of the sample. This is not the case for tips made from anti-ferromagnetic materials. One type of magnetic tip used in the current work is made from bulk Cr. To generate such a tip in a reproducible way the etching procedure described in the previous section is modified. Instead of a round wire, the starting point is now an $0.5 \times 0.5 \times 10\,\text{mm}$ Cr rod. First, the rod is electrochemically etched into a round $\approx 0.25\,\text{mm}$ diameter cylinder. The reaction products, which in the case of Cr are buoyant, dissolve less
readily into the etchant as compared to the case of W tips and tend to stick to the wire. This result in uniform etching of the wire and bending when it is almost etched through. The problem can be solved by the application of a polymer tube to the wire, see figure 2.10c. The polymer tube protects a large part of the wire from being etched and will due to its relatively high mass-density pull the wire down during the final stage of the drop-off. Note that a small part of the wire extends beyond the polymer tube. This part provides a notable drop in the current at the moment of drop-off, which is needed for the automatic switch to cut the voltage at the right moment.

The second class of magnetic tips is comprised of non-magnetic tips that are coated with a thin magnetic film. However, there is a complication in this scheme. In case a thin magnetic film is applied to sharp tips the resulting direction of magnetization will be random. This randomness is unwanted and can be avoided by using tips with a rounded apex. In case the radius of curvature at the apex is > 100 nm the surface can locally be considered as flat. It is known that thin films of (anti-)ferromagnetic material on flat surface exhibit a preferential direction of magnetization. For example, 3–10 mono layers (MLs) of Fe are known to exhibit an in-plane direction of magnetization, whereas 25–45 MLs of Cr result in an out-of-plane direction of magnetization.

Two methods, one \textit{ex situ} and \textit{in situ}, have been developed to generate tips with a round apex. The \textit{ex situ} method is a continuation of the electrochemical etching process for \(\approx 1\) s after the drop-off. Tips generated in this way are found to have a radius of curvature of 350–650 nm, see figure 2.11a. Although this is a very simple procedure, the \textit{ex situ} nature of this method results in a high number of contaminants being present on the tip which subsequently have to be removed. This is circumvented in the \textit{in situ} method, in which a tip oven is used to melt the apex of sharp tips, and thereby rounding them. The tip oven has two modes of operation: heating mode and field emission mode, see figure 2.12a–b. In the heating mode, electrons ejected by the filament are accelerated towards the apex of the tip, losing their energy on impact. At high enough

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.12.png}
\caption{Schematic representation of the workings of the tip oven. (a) Heating mode. (b) Field-emission mode.}
\end{figure}
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currents and fields, this so-called e-beam heating will result in the melting of the apex. To check whether the rounding/melting of the apex was successful the oven can be operated in the field emission mode. In this mode electrons are extracted from the tip. The magnitude of the field emission current is a measure for the radius of curvature of the apex. With the tip oven it is possible to generate smooth contaminant free tips with a radius of curvature of 80–220 nm, see figure 2.11b.

Throughout the current work three different magnetic tips are used: 1) sharp electrochemically etched bulk anti-ferromagnetic Cr tips which have a predominately but somewhat canted out-of-plane direction of magnetization. 2) By electrochemical etching and 3) by e-beam-heating rounded W tips, both coated with a thin film of Fe that has an in-plane direction of magnetization.

2.2 Atom probe tomography

The second nanoprobing technique under consideration is atom probe tomography (APT). This is the latest evolution of the venerable field emission microscope whereby a field ion microscope is combined with a spatially resolved time-of-flight mass spectroscope, creating a device known as a three-dimensional atom probe (3DAP). In APT, the specimen is made up by a needle-shaped piece of material that contains the nanostructures of interest, this in contrast to STM where an atomically sharp needle is used to scan the surface of the specimen. In APT the needle-shape specimen is brought in close proximity (typically ≈ 1 mm) of a local electrode to which a high standing voltage (≈ 10 kV) is applied, see figure 2.13. The specific needle shape of the specimen is required in order to locally enhance the electrical field. Above a certain threshold value the electric field will ionize and pull out atoms from the outermost layer of the specimen. The evaporated ions accelerate towards the local electrode where they pass through a hole. From there on, the ions move ballistically towards a microchannel position detector that registers their position of impact. With this information and the sequence in which the atoms arrive at the detector, the original position of the atoms in the specimen can be worked out. However, in the scheme described above it is not possible to reconstruct a full three-dimensional composition profile of the specimen. One piece of information is missing: the chemical species of the ions. To obtain this information the following scheme is applied. The standing voltage between the specimen and the local electrode is lowered to such a value that evaporation does not occur anymore. The specimen is then subjected to an additional nanosecond high voltage pulse or is targeted by a short laser pulse. The temporary rise of the voltage, or in case of the laser pulse of temperature, provides the atoms with the last bit of the energy required to break free from the surface. If the settings are chosen right, the evaporation progresses atom by atom, and layer by layer. The mass-charge ratio of the ion, and thus the chemical species, can then be worked out by recording the time between the voltage or laser pulse and impact of the ion on the detector. With this additional information a complete three-dimensional composition map of the specimen can be reconstructed, see for example figure 2.14. In the remainder of this section both the theoretical and experimental backgrounds of APT are discussed. For a good historical overview of the technique of APT see the review article by Kelly and Miller.
2.2.1 Theoretical background

Field evaporation

The main underlying physical process of APT is field evaporation in which atoms are evaporated, or "pulled-out", from the specimen’s apex. For this process to occur a high electric field, typically $10^{-40} V \text{ nm}^{-1}$ depending on the material, is needed to break the surface-atom bonds and ionize the atoms. Such high field strengths can be achieved by local field enhancement due to the geometry of the specimen. The field strength at the apex of a needle-shaped specimen with a round apex is given by:

$$F_0 = \frac{V_0}{k_f r_0},$$

(2.11)

where $V_0$ is the applied potential, $k_f$ a numerical constant determined by the specimen geometry and the instrument configuration (typically 2-5), and $r_0$ the radius of curvature of the specimen. An evaluation of equation (2.11) shows that for an applied voltage of 10 kV a radius of curvature in the order of 100 nm is required to achieve field evaporation.

Two stages can be distinguished in the process of field evaporation. In the first stage an atom is pulled from the surface of the specimen, losing one or more electrons in the process. Immediately after the escape from the surface, the ion has a charge of $se$ where $s$ is a positive integer and $e$ the positive elementary charge. In the second stage the ion reaches a critical distance from the surface and may thereafter be post-ionized one or several times. This post-ionization is the result of electrons tunneling from the ion to the substrate while it is still in the vicinity. After one or more post-ionization steps the ion departs with a final charge given by $ne$ with $n \geq s$. The rate at which the atoms are pulled from the surface is given by an Arrhenius-type equation:

$$k = A \exp \left(-\frac{Q(F)}{k_b T}\right),$$

(2.12)

where $A$ is a constant, $Q(F)$ the activation energy for escape into the charge state $se$, $F$ the electric field, and $k_b$ the Boltzmann factor. The field at which $Q(F) = 0$ is called
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the zero-Q evaporation field and is denoted by $F^E$. In practice the operating field $F^0$ is set such that $Q(F)$ has a small non-zero value, and is thus slightly less than $F^E$. To evaporate an atom, $k$ must temporarily be raised to a much higher value. Classically, this is done by the application of a voltage pulse. However, for this scheme to work the specimen material must have an electrical conductivity greater than about $10^2 \text{ S cm}^{-1}$ (metal of highly doped semiconductor) to transmit the nanosecond high voltage pulse $^7$. For this reason there has been little use for this technique outside of metallic systems. The problem can be circumvented with laser pulsed APT. In this technique, the voltage pulse is substituted for a laser pulse that thermally excites the specimen and thereby provides the atoms with the last bit of energy required to break free from the surface. Where semiconductors were previously out of bounds, this recent development makes APT on these materials feasible.

Data reconstruction

In APT the recorded information is a sequence of impact coordinates and the time-of-flight of all collected ions. The original $(x, y)$-coordinates of the atoms in the specimen can be derived from the $(X, Y)$-coordinates of impact on the detector. Since the atom probe is a point projection microscope, the original coordinates are to a first approximation given by $(x, y) = (X, Y)/\eta$ with $\eta$ the magnification factor$^7$. From the order in which the atoms arrive at the detector the original $z$-coordinate can be worked out. In general the $z$-coordinate has to be corrected to account for the shape of the specimen. Several protocols for such corrections exist$^7$. One of the simplest assumes a constant radius of curvature of the specimen during evaporation. Considering the specimen geometry leads to a correction of the $Z$-coordinate of:

$$Z’ = r \left( 1 - \sqrt{1 - \frac{X^2 + Y^2}{r^2}} \right),$$

(2.13)

with $r$ the radius of curvature of the specimen. In modern atom probes the radius of curvature can be determined periodically by means of a scanning electron microscope during evaporation. This information can then be employed for the reconstruction of the specimen.

With the original $(X, Y, Z)$-coordinates known, only the chemical species needs to be determined in order to reconstruct a full three-dimensional composition map of the specimen. The mass-to-charge ratio, and thus the chemical species, can be worked out from the time-of-flight and the applied voltage. The potential energy of a surface resident atom is given by $E_{\text{pot}} = neV$, with $V$ the standing voltage. As the ion arrives at the local electrode all its potential energy will have been converted into kinetic energy $E_{\text{kin}} = 1/2mv^2$. Given the time-of-flight $t$ and the distance between the local electrode and the detector $d$, the ion-velocity $v = d/t$ can readily be worked out. The substitution of these results yields a mass-charge ratio of:

$$\frac{m}{n} = \frac{2e}{d^2Vt^2}.$$

(2.14)

With this last piece of information it now possible to reconstruct a complete three-dimensional composition map of the sample, see for example figure 2.14.
Figure 2.14: (a) $25 \times 25 \times 13 \text{nm}^3$ atom map of a volume of an (In,Ga)As QD layer. For clarity, only gallium (gold) and indium (indigo) atoms are shown. (b) Taking a cross-section through the data set reveals the core of a QD, demonstrating the three-dimensional nature of APT.

2.2.2 Experimental background

Needle-shaped specimens can be fabricated via the so-called lift-out technique in which a scanning electron microscope, micro manipulators, Pt welding, and focus ion beam (FIB) milling are used to extract and mount a small piece of the original specimen on a Si micropillar. With this technique it is possible to produce needle-shaped specimens that have an uniform circular cross-section, an apex radius of less than $50 \text{nm}$, a smooth surface, a taper angle of less than $5^\circ$, and a length of several hundred nanometers. A detailed review of the preparation technique is beyond the scope of this thesis, but a good overview can be elsewhere\textsuperscript{14}. The specimens studied in this thesis were fabricated with a dual-beam FEI Nova 200 NanoLab system\textsuperscript{78,79}. To protect the specimens during fabrication, a protective 100–150 nm Ni layer was sputtered on top of the specimens prior to the FIB sharpening. Inside the FIB system, a further 100–150 nm thick protective Pt layer was deposited on the Ni using the ion beam deposition capabilities of the FIB.

All the APT measurements presented in this thesis were performed using an LEAP 3000X Si instrument, operated in laser mode. The laser wavelength was 532 nm and the pulse frequency $0.5 \text{MHz}$. The target evaporation rate was set to 0.2%, which means that on average only one atom is evaporated every 500 laser pulses. Such a low evaporation rate is important to maintain a high ratio of single ion events, because the position sensitive detector is not able to accurately distinguish multiple impacts. Accordingly, the laser pulse energy was chosen to be less than $0.01 \text{nJ}$. The evaporation field was dynamically altered during the measurement in order to maintain a constant evaporation rate. This is necessary because the radius of the specimen becomes larger as it is evaporated down. The typical detection efficiency of the used detector is approximately 50–60%. The loss is mainly due to ions impacting on the interchannel regions of the microchannel plates in the detector. The flight length between specimen and detector was 90.0 mm and the typical time-of-flight of an evaporated ion 0.6–1.6 $\mu$s, depending on the species. The sample stage temperature was set to 50 K.
Simple and efficient detection of scanning tunneling luminescence at low-temperature

In Scanning Tunneling induced Luminescence microscopy (STL), photons created by the recombination of minority carriers injected in semiconductors or by the decay of a locally excited plasmon state on metals, are collected and analyzed. Since the process of electroluminescence emission is governed by the size and position of the STM tip, STL has the potential to study the optical properties of a surface at the atomic-scale. Several STL-modes of operation have been reported in literature, ranging from relatively straightforward intensity measurements\(^{80,81}\) to more experimentally demanding spectrally and spatially resolved photon mapping\(^{61,62}\). In the latter technique luminescence spectra are collected during scanning, yielding a map of luminescence spectra that can be directly linked to the topography of the studied surface. This chapter reports on the adaptation of a commercial Omicron low temperature STM to allow for spectrally resolved STL-measurements. STL-measurements on the Au(110) surface are presented in detail and should be considered as an experimental proof-of-principle. This chapter focuses on the technological aspects of STL-implementation. It is shown that STL-capability can be achieved in a relatively simple and cost-effective manner with the purposed luminescence collection system, opening up the possibility of simultaneously recording the surface topography and the corresponding spectra. Due to the fact that a large part of the properties of the STM-induced luminescence are governed by the local properties of the sample directly underneath the tip, the luminescence spectra can be collected with an atomic-scale spatial resolution.

3.1 Instrument design

3.1.1 Collection system

The proposed luminescence collection system can be divided in two parts: two in situ lenses providing two optical access points and an ex situ optical collection system.

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In figure 3.1, the in situ part of the luminescence collection system is schematically depicted. The STM-head of the Omicron low temperature STM provides two optical access points that are tilted at an angle of 20° toward the sample face and can hold two in situ lenses. At present, only one of the arms is used for luminescence collection.

In figure 3.1, the in situ part of the luminescence collection system is schematically depicted. The STM-head of the Omicron low temperature STM provides two optical access points that are tilted at an angle of 20° toward the sample face and can hold two in situ lenses. At present, only one of the arms is used for luminescence collection. The other arm is meant for future excitation or detection experiments. The diameter of the lenses (Thorlabs al2520, $f = 20.0\, \text{mm}$, $\text{NA} = 0.543$) was trimmed to 10 mm to fit the special designed lens holders, which fit into the optical access points on the STM-head. These lenses were selected to direct the STM-induced luminescence in a parallel bundle through a kodial glass viewport out of the vacuum chamber. This viewport has above 90% transmittance in the wavelength range 350–2000 nm and will therefore allow most STL-experiments. However, before reaching the viewport, the luminescence bundle has to pass two in situ Schott KG5 glass filters that are installed by default to shield the STM-head from infrared radiation. These filters have a cutoff wavelength of $\approx 700$ nm. For future STL-experiments on for example semiconductors, these filters should be removed or replaced by filters that allow transmittance at higher wavelengths.

Outside the vacuum chamber, the bundle enters a lens system where it is narrowed and focused onto an optical fiber. The ex situ part of the luminescence collection system consists of a CCD camera, three lenses, a diaphragm, a beam splitter, a collimator, a multi-mode fiber, and a monochromator, see figure 3.2. Once the luminescence is coupled into the optical fiber (Thorlabs, $d = 600\, \mu\text{m}$) it is directed into the monochromator (Acton Research Corporation SpectraPro-300i) which is fitted with a liquid nitrogen cooled $576 \times 384$ Si CCD camera. The detector is operated at a temperature of 100 K. To ease the alignment, the ex situ optical system is designed with three translational and two rotational degrees of freedom, see figure 3.3. These five degrees of freedom facilitate the focusing of the beam onto the fiber. Although not necessary for STM-induced luminescence collection, the beam splitter (8:92) and CCD camera have the
advantage that they allow visual tracking of the tip during coarse approach with a resolution of $\approx 2 \mu m$. In figure 3.4, a screenshot of the STM-tip and its reflection on the sample surface as recorded by the CCD camera is shown. The STM and the entire luminescence collection system, including the monochromator, are located inside a light-tight box to reduce the collection of unwanted stray light.

The main advantage of the proposed design is its simplicity. To begin with, only one lens has to be installed on the STM-head. The fact that this lens is fixed and that the complete optical alignment is done outside the STM-chamber makes the use of complicated (cooled) motion-feedthroughs\textsuperscript{82,83} to \textit{in situ} align the lens redundant. This eliminates the need to install any additional cooling systems to prevent radiative heating of the tip and sample by the lens and its holder/stage. The simplicity of the current design is also reflected by the fact that it does not interfere with normal STM operations. This is not the case in more complicated collection schemes that use specially designed tip-holders with an integrated parabolic mirror\textsuperscript{84}. Since \textit{in situ} moving parts, additional cooling systems, or specially designed tip-holders are unnecessary, current collection scheme is relatively robust, low cost, and straightforward to install. Due to the use of \textit{ex situ} free space optics, the fixed \textit{in situ} lens does not restrict the luminescence collection to a specific point inside the STM-head. In fact, the five degrees of freedom of the \textit{ex situ} free space optical system allow luminescence collection from a $\approx 4 \times 4 \times 4 \text{mm}^3$ volume, relaxing the necessity for precise alignment of the sample. Another advantage of the current design over other collection systems described in literature is the presence of a second \textit{in situ} lens that can be used separately from the lens used for luminescence collection. This opens the possibility to do excitation experiments such as low temperature tip-enhanced Raman spectroscopy. Yet another advantage of the current design over ones employing an \textit{in situ} optical fiber to collect the luminescence\textsuperscript{59,81,85} is the ease with its \textit{ex situ} part can be adapted to allow polarization sensitive measurements. This removes the need for installing complicated \textit{in situ}
3.1.2 Detection efficiency

Performance grading and comparison of STM-induced luminescence collection systems is best done by means of their detection efficiency. In this case, the analysis of the detection efficiency can be split into two parts: 1) collection yield of the first optical positioning stages, rotation mounts, and polarization filters as necessary in fiber based luminescence collection systems. Although, fiber based collection systems generally have the benefit of high collection yields, their disadvantages outweigh their benefits in most cases. This is indeed the case for the current STM were the initially opted for luminescence collection system consisted of a fiber installed in close proximity to the tip-sample cavity. This collection design introduced unwanted vibrations in the STM and proofed nearly impossible to align.
element, and 2) collection efficiency of the remainder of the optical system. In our case the first optical element is the in situ lens which has a diameter of 10 mm and is placed 15.7 mm from the tunnel contact. This yields a collection solid angle of \(\approx 0.3 \text{Sr}\), which corresponds to 4.8% of the hemisphere. In order to quantify the collection efficiency of the remainder of the optical system we assume that each electron injected by the tip induces a plasmon that radiatively decays with a quantum efficiency of \(1 \times 10^{-4}\). Given the collection yield of the in situ lens this implies that at a tunnel current of 10 nA, a total of \(\approx 1.5 \times 10^5\) photons s\(^{-1}\) will enter the optical system. At this tunnel current count rates up to \(4 \times 10^4\) s\(^{-1}\) are routinely achieved, yielding an estimated efficiency of the collection system of \(\approx 27\%\). This value includes the losses in the monochromator and the detection efficiency of the Si CCD camera in the wavelength range of 500–750 nm. Note that, at the cost of spectral information, the collection efficiency can be greatly increased by using a photomultiplier instead of the monochromator and a Si CCD camera. Given the collection yield of the in situ lens and the estimated collection efficiency of the optical system, the total detection efficiency, i.e. the number of collected photons divided by the number of total emitted photons, is estimated to be \(\approx 1.3\%\), a value that is comparable to the estimated collection efficiency (\(\approx 2.5\%\)) of the lens detection system described by Hoffmann et al.\(^{82}\).

3.1.3 Experimental procedure

In order to spatially map the STM-induced luminescence, the normal topography scanning mode of the STM is interrupted at discrete points on a grid, see figure 3.5a. During these interruptions the feedback loop is kept on, resulting in the tip being fixed at a constant height above the surface. In this static situation luminescence spectra are collected. The STL-collection is started by a trigger signal sent by the STM-electronics at the moment the scanning mode is interrupted. The duration of STL-collection is chosen such that the recording is ended before the scanning mode of the STM is resumed. The advantage of interrupting the STM at discrete points for STL-collection is that both the surface topography and the luminescence spectra are extracted in one scan, eliminating the influence of drift and, consequently, the need for a post-scan overlay correction of the surface topography with the recorded luminescence spectra.

The surface topography is typically collected at scan speeds on the order of 50 nm s\(^{-1}\) and the duration of the scan interruptions for luminescence spectra collection is on the order of seconds. Typically, a few thousands of photons are collected during one second with the current luminescence collection system, which is comparable to count rates reported elsewhere in literature\(^{90–94}\) and sufficient to achieve a decent signal-to-noise ratio. For a 50 \(\times\) 50 nm\(^2\) scan area consisting of 500 topographic lines and a 100 \(\times\) 100 luminescence grid the total measuring time would amount to \(\approx 3\) hours. Note that, recording the topography only takes up 10% of the total measuring time.

One way to visualize the luminescence spectra is in a so-called photon map. In such image each pixel is obtained by integrating the number of counts in the individual spectra over the wavelength, either a selected band or the whole recorded range. Subsequently, the result is spatially mapped to the position where the specific luminescence spectrum was recorded. An example of a photon map is shown in figure 3.5b.
3.2 Experimental results

The sample consists of a clamped glass plate on which a $\approx 1\,\mu m$ thick gold film is deposited. This is done in a dedicated evaporation chamber that is not connected to the STM. Consequently, the thin gold film is exposed to ambient conditions during transfer to the STM. In order to remove possible contaminants, the sample is heated to $\approx 160^\circ C$ in the preparation chamber before its transfer to the STM chamber. All the measurements that are presented in this chapter are performed at a temperature of $\approx 5 K$. Standard electrochemically etched tungsten tips were used, see section (2.1.6) for a detailed description of the preparation procedure of these tips.

As it turns out, the surface in the current measurements is an Au(110)-surface with a $\{1 \times 3\}$-reconstruction. This is illustrated in figure 3.6, which shows a $100 \times 100 \, nm^2$ topographic image of the gold surface (top) and a schematic side view of the Au(110) $(1 \times 3)$-reconstructed surface (bottom). Although, a lot of different mono-atomic layers are visible in the image and give the surface a quite rough look, the $(1 \times 3)$-reconstruction is clearly visible on the plateaus. The peak to peak distance of the surface reconstruction as measured by STM is 1.26 nm, which is in agreement with the value reported in literature$^{95}$.

A first demonstration of scanning tunneling luminescence microscopy is shown in figure 3.7, which shows (a) the topography of a part of the Au(110)-surface, (b) the corresponding current image, and (c) a photon map recorded on the same area. The three channels are recorded simultaneously. Note that, the plotted current image shows the averaged tunnel current as measured during the collection of the luminescence and not the tunnel current during the scanning of the tip in between grid points. Features can be seen in the current image. In principle this should not be the case; ideally...
Figure 3.6: 100 × 100 nm² topographic image (top) of the Au(110)-surface ($V = +0.8\,V$, $I = 0.5\,nA$) and a side view cartoon (bottom) of the (1 × 3)-reconstructed surface.

The feedback loop of the STM should keep the tunnel current fixed at the value of the set-point. However, in this case the tunnel current is found to vary by ±10% across the whole image. As a result, structures can be observed in the current image. Comparing the positions of these structures with the topographic image, it becomes immediately clear that the observed structures are correlated with the step-edges present on the surface. Apparently, the feedback loop has trouble keeping the tunnel current constant at these positions. Since, this can potentially have consequences for the luminescence intensity, a careful review is needed. First, let us consider the difference in tunnel current at the various step-edges. In figure 3.7a, the slow scan direction is indicated by the white arrow. This corresponds to the direction in which the tip is moved across the surface between the points where the luminescence is collected. Although, the movement of the tip is halted at these points, it is expected that tip will continue to drift in the direction of scanning. This will, due to the limited response time of the feedback loop, result in an under- and overshoot in the tunnel current at down- and
Simple and efficient detection of scanning tunneling luminescence at low-temperature

Figure 3.7: (a) 40 × 50 nm² topographic image, (b) the averaged tunneling current as measured during luminescence collection, and (c) photon map of the Au(110)(1 × 3)-reconstructed surface (V = +3.2 V, I = 100 nA). Two exemplary step-edges are indicated by the blue and yellow arrows. An plateau is indicated by the red arrow.

Figure 3.8: Schematic breakdown of the tunnel current at step-edges going down (left) and going up (right). The values are extracted from figure 3.7.

up-going step-edges, respectively. This is schematically illustrated by the red dashed line in figure 3.8. However, the careful examination of the current image shown in figure 3.7b, shows that the drift of the tip can not entirely explain the observed features; at down-going step-edges the tunnel current drops by 10% while at up-going step-edges it drops only 3% (marked for two exemplary cases by the blue and yellow arrows, respectively). If only the drift of tip were to be responsible for the observed variations in the tunnel current, the down- and up-going step-edges are expected to yield an equal but opposite variation in the tunnel current. Since this is not the case, another unknown effect is acting on the tunnel current. Given that a decrease in tunnel current is observed at both down- and up-going step-edges, the mechanism responsible has to always act negatively on the tunnel current. This is illustrated by the blue dashed
line in figure 3.8. From the difference in tunnel current at the various step-edges, the magnitude of this mechanism and the influence of drift on the tunnel current is estimated to be 6.5% and 3.5%, respectively. Although an estimate can be made, the source of the involved experimental mechanism is still unclear. The next question to be addressed is, whether the variations in tunnel current influence the luminescence intensity. First, the maximum drop in tunnel current at step-edges is 10% and while this is more than one wishes for, it is much less than the variation found in the luminescence intensity across a step-edge where a drop in intensity of \( \approx 60\% \) is observed. Given that the luminescence intensity is proportional to the tunnel current on metallic surfaces\(^{52}\), this already is an indication that the observed structure in the photon map is not solely the result of variations in tunnel current and another physical cause is to be expected. Secondly, structures can be observed on the plateaus in the photon map (indicated by the red arrows). As no corresponding structure is observed at these positions in the current image (the tunnel current only varies by \( \pm 1\% \) on the plateaus), this again indicates that the variations in the tunnel current during the luminescence collection are not the dominant factor governing the luminescence intensity on this material system.

In principle, the spatial resolution of the tip induced luminescence is limited by the spatial extend of the tunneling region; the properties of the sample directly underneath the tip are the major factor governing the properties of the emitted light. To investigate the spatial resolving power of the current luminescence collection system a closer look is taken at the structures observed on the plateaus. In figure 3.9a–b, a close-up of the topography and the corresponding photon map of one of these plateaus is shown, respectively. The Au(110)(1 x 3)-reconstruction is nicely resolved in the topographic image, and a quick comparison with the photon map reveals a similar structure in the luminescence signal. To check to which extent the two signals match, a cross-section is taken along the plateau for both channels and compared in figure 3.9c. The peaks and troughs in the topography (blue line) are found to correspond to the troughs and peaks in the luminescence intensity (red line). To explain similar results on similar metallic material systems, various models have been put forward by other teams in literature. In one of the proposed models the correlation between topography and luminescence intensity is ascribed to local variations of the electromagnetic coupling between the tip and sample\(^{61,96}\), while in another model it is attributed to changes in the relative strength of the excitation mechanisms involved\(^{63,97}\). A better model, that also explains conflicting results observed at the step-edges on several different surfaces, e.g. Ag(111)\(^{98}\) and Au(110)\(^{61}\), might be the one suggested by Hoffmann et al.\(^{62}\). In this model, which is completely independent of the tip–surface geometry, the variations in the luminescence intensity are a consequence of the local electronic structure directly underneath the tip and the effect on the elastic and inelastic tunneling channels. STL-measurement on the Au(110)(1 x 3) surface might in the future provide further support for this model.

Besides studying the spatial correlation of the luminescence intensity with the surface topography, it might for certain material systems also be worthwhile to investigate the spatial dependence of the spectra shape. Because in the current luminescence collection scheme a full spectrum is recorded at each grid point, this can be done easily. As a demonstration a brief spectral analysis of the Au surface is presented here. As it turns out, the shape of the recorded spectra shows no strong change as function of the position on the surface; all are found to have a shape similar to the spectrum presented in 3.5a. However, the position of the peak does shift depending on the surface topography. This
Figure 3.9: (a) $15 \times 15$ nm$^2$ topographic image and (b) corresponding photon map of the Au(110)($1 \times 3$)-surface ($V = +3.2$ V, $I = 100$ nA). (c) Averaged cross-section along the marked areas in figure (a) and (b). The dotted vertical lines indicate the periodicity of the ($1 \times 3$)-reconstruction on the plateau.

is best illustrated in a so-called spectral map, which is generated by assigning a color scale to the position of the peak in the luminescence spectra and subsequent spatial mapping of the result. In figure 3.10, the surface topography and the corresponding spectral map of a relatively large surface region is shown. On the scale of the plateau that is shown in figure 3.9a (and indicated in the current figure with the yellow arrow), no spectral shifts are observed. However, pronounced structures can be distinguished in the spectral map on a larger scale. Four distinct regions are observed; three exhibiting regular facets (blue arrows), and one polycrystalline grain (red arrow) that is probably the result of a tip crash prior to the presented measurement. Although there is no substantial spectral shift observed within the regular faceted regions, there is a relatively large ($\approx 7$ nm) spectral shift between them. The spectral homogeneity within
regular faceted regions is not found in the polycrystalline Au grain; within the grain large spectral shifts (≈ 20 nm) are observed over relative short distances. Unfortunately, it is not possible to construct a consistent model with the available data. Further measurements on larger regions, including more grains and facets, are required. Literature also does not provide any solace in this respect. The luminescence from polycrystalline Au grains has been studied by several groups in the past. However, research is mainly focused on the luminescence intensity as a function of grain size and position. The available spectral information for the grains, and also for regions with the more regular facets, is limited due to the experimental difficulties involved. What is known comes from two other studies that do focus on the spectral properties of the Au grains, but suffer from the lack of spectral resolving power due to the use of spectral filters. Although, these studies find evidence that the spectral shifts can be attributed to the geometry of the tip, the results are by no means conclusive. In this respect, the presented luminescence collection system can be of great value in future studies.

3.3 Semiconductors: Zn-doped GaAs

After having shown in the previous section that the proposed luminescence collection system is able to record the STM-induced luminescence on an Au(110)(1×3)-reconstructed surface, the same setup will now be used to demonstrate atomically resolved luminescence collection from a semiconductor material system. Highly (≈ 2.519 cm−3) Zn-doped GaAs was chosen as a test sample. This material system is known to have a strong luminescence emission around 835 nm. Furthermore, the high dopant concentration ensures that a relatively high tunnel current (up to ≈ 1 nA) can be applied without crashing the tip. The integration time to obtain a decent signal-
Simple and efficient detection of scanning tunneling luminescence at low-temperature

Figure 3.11: a) Typical electroluminescence spectrum ($V = 2.1 \text{ V}$, $I = 0.7 \text{ nA}$, $T = 5 \text{ K}$, $t = 4 \text{ min}$, peak intensity 200 counts). b) Luminescence intensity as function of the bias voltage. The threshold bias voltage for STM-induced luminescence on highly Zn-doped GaAs lies at $V \approx 1.5 \text{ V}$. The red point in the graph corresponds to the spectrum shown in a). c) Idealized $I(V)$-characteristic of a highly $p$-doped semiconductor.

A threshold bias voltage ($V \approx 1.5 \text{ V}$) for the onset of luminescence was found. This value closely corresponds to the direct band gap of GaAs ($1.52 \text{ eV}$). The threshold behavior can be explained as follows. Zn-dopants in GaAs are acceptors and as a result the Fermi level will be located close to the top of the valence band. As explained in section (2.1.3), the predominant mechanism of STM-induced luminescence in semiconductors is the recombination of injected minority carriers with majority carriers of opposite type present in the sample. In the current case, the minority carriers (electrons) injected into the conduction band recombine radiatively across the band gap with the majority carriers (holes) present in the valence band. However, to inject electrons in the conduction band, the application of a threshold bias voltage is required, which in the current highly $p$-doped sample closely corresponds to the band gap, see figure 3.11c.

Just as in the previous section, the highly localized injection of electrons by the STM-tip can be used to probe the optical properties of the semiconductor sample on the atomic-scale. However, the diffusion length of $e\text{V}$ electrons in intrinsic semiconductors can be in the micrometer range but depends strongly on the material properties (e.g., defects and doping level), the nature of the probed nanostructures, and the tem-
Figure 3.12: a) 40 × 40 nm² topographic X-STM map of the Zn-doped GaAs (110)-surface ($V = 1.5 \text{ V}, I = 50 \text{ pA}$). Zn-dopants appear as bright features. b) Luminescence spectra recorded ($V = 4 \text{ V}, I = 0.4 \text{ nA}, t = 5 \text{ min}$) at the marked positions.

Figure 3.13: a) 32 × 12 nm² topographic X-STM map of the Zn-doped GaAs surface ($V = 1.5 \text{ V}, I = 50 \text{ pA}$). The luminescence spectra were recorded along the semi-transparent yellow line ($V = 2 \text{ V}, I = 0.7 \text{ nA}, t = 1 \text{ min}$). b) Topography signal (orange line), peak wavelength of the luminescence signal (red points), and integrated intensity around this peak (blue points).
Simple and efficient detection of scanning tunneling luminescence at low-temperature. These factors can greatly reduce the diffusion length. For example, it has been demonstrated that a luminescence spatial resolution of \( \approx 2 \) nm could be achieved on semiconductor quantum well structures\(^{38}\) and single Zn-dopants\(^{59}\). In figure 3.12a, the topography of the Zn-doped GaAs (110)-surface is shown. At these tunnel conditions the bright anisotropic features correspond to the Zn-dopants: triangles of various size for dopants in sub-surface layers, and crab-like features for dopants in the surface layer\(^{100,101}\). Luminescence spectra were recorded at several positions on the surface for various dopant configurations. For this, the bias voltage was temporarily raised above the threshold voltage and the tunnel current increased. The recorded luminescence spectra are shown in figure 3.12b. A quick comparison reveals that there is apparently no positional dependence; all the spectra seem to have an emission peak at \( \approx 835 \) nm and are equal in intensity. To make this more quantitative, another set of luminescence spectra were recorded along a 32 nm stretch of sample, see the semi-transparent line in figure 3.13a. This line crosses both the position of subsurface dopants and regions free of any dopants. In the graph of figure 3.13b, the surface topography (orange line), the peak wavelength of the luminescence signal (red points), and the integrated intensity around this peak (blue points) are plotted. The averaged current recorded during STL-collection (not plotted) was found to fluctuate less then 0.1% along the line. Again, no correlation between the surface topography, i.e. the position and the configuration of dopants, and the recorded luminescence spectra is found. Given the high dopant concentration and the large Bohr radius of a Zn-dopant in GaAs (\( \approx 10 \) nm) this is not surprising; the hole wave function of individual dopants overlap and form an impurity band. The injected electrons recombine across the band gap into this position independent impurity band and not into position dependent hole states as found in samples with lower dopant concentrations.

3.4 Summary

The measurements presented in this chapter show that it is possible to relatively easily and cost-effectively implement luminescence detection into a commercially available Omicron low temperature STM. It was shown that the STM-induced luminescence could be collected efficiently from an Au(110)(1 × 3)-reconstructed surface. Furthermore, it was demonstrated that it is possible to simultaneously record the surface topography and the corresponding photon map, both with atomic resolution. The fact that a full luminescence spectrum is recorded at each grid point allows for a spatially resolved spectral analysis. Besides a metallic surface, the collection of luminescence from a highly Zn-doped GaAs semiconductor sample was demonstrated. Here, a threshold bias voltage for the onset of electroluminescence was found. No correlation between the shape, the position, and the intensity of the luminescence spectra with the positions of the dopants was found. The results show that the proposed collection system can be used to spectrally collect and analyze the STM-induced luminescence from both metallic and semiconductor material systems with atomic-scale resolution.
Demonstration of spin-polarized scanning tunneling microscopy

In scanning tunneling microscopy (STM) the surface topography of an electrically conductive sample can be imaged with atomic resolution. Besides mapping the local density of states (LDOS), the technique of STM can be adapted to detect the local magnetization of a surface. This technique, called spin-polarized scanning tunneling microscopy (SP-STM), requires a tip that is sensitive to the spin of the electrons that constitute the tunnel current. In addition to magnetic sensitive tips, a demonstration of SP-STM requires a sample exhibiting a laterally varying direction of magnetization. In the current work the material system consists of thin layers of iron deposited on a vicinal tungsten (110)-surface. The surface of this material system is known to exhibit an alternating in-plane and out-of-plane direction of magnetization, making it well-suited for a proof-of-principle SP-STM experiment. In the first section of this chapter the experimental details, i.e. the chosen material system and the preparation procedure, are described. In the following section the origin of the contrast in $dI/dV$-maps of the surface is discussed. The chapter is concluded with a section presenting results that conclusively demonstrate SP-STM.

4.1 Experimental details

All the STM measurements presented in this chapter were performed with the low temperature STM described in section (2.1.5). The operating temperature was 77 K, which is well below the Curie temperature of the studied material system (210 K). Two types of magnetic tips were used. Sharp anti-ferromagnetic chromium tips with an canted out-of-plane direction of magnetization, and blunt rounded tungsten tips covered with a thin film of iron with an in-plane direction of magnetization. The details of the preparation procedure of both type of tips is given in section (2.1.6). The magnetic properties of the sample are investigated by means of $dI/dV$-maps that were recorded simultaneously with the topography by using a lock-in amplifier. If not specified otherwise, the amplitude of the modulation signal was 30 meV.
4.1.1 Material system

The material system chosen to demonstrate SP-STM consists of a vicinal W(110)-surface covered with 1.5 ML of Fe. The angle of miscut was chosen such that the average terrace width is \( \approx 9 \) nm, just below the critical width for the formation of misfit-dislocations\(^{103}\). The thin layer of Fe was epitaxially grown at room temperature and subsequently annealed to \( \approx 550 \) K (4 min). The post annealing leads to so-called step flow growth in which, the increased mobility of the Fe adatoms prevents the formation of nuclei on the middle of the terraces. Instead, the Fe adatoms settle on the energetically more favorable adsorption sites at the step-edges. For a coverage below one monolayer this results in the formation of parallel stripes (“nanowires”) of Fe along the step edges. After the completion of the first layer of Fe, the process of step flow growth repeats itself for the second layer. This means that in case 1.5 ML of Fe is deposited the surface will consist of alternating mono/bilayer Fe nanowires of equal width, see figure 4.1. Previous studies on this material system show that the bilayer nanowires have an out-of-plane direction of magnetization and are anti-ferromagnetically coupled\(^{68,104,105}\). In contrast, the monolayers were found to have an in-plane direction of magnetization. Note that since all previously reported experiments were done with tips having out-of-plane direction of magnetization, the specific configuration of the in-plane direction of magnetization in the monolayers is not known. In the current work between 1.25–1.75 ML of Fe was deposited on the W(110)-surface.

4.1.2 Cleaning the W(110)-surface

Prior to the growth of the Fe nanowires, the W(110)-surface needs to be cleaned. For this purpose a high temperature oven capable of sustained heating up to \( \approx 1500 \) K and flashing up to \( \approx 2300 \) K was designed, see figure 4.2. The oven can be classified as an electron-beam heater; free electrons are ejected from a filament and directed toward the sample by the application of a high electric field and heating it upon impact. In the current design a triode, with which the electron beam can be squeezed and focused on the sample, has been included. The high temperature oven consists of numerous parts of which most are made out of material that are electrical isolators and/or have a high melting point, see the explosion view of figure 4.2. In table 4.1, the
Figure 4.2: Three-dimensional rendering of the high temperature oven. a) Final assembly, and b) explosion view indicating the material composition of the various parts.

Table 4.1: Cleaning procedure of the W(110)-surface. The first four steps are only needed in the case if the W(110)-surface and/or if the high temperature oven was exposed to ambient conditions. For better results step 4 and 5 might be repeated.

<table>
<thead>
<tr>
<th>Step</th>
<th>Duration</th>
<th>Pressure</th>
<th>Temperature</th>
<th>Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 day</td>
<td>UHV</td>
<td>&lt;1000 K</td>
<td>50–100 W</td>
</tr>
<tr>
<td>2</td>
<td>1 day</td>
<td>$1 \times 10^{-6}$ mbar O$_2$</td>
<td>$\approx$ 1500 K</td>
<td>100–150 W</td>
</tr>
<tr>
<td>3</td>
<td>10 × 15 sec</td>
<td>UHV</td>
<td>$\approx$ 2300 K</td>
<td>400 W</td>
</tr>
<tr>
<td>4</td>
<td>4 hours</td>
<td>$1 \times 10^{-6}$ mbar O$_2$</td>
<td>$\approx$ 1500 K</td>
<td>150 W</td>
</tr>
<tr>
<td>5</td>
<td>10 × 15 sec</td>
<td>UHV</td>
<td>$\approx$ 2300 K</td>
<td>400 W</td>
</tr>
</tbody>
</table>

steps involved in the cleaning procedure are listed. During heating of the sample under an oxygen atmosphere at $\approx$ 1500 K, carbon compounds, which constitute the bulk of the contaminants, are burned off. The oxygen layer now covering the surface is subsequently removed by flashing the sample several times to a temperature of $\approx$ 2300 K.

4.2 Results

It the following subsections the results of SP-STM experiments are presented. First, the observed contrast in the dI/dV signal is discussed, followed by a subsection focusing on the identification of the magnetic domain structure. In this subsection, two different kind of magnetic tips, i.e. with an in-plane and canted out-of-plane direction of magnetization, were used.
4.2.1 \( dI/dV \) contrast between mono- and bilayers of Fe

All the results presented in this subsection were obtained with a rounded tungsten tip coated with 9 ML of Fe. Such tips are known to possess an in-plane direction of magnetization. In the current experiment the same surface area was scanned at different bias voltages. At each bias voltage the topography and the \( dI/dV \)-signal was recorded. The results for two exemplary bias voltages will be presented. First, the data recorded at a bias voltage of \( V = -1.0 \) V is considered. In the topographic map of the scanned area, see figure 4.3a, 10 terraces can be identified. However, the corresponding \( dI/dV \)-map, see figure 4.3b, shows 16 different areas, alternating between bright and dark regions. This contrast does not have a magnetic origin, at least not for a large part, but stems from the difference in electronic properties between mono- and bilayer nanowires. Note that, this contrast can also be observed with non-magnetic tips and can be explained by the spin-orbit coupling effect that makes the spin-averaged electronic structure magnetization direction dependent. Given the observed contrast and the knowledge about the locations of the step-edges from the topographic map, it is possible to work out the location of the mono–bilayer transitions and, subsequently, the topography of the underlying W(110)-surface. The result of this analysis is shown in figure 4.5. The dark and bright regions are found to correspond to monolayers and bilayers of Fe, respectively. At this bias voltage the topography signal shows discrete steps with mono-atomic height. This is not the case for \( V = +0.3 \) V, the other exemplary bias voltage. In the topographic map of the same area, see figure 4.4a, a total of 15 terraces can now be identified for this bias voltage, while the \( dI/dV \)-signal is nearly identical, see figure 4.4b. As a guide to the eye, the edge of one of the newly appeared terraces is marked with an arrow both figures. Again, the correlation between the topography and the \( dI/dV \)-signal is analyzed, see figure 4.6. The additional terraces coincide with regions of monolayer coverage and where the topography signal is increased by approximately the height of half a mono-atomic step. As mentioned above, the contrast in the \( dI/dV \)-map is not necessarily the result of a difference in direction of magnetization between mono- and bilayers. Since the topographic signal is proportional to the integrated LDOS, see equation (2.4), with the LDOS in turn being proportional to the \( dI/dV \)-signal, see equation (2.6), the same reasoning holds for the newly appeared terraces. If the integrated LDOS is higher on the monolayers than on the bilayers, for example at a bias voltage of \( V = +0.3 \) V, more sample states are available for tunneling. This will result in an enhancement of the tunneling current at a given bias voltage and sample–tip distance. Since the STM is operated in constant current mode, the feedback-loop will retract the tip to compensate, resulting in a rise of the topography signal.

Although part of the contrast in the \( dI/dV \)-maps might be the result of a different direction of magnetization between the mono- and the bilayers, it is not yet possible to claim that the presented measurement is a demonstration of spin-polarized tunneling. An conclusive proof of spin-polarized tunneling requires a change in direction of magnetization between electronically identical regions, i.e. between or within the monolayers when probing with a tip having an in-plane direction of magnetization. At the moment the interpretation of the current results remains open, as they can be explained by several options. First, the preparation of the magnetic tip could have failed and spin-polarized tunneling can then not be observed, the contrast being purely of electronic
Figure 4.3: a) 40 × 40 nm$^2$ topographic and b) corresponding $dI/dV$-map of the 1.5 ML Fe / W(110)-surface ($V = -1.0$ V, $I = 0.2$ nA). The $dI/dV$-map was recorded simultaneously with the topography. The arrow in the topographic image indicates the position of an additional edge that will appear in the topographic image at other bias voltages, see figure 4.4a for comparison.

Figure 4.4: a) 40 × 40 nm$^2$ topographic and b) corresponding $dI/dV$-map of the same surface area of the 1.5 ML Fe / W(110) surface shown in figure 4.3 ($V = +0.3$ V, $I = 0.2$ nA). The $dI/dV$-map was recorded simultaneously with the topography. The arrow in the topographic image marks the position of an additional edge that has become visible at this bias voltage, see figure 4.3a for comparison.
Figure 4.5: Topographic height profile (blue line) as extracted from figure 4.3a and taken along the same path as the line as shown in the $dI/dV$-map inset. The dark and bright regions in the $dI/dV$-signal are schematically indicated in the graph by rectangles with corresponding colors. The red line indicates the underlying tungsten surface. All the steps-edges are found to be of mono-atomic height.

Figure 4.6: Topographic height profile (blue line) as extracted from figure 4.4a and taken along the same path as the line shown in the $dI/dV$-map inset. The dark and bright regions in the $dI/dV$-signal are schematically indicated in the graph by rectangles with corresponding colors. The red line indicates the underlying tungsten surface. Compared to figure 4.5, additional terraces that coincide with the bilayers are found. The apparent topographic enhancement of these terraces is highlighted by the green rectangles.
nature. Secondly, the magnetization direction might be the same for all monolayers, which would make the current material system unsuited for a demonstration of spin-polarized tunneling with tips having an in-plane direction of magnetization. Thirdly, the specific in-plane direction of magnetization of the tip with respect to the direction of magnetization of the monolayers might be unfortunate, yielding an equal contrast for monolayers with different direction of magnetization.

The next experiment was performed on the 1.25 ML Fe/W(110)-surface with a rounded tungsten tip coated with 9 ML of Fe. Again, such tips are known to have an in-plane direction of magnetization. Figure 4.7 illustrates the sensitivity of the contrast in the $dI/dV$-map to the bias voltage and the modulation amplitude of the lock-in amplifier. In this figure, a $dI/dV$-map recorded at four different bias voltages and two different modulation amplitudes is shown. As can be seen, switching the polarity at the low bias voltage ($V = \pm 0.3 \text{ V}$) has very limited impact on the contrast. This is not the case at the high bias voltage ($V = \pm 0.7 \text{ V}$), where several contrast reversals are observed. A first glance at the contrasts and the reversals recorded at the high bias
Demonstration of spin-polarized scanning tunneling microscopy

Figure 4.8: 60 × 55 nm² area of the Fe 1.25 ML / W(110)-surface. a) Surface topography (V = +0.7 V, I = 100 pA), and b) dI/dV-map. c) The same dI/dV-map with a color coded superposition of the magnetic domains. The mono-atomic step-edges are marked with black lines. As a guide to the eye, the locations of a step-edge (dark arrow), a mono / bilayer transition (white arrow), and a transition within a monolayer (gray arrow) are marked.

voltage shows that at least four distinct regions can be classified (marked in figure 4.7). Given the fact that only two electronically different regions are present on the surface, i.e. the mono- and bilayer nanowires, a higher number of contrasts is a clear indication that magnetic information is being recorded and thus a demonstration of SP-STM. This will be investigated in more detail in the next subsection.

4.2.2 Spin-polarized scanning tunneling microscopy

In figure 4.8a, a topographic map of the 1.25 ML Fe / W(110)-surface recorded with a rounded Fe coated tungsten tip. As mentioned before, such tips are known to have an in-plane direction of magnetization. Note that, similar to figure 4.4a, additional non-atomic height differences are observed in the topographic map. As a guide to the eye the location of one ‘real’ step-edge (dark arrow) and one apparent step-edge (white arrow) are marked in the figure. As shown in the previous section, the additional terraces are, at least for a large part, due to the different electronic properties of the monolayers and the bilayers. So far everything is analog to the first part of the previous experiment.
The situation changes for the $\frac{dI}{dV}$-map, see figure 4.8b. Instead of just two contrasts, three different contrast levels are observed. An analysis of the correlation between the topography and the contrast in the $\frac{dI}{dV}$-map shows that each monolayer of Fe exhibits two contrasts separated by a sharp boundary. One of these transitions within a monolayer is marked by a gray arrow in all the images of figure 4.8. Given the fact that the electronic properties do not change within one monolayer, the observed contrast should be of magnetic origin and thus constitute a conclusive demonstration of SP-STM. In case the direction magnetization within the monolayer is aligned with (opposite to) the direction of magnetization of the tip, regions with bright (dark) contrasts are observed in the $\frac{dI}{dV}$-map. No difference in contrast is observed between or within the bilayers. Since the bilayers are known to have an out-of-plane direction of magnetization\textsuperscript{105}, and given that the tip has an in-plane direction of magnetization, this was expected. In order to make the geometrical extend and the configuration of the various magnetic domains more tangible a semi-transparent color coded layer has been overlain on the raw $\frac{dI}{dV}$-map, see figure 4.8c.

As shown in figure 4.8b, the width over which the contrast and thus the direction of magnetization switches within a monolayer, i.e., the domain wall width, is sharply defined. To make this more quantitative, the profile of the $\frac{dI}{dV}$-signal along a typical stretch of sample surface perpendicular to the nanowires is plotted in figure 4.9. Analog to the results of other groups\textsuperscript{9}, the observed domain walls within the monolayers are assumed to be 180° domain walls. From micromagnetic theory it is known that the profile of such a domain wall is determined by a competition between the exchange stiffness energy, i.e., the energy penalty imposed by a change in the direction of two neighboring spins, and the magnetic anisotropy energy. The latter depends on the direction of magnetization relative to the crystallographic axis of the material, and is affected by lattice defects and deformations. For 180° domain walls in bulk material the profile can be described in micromagnetic theory by\textsuperscript{9,106}.

**Figure 4.9:** Cross-sectional $\frac{dI}{dV}$-profile (red line). From left to right: monolayer with bright contrast, monolayer with dark contrast, and the bilayer. An analytical function (blue line) is fitted to the domain wall.
Figure 4.10: 50 × 40 nm² area of the Fe 1.25 ML/W(110)-surface. a) Surface topography (V = −1.5 V, I = 150 pA), and b) the accompanying dI/dV-map in which the four contrast levels are marked. c) The same dI/dV-map with a color coded superposition of the magnetic domains. The mono-atomic step-edges are indicated with black lines.

\[
y(x) = y_0 + y_{sp} \cos \left\{ \arccos \left[ \tanh \left( \frac{x - x_0}{w/2} \right) \right] + \phi \right\},
\]

with \(y(x)\) the dI/dV-signal at position \(x\), \(x_0\) the position of the domain wall, \(w\) the domain wall width, \(\phi\) the angle between the directions of magnetization of the tip and surface (\(\phi = 0\) for in-plane sensitive tips on the monolayers), and \(y_0\) and \(y_{sp}\) the average and the amplitude of the dI/dV-signal, respectively. A domain wall width of 0.45 nm, which is roughly the extend of 3 atomic-sites, was found. Within micromagnetic theory this very narrow domain wall width can be explained by assuming a large magnetic anisotropy\(^9\). However, note that the basic assumption in micromagnetic theory is that the angles between adjacent spins are small. The fact that in the current case the spins turn 180° in a couple of atomic-sites renders this assumption invalid and it is therefore not clear if micromagnetic theory can be applied here. First of all, the electronic and magnetic structures of films with a thickness of a couple of monolayers is known to strongly differ from bulk layers\(^{109,110}\). Furthermore, the exchange stiffness of an atomic-scale domain wall depends strongly on its width\(^{111}\). For these reasons, it might be more appropriate to treat the observed domain wall within the framework of first principles quantum mechanics. In a recent study in which the domain wall profile in a monolayer Fe was calculated from first principles quantum mechanics the width of the domain wall was found to be 8 Å\(^{112}\). Although, the calculation is outside the scope of the current...
work, the results are quantitatively consistent with the SP-STM measurements.

Besides tips with an in-plane direction of magnetization, bulk Cr tips with a predominant out-of-plane direction of magnetization were used to image the 1.25 ML Fe/W(110)-surface. In figure 4.10a–b, a topographic map and the accompanying $dI/dV$-map recorded with such a tip are shown. The number of different contrasts in the $dI/dV$-map is striking. Four levels are observed: a dark, an intermediate, and two levels of bright contrast. Since the latter two are always located next to each other and differ only slightly in intensity, it is hard to distinguish one from the other. However, by analyzing the correlation between the topography and the $dI/dV$-map, the magnetic configuration of the surface can still be precisely retrieved. In figure 4.10c, the configuration of the various magnetic domains is made more tangible by overlaying a semi-transparent color coded layer on the raw $dI/dV$-map. A difference in contrast between the individual bilayer nanowires is expected. This is expected with a tip that has an out-of-plane direction of magnetization and bilayers that are anti-ferromagnetically coupled. However, the contrast transition within the monolayer that were observed with the in-plane sensitive tip are still observed. Since no other studies using tips with a purely out-of-plane direction of magnetization report a change in contrast within a monolayer\textsuperscript{105,113,114}, the current tip has most likely a slanted direction of magnetization with respect to the out-of-plane axis. This is supported by the results of other groups that have used bulk chromium tips\textsuperscript{9}.

### 4.3 Summary and discussion

In this chapter spin-polarized tunneling microscopy was achieved on a vicinal W(110)-surface covered with 1–2 ML Fe. This material system consists of alternating mono- and bilayer magnetic nanowires. Tips having an in-plane direction of magnetization and tips that proofed to have a slanted direction of magnetization were used. Respectively, three and four levels of magnetic contrast were observed with these tips, unambiguously demonstrating SP-STM. Although, the global direction of magnetization of the tip can be determined (in-plane, out-of-plane, or slanted) on the 1–2 ML Fe/W(110)-surface, it is from an experimental point of view not the most convenient material system for tip characterization. The preparation involves high temperature annealing, deposition of a calibrated amount of Fe, and step-flow growth. All these steps are experimentally very challenging. In this respect, >8 ML thick Fe islands on W(110) might proof more forgiving\textsuperscript{11}. In this material system the direction of magnetization of the islands is in-plane and spirals around the center. This allows the determination of the exact direction of magnetization of tips having an in-plane direction of magnetization. In addition, it can be checked whether tips have a pure out-of-plane direction of magnetization. Since the Fe islands are relatively thick compared to the thin films (>9 ML vs. 1–2 ML), the condition of the surface is of less importance and the cleaning step therefore not as crucial. Furthermore, the deposition of the proper amount of Fe is not nearly as critical as for the thin films. The next step along the lines of the current work is to extend SP-STM to dilute magnetic semiconductors, e.g. Mn in GaAs. Atomic-scale resolution with magnetic chromium tips has already been observed (not in the thesis) on this material system in X-STM measurements, a hopeful first step towards probing the magnetic properties of dilute magnetic semiconductors in the future.
Composition profiling of InAs quantum dots and wetting layers by atom probe tomography

In this chapter a study comparing the techniques of cross-sectional scanning tunneling microscopy (X-STM) and atom probe tomography (APT) is presented. Epitaxially grown self-assembled InAs quantum dots (QDs) in GaAs are chosen as an exemplary material system with which to compare these two nanostructural analysis techniques. The composition of the QD layers is studied, and quantitative comparisons of the indium concentration profiles as measured by each method are performed. It is shown that computational models of QD layers, based on experimental data, are consistent with both analytic approaches. This establishes a link between the two techniques and shows their complementary behavior, an advantage which is exploited in order to highlight unique features of the examined QD material.

5.1 Introduction

Accurate and high-resolution structural imaging and compositional analysis techniques have been the key driving technological force behind recent advances in nanotechnology and nanoanalysis. Today, a multitude of analysis tools are employed by scientists and engineers studying nanostructures, each offering its own specific capabilities and advantages. Because each technique can supply different data, it is common that several methods will be used together in order to build a more complete and accurate understanding of the studied subject. Of the various methods in use, two techniques are of particular interest thanks to their unparalleled ability to provide atomic-level imaging. The first technique, cross-sectional scanning tunneling microscopy (X-STM), which belongs to the family of scanning probe microscopy techniques, is well suited for...
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studying semiconductor materials, particularly in the III-V arena. The key strength of X-STM is that it can directly visualize the atomic structure of a material, allowing detailed structural analysis. However, analysis of nanostructures can be difficult due to the complicated contrasts of the various atomic species, the outward relaxation of the cleaved surface, and the two-dimensional nature of the technique. Despite this, the great precision of the measurements makes it feasible to infer details that otherwise can not be directly visualized. For example, statistical analysis and finite element (FE) calculations can be used to create three-dimensional models of the atomic structure. However, this FE approach, in which the outward relaxation of a strained surface is calculated, has the inherent limitation that it is not injective; any measured dataset can be simulated by a range of different input models.

The second technique under consideration is atom probe tomography (APT). This is the latest evolution of the venerable field emission microscope, where a field ion microscope is combined with a spatially resolved time-of-flight mass spectroscopy, creating a device known as a three-dimensional atom probe (3DAP). In 3DAP, a large pulsed voltage is applied to a needle shaped specimen of material, causing the emission of single ions from the specimen's apex and their acceleration towards a detector screen. The data collected after each voltage pulse can be combined to form a three-dimensional tomographic image of the specimen. This technique works best for materials with a high conductivity, where sub-atomic precision can be achieved, and so far there has been only little use of the technique outside of metallic systems. However, the re-emergence of laser based 3DAP has greatly extended the range of materials that can be analysed. Where semiconductor materials were previously out of bounds, now the additional thermal excitation from a pulsed laser makes performing APT on these materials feasible, although with a reduced analytical quality. Consequently, pioneering work on semiconductor nanostructures, such as quantum dots (QDs) and nanowires, has started.

In terms of capabilities, APT seems to complement X-STM very well. Where X-STM can only image two-dimensional cross-sections, APT provides a full three-dimensional tomographic reconstruction, and where X-STM has limited capabilities to distinguish between chemical species, the mass-spectral analysis offers the ability not only to distinguish between different elements but also different isotopes. Naturally, these capabilities do not come without a price. The volume that can be measured by the 3DAP is typically of the order of tens of nm laterally and hundreds of nm vertically, which is far more restrictive than the many µm that can be imaged with X-STM. Furthermore, the spatial precision is not as high as with X-STM, and not all emitted ions can be detected. Even in ideal conditions, the detection efficiency is less than 60%. Finally, a particular weakness of APT is that the images are reconstructed in a process requiring many assumptions about factors such as apex shape, radius, evaporation conditions and so forth. The result is that, whilst the 3DAP provides a very unique dataset, its reliability and its spatial accuracy is inherently inferior to X-STM.

5.2 Experimental details

The studied material consists of (In\textsubscript{x}Ga\textsubscript{1-x})\textsubscript{As} self-assembled QD layers in GaAs, grown on an (001)-oriented GaAs substrate via molecular beam epitaxy. The QD layers were...
grown by deposition of 2 ML of InAs at a rate of 0.1 ML s\(^{-1}\) and at a substrate temperature of 500°C. Vertically, the five QD layers are separated by 50 nm of GaAs with a final capping layer of 20 nm. This separation distance between QD layers is considered sufficient to suppress strain induced nucleation in this material system. From atomic force microscopy (AFM) measurements on uncapped material grown under the same conditions, the areal density of the QDs was determined to be \(\approx 3.0 \times 10^{10} \text{ cm}^{-2}\). Low temperature (5 K) macro photoluminescence measurements show that the QDs emit at an energy of 1.229 eV with a FWHM of 59 meV. All X-STM measurements were performed with the room temperature STM described in section (2.1.5). Standard electrochemically etched tungsten tips were used, see section (2.1.6) for the details of the preparation procedure. The STM was operated in constant current mode on \textit{in situ} cleaved \{110\} surfaces. To ensure that the electronic contribution to the apparent height measured by X-STM, is minimized, a high negative bias voltage (\(V \approx -3\) V) was applied during all measurements. The resulting signal is almost purely topographic, allowing the recording of the outward relaxation of the surface and the identification of individual indium atoms. The strain relaxation, induced by the lattice mismatch between InAs and GaAs, of the wetting layers (WLs) and the QDs was modeled with the finite element (FE) method. The FE calculations were performed using the MEMS module of COMSOL Multiphysics. To calculate the strain relaxation of the WL and the QDs a two- and three-dimensional model was used, respectively. The APT measurements were performed using an LEAP 3000X Si instrument. The 3DAP, operating conditions, and specimen preparation are described in more detail in section (2.2.2).

5.3 Results

For a direct comparison a representative view of typical data obtained with the two techniques of X-STM and APT is shown in figure 5.1. From this figure, the different nature of the two techniques becomes apparent; where the X-STM measurement is restricted to the cleavage plane and thus yields information that is two-dimensional in nature, the APT measurement provides a fully three-dimensional data set. Even without any further analysis, the WLs and QDs can already be distinguished in the figure. In the following sections a detailed comparison of the WLs and the QDs as measured by X-STM and APT is given.

5.3.1 Wetting Layer

An atomically resolved 52 \(\times\) 19 nm\(^2\) local mean equalization filtered current X-STM map of a representative part of the WL is shown in figure 5.2a. The positions of individual indium atoms can be distinguished. The WL is found to start abruptly (within one bilayer), followed by a decay of the indium concentration in the growth direction. From previous work it is known that the decay of the indium concentration can be modeled by an exponentially decaying function. The function \(a \exp(-z/b)\), with \(z = 0\) nm corresponds with the start of the wetting layer and positive \(z\)-direction represents the growth direction, is used as an input for the FE modeling that is employed to calculate the outward relaxation of the cleaved surface due to the strain in the WL. By adjusting the initial indium fraction, \(a\), and the inverse decay constant, \(b\), until the calculated...
Figure 5.1: Representative view of typical data sets as obtained with the two techniques under consideration. The five In$_x$Ga$_{1-x}$As layers are clearly visible with both methods. All the scale bars are 50 nm. a) 190 × 175 nm$^2$ topographic X-STM map ($V = -3$ V, $I = 30$ pA). Several QDs can be distinguished as bright features in the WLs. b) Atom map showing only the indium atoms (indigo pixels). The indium atoms between the WLs are background noise and account for approximately 0.1–0.6% of the detected atoms. Red isosurfaces (25% indium) mark the location of QDs. c) The top image shows the reconstruction, now also with 20% of the detected Ga atoms (yellow pixels), overlaid on an SEM image of the specimen prior to evaporation. The bottom image shows the remains of the specimen after evaporation.
Figure 5.2: WL analysis. a) $52 \times 19 \text{ nm}^2$ local mean equalization filtered current X-STM map ($V = -3\text{ V}, I = 40\text{ pA}$). The start of the WL (red arrow) occurs within one bilayer and is followed by an exponential decay of the indium concentration along the growth direction. b) Outward relaxation profile, averaged over 90 nm of WL, as measured by X-STM (red line) and the result of the FE calculation (blue line). c) top) Indium fraction in the WL as a function of the position along the growth direction as measured by APT and the used deconvolution function (yellow line). c) bottom) Deconvolved APT data and its fit using an exponentially decaying function (yellow line), to the data. To ease comparison, the input for the FE calculation is also plotted (red line).
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Figure 5.3: Example of an atom probe data set showing a $20 \times 20 \times 30$ nm$^3$ volume through a section of the (In,Ga)As WL. For clarity, only the group-III elements are shown. The indium atoms are represented by purple spheres with a radius of 0.2 nm and the gallium atoms by yellow spheres with a radius of 0.1 nm. The indium concentration along the growth direction is extracted by sampling a binned cylinder with a diameter of 20 nm.

outward relaxation profile (blue line, figure 5.2b), matches the outward relaxation profile as measured by X-STM (red line, figure 5.2b), the decay of the indium concentration can be determined. The final values are determined to be $a = 0.188 \pm 0.002$ and $b = 1.95 \pm 0.05$ nm.

The indium concentration along the growth direction can also be determined from the APT data. This is done by sampling the composition of 20 nm diameter cylinders along the $z$-axis, see figure 5.3. A small bin length was chosen in order not to lose detail of the sharp concentration changes. A thin diameter was chosen so that the cylinder could be positioned without overlap with with any of the QDs and yet remain close to the core of the specimen, where the reconstruction is most the accurate. The thin diameter also helps to reduce the effects of curvature in the reconstruction and misalignment of the cylinder to the normal axis, both of which could result in loss of detail in the sharp onset of the WL. In order to avoid systematic errors in the reconstructions, volumes from different layers and different specimens were compared. To improve the signal-to-noise ratio, the concentrations of these different sampling volumes were averaged together; this averaged data is shown in figure 5.2c (top).

From the X-STM measurements it is unambiguously determined that the onset of the WL is abrupt (within one bilayer). This is not the case in the APT data, where the indium fraction rises from $x = 2\%$ to 15\% over a distance of $\Delta z \approx 0.7$ nm. Despite the measures taken to ensure a good alignment of the cylinders and data reconstruction of the interface, this artifact is considered to arise from three effects. First, averaging over
several volumes, which individually also do not have completely sharp interface reconstructions. Secondly, the alignment of the cylinders perfectly parallel to the growth direction, and thirdly, possible problems with the reconstruction of the APT data. Combined, these errors smear out the onset of the WL. However, since it is known that the WL starts abruptly, a deconvolution of the APT profile can be performed in order to compensate for this. The deconvolution function was determined by fitting a Gaussian function to the onset of the WL in the APT data, see figure 5.2c (top). The FWHM of this Gaussian function is 0.8 nm and thus can be considered as the instrument profile. This value is in good agreement with the resolution obtained from laser-assisted evaporation of Si isotope superlattices. An alternative technique, known as z-density correction, can also be used to improve interface sharpness in the depth direction.

The deconvoluted APT data is shown in figure 5.2c (bottom). The onset of the WL is now found to occur within ≈ 0.35 nm, which is well within one bilayer (0.565 nm), and the peak Indium fraction, x, has risen by ≈ 2%, in agreement with the X-STM data. An exponentially decaying function in the same form as the input for the FE calculations was used to fit the deconvolved APT data. The final values are determined to be a = 0.189 ± 0.004 and b = 1.95 ± 0.05 nm.

By comparing the two techniques an excellent match of the indium segregation profiles is found. However, to arrive at this result the deconvolution of the APT data was necessary. In case that no deconvolution function is known and z-density correction is not applicable, the APT's ability to image sharp interfaces is limited by the data reconstruction technique.

5.3.2 Quantum Dots

Having shown, with the aid of FE calculations, that the two techniques give comparable results for the WLs, the QDs case is now considered. A total of 55 QDs were characterized, among which 43 by X-STM and 12 by APT. The various ways of data analysis used on the APT data sets are shown in figure 5.4. Each of the depicted methods has its own merits and disadvantages, and are therefore used in conjunction. In figure 5.5, the height and width of all observed QDs is plotted. The height of the QDs was determined from the X-STM data by counting the number of bilayers in the current maps, resulting in the discrete nature of the plotted data. In APT the height of the QDs is determined from a one-dimensional composition profile sampled by a 10 nm diameter cylinder going through the center of the QD, see figure 5.4a. The width is determined from the cross-sectional contour maps with a 1 nm projection taken through what is estimated to be the longest part of the dot, see figure 5.4b–c. The thickness of the highest QD as measured by X-STM is in agreement with the highest QD observed by APT (2.8 nm vs. 2.7 nm). At the lower end of the observed height distribution a discrepancy between the two techniques is observed; the thinnest QD found by X-STM is significantly lower than the thinnest QD observed by APT (1.1 nm vs. 1.5 nm). This can be explained by the two-dimensional nature of the X-STM technique and the arbitrary position of the cleavage plane. There is no a priori way of knowing where a QD is cleaved and if a QD is cleaved near its edge it will appear thinner. The same holds for the width of the QDs. This results in a wide range (7–22 nm) of observed QD widths and in the trend of increasing QD height with increasing QD width in the X-STM data as seen in figure 5.5a.
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Figure 5.4: 25 × 25 × 13 nm³ atom maps of a volume of (In,Ga)As containing a QD. For clarity only the group-III elements are shown. Various ways of analyzing the data are shown. a) 10 nm diameter cylinder through the center of the QD to sample a one-dimensional compositional profile. b) Cross-section taken in-plane, and (c) parallel to the growth direction through the center of the QD. From these cross-sections, two-dimensional composition profiles, sampled from a 1 nm deep projection, are extracted.

In the fully three-dimensional technique of APT the height and width of the QDs can be determined with less ambiguity. It is therefore not surprising that the height/width distribution of the QDs as measured by APT is clustered in the top right of figure 5.5a. The spread in the distribution reflects the non-uniformity of the growth process. By taking cross-sectional contour maps through non-central positions of the QD, as shown in the upper-right panel of figure 5.5b, the effect of off-center cleavage can be emulated.
Figure 5.5: a) QD height vs. width distribution as measured with X-STM (red) and APT (blue). The yellow APT data is extracted from indium concentration contour plots made at 2 nm intervals from the center of the QD shown in the upper-right panel of figure b). In this way the random position of the cleavage plane in X-STM is simulated. b) Indium concentration contour maps ($25 \times 25$ nm$^2$) of six different QDs looking at the (001)-surface. The upper-left panel shows the center position used to make the cross-sectional contour of figure 5.6c. The upper-center panel illustrates how the width is estimated from cross-sectional contour plots. The arrows in the upper-right panel mark the length as measured for the yellow data points in figure a). Three more QD footprints are depicted in the bottom panels.
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Figure 5.6: Comparative views of two QDs. All images are 25 × 13 nm². a) Topographic and b) local mean equalization filtered current X-STM map (V = -3 V, I = 40 pA). The QD height was determined to be 2.8 nm. c) Contour plot of the indium concentration of a 1 nm thick slice through the center of a QD as measured by APT. The three-dimensional grid parameters used to create the two-dimensional profile are a delocalization of 1.5 nm along the in-plane axes and 0.75 nm in the growth direction. The contour lines are every 5%, ranging from 0% to 65%. The height of the QD as measured by APT was determined to be 2.3 nm. The APT data was used to construct a model (d) which serves as an input for the FE calculations. The two marked regions were found to be crucial for modeling the QD.

The yellow points in figure 5.5a show the width and height, measured as the contour map is moved towards the edge of the QD. In contrast to the blue points, for which a one-dimensional profile was used to determine the height, the height was determined from the x = 25% indium contour of a cross-section taken along the growth direction (analog to figure 5.4c). Although this is not as accurate, it yields more localized measurements.

It should also be noted here that there is a substantial error in the determination of the width of the QDs with both techniques. Due to the gradual transition of WL to QD it is hard to pinpoint where the QD exactly starts. In an effort to increase the accuracy, a combination of current and topographic data was used to determine the width of the QDs with X-STM. In the case of the APT the WL profile is first subtracted from the data. However, with both techniques, an error of ≈ ±2 nm remains in the width of the QDs. For clarity these error bars are omitted from figure 5.5a.

Figure 5.6a–b shows the topographic and the local mean equalization filtered current X-STM maps of a cleaved QD. The height and width of this QD were determined to be 2.8 nm and 18.0 nm, respectively. As mentioned above, it is normally not known how the cleavage plane intersects the QDs in the X-STM technique. However, the statistics of figure 5.5a show that this QD is one of the highest and widest that was observed. Therefore, it is reasonable to assume that this particular QD was cleaved through its center. Since not all the individual indium atoms can be resolved in the X-STM...
images, it is not possible to extract directly an indium profile from figure 5.6a–b, and an indirect route via APT and FE calculations has to be taken. With APT the indium profile of the QDs can readily be obtained. A contour plot of the indium concentration of a slice through the center of a QD as observed by APT is shown in figure 5.6c. The QD and the slice position are shown in the upper-left panel of figure 5.5b. This particular QD was located near the middle of the APT specimen. As it is the least affected by reconstruction artifacts, it was chosen to link the two techniques of X-STM and APT. The height and the width were determined to be 2.3 nm and 16.7 nm respectively, making this a typical QD. It has to be noted that a previous APT study reported the peak indium concentration in InAs QDs to be off-centered and towards the top of the QDs. This is not the case in the current QDs where the peak indium concentration is slightly shifted towards the top and laterally located in the center.

Conventionally, InAs / GaAs QDs are modeled by a disk or a truncated pyramid with increasing (from bottom to top) or inverted-triangular shaped indium profiles. Given the X-STM and APT data, such an approach cannot be followed with the current QDs. Figure 5.5b shows no strong evidence of faceting or any particular footprint for these QDs. As the contour concentration maps show, the QDs merge into the WL, making edges indistinct. Furthermore, each QD footprint has a unique irregularity. Therefore, modeling these QDs as long thin spheroids with a circular footprint is considered to be the most reasonable first approximation.

The size and the shape of buried InAs / GaAs QDs are determined by a delicate interplay between driving and quenching of QD leveling during overgrowth. Depending on the growth rate, the growth temperature, and the application of a growth interrupt, various geometrical and compositional configurations of the WL and the QDs are possible. Generally, two main classes can be identified: 1) QDs grown at low temperature and 2) QDs grown at high temperature. Low temperature reduces the indium segregation (both vertically and laterally) during the overgrowth of the QDs. Consequently, the wetting layer will be relatively thin and the interfaces of the QDs will be sharply defined. In contrast, a higher growth temperature will result in a stronger indium segregation and therefore yields a more pronounced WL and softer QD interfaces.

Figure 5.6a–b shows that the interfaces of the studied QDs are not sharp and that a pronounced WL is present. Clearly, these QDs belong to the second class. Here it should be noted that, due to the averaging nature of the technique, it can be difficult to distinguish between the two QD classes in most TEM studies of InAs / GaAs QDs. Thus, particular care must be taken when trying to model QDs based only on this imaging technique. To aid in the construction of a model for the current QDs, two one-dimensional indium profiles were extracted from the APT data shown in figure 5.6c: one through its center along the growth direction, shown in figure 5.7, and one laterally through the center, perpendicular to the growth direction (not shown). This data was fitted with analytical functions and scaled to match the width and height of the QD observed by X-STM depicted in figure 5.6a–b. The analytical expressions were then used to generate a fully three-dimensional model of the QD. The result is shown in figure 5.6d, and in more detail at the end of the chapter in figure 5.9 and table 5.1.

Besides the indium profile in the core of the QD, two other regions (marked in figure 5.6d) proved to be crucial in the modeling of the QD. The first is the exponential decay of the indium concentration in the growth direction above the QD. From the one-dimensional indium profile taken through the center of the QD, it is determined that this
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Figure 5.7: One-dimensional indium profile in the direction of growth through the center of the QD shown in figure 5.6c. Analytical functions (solid lines) are fitted to the APT data (points). The indium found above the QD is marked in this profile by the blue shaded area and amounts to 16% of the total amount of indium.

amounts to 16% of the total number of indium atoms present; see the marked area in figure 5.7. Note that in the X-STM images of figure 5.6a–b, only a few individual indium atoms are visible above the QD and that no exponential decay can be distinguished. Because the area above the QDs measured by X-STM is very limited a meaningful statistical analysis is not practicable. Consequently, the presence of indium in this region is often neglected/neglected. However, the APT data reveals that these indium atoms actually form a significant part of the indium profile and should thus be included in the model. Note that, the best estimate based on directly counting the number of indium atoms in the X-STM data evaluates to an indium concentration of $\approx 5–10\%$, which is in nice agreement with the APT data. The second region crucial for modeling the QDs is the gradual transition from the QD to the WL. The X-STM and APT images of figure 5.6a–c show that the indium concentration at the sides of the QD is more substantial for the WL profiled in the previous section. It was chosen to model this feature as a region of $x = 15\%$ indium fraction extending well beyond the QD and eventually merging with the WL (not shown in figure 5.6d).

In figure 5.8, the outward relaxation profile of the cleaved surface (as measured by X-STM) across the center of the QD and 7 nm off-center are plotted together with the result of the FE calculations. A close match between the measured and the calculated profile is observed. It should be noted that different input models, e.g. the models with a linear indium profile mentioned above, can yield a similar match. However, such models would not resemble the APT data. From this it is concluded that great care is required when constructing QD models based on X-STM measurements only. Recently, it has been shown$^{43}$ that PL measurements in combination with extensive theoretical modeling and X-STM measurements had to be combined to yield a realistic QD model. However, subtleties as the decaying indium concentration above the QD
and the extension of the QD into the WL might be overlooked in such an approach, and thus some ambiguity remains. In this respect, the abilities of APT in providing a fully three-dimensional indium compositional profile are at the moment unique, and an essential tool to construct an valid three-dimensional QD model.

5.4 Summary

X-STM and APT are used to characterize InAs/GaAs QD layers from a unique sample. A good agreement between the segregation profiles of the WL obtained by both techniques is found. To obtain at this result it was necessary to deconvolve the APT data with an instrument profile. The height and length of the QDs determined by both techniques are also comparable, both in the case where cross-sections are taken through the center of the QD and where they are taken off-center. This highlights the versatility of APT whereby the three-dimensional data can be processed in a number of ways to show a variety of details. Exploiting this advantage, the indium profile as measured by APT is used to make a three-dimensional model of a typical dot. This model is in agreement with the outward relaxation measured by X-STM, and is therefore considered to be a unique solution. This analysis method emphasizes structural features of the QDs that were not detected or neglected in previous measurements. The juxtaposition of the two techniques shows the benefits and the unique capabilities of each one; where X-STM provides unmatched atomic resolution, APT provides a fully three-dimensional composition profile. Thanks to their very different natures, using the combination of X-STM and APT on semiconductor nanostructures allows an analysis with a level of detail which was not available before.
Figure 5.9: Details of the QD model used as input for the FE calculations. The dimensions of the box that encloses the QD in the FE calculations are $100 \times 100 \times 100 \text{nm}^3$. The dimensions in the figure are given in nm. Regions with different indium concentrations profiles are marked in the figure and described in table 5.1. The contour plot of this model is shown in figure 5.6d.

Table 5.1: Analytic expressions for the indium fraction in the areas as indicated in figure 5.9. The coordinate system is Cartesian.

<table>
<thead>
<tr>
<th>Area</th>
<th>Expression</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$0.21 \exp((x + 1.47)/0.43)$</td>
<td>transitional region</td>
</tr>
<tr>
<td>2</td>
<td>$((0.0003(x^2 + y^2)^2 - 0.0088(x^2 + y^2)^{\frac{3}{2}} + 0.0269 \left(x^2 + y^2\right) - 0.0645(x^2 + y^2)^{\frac{3}{2}} + 1)(-0.1023 z^2 + 0.1243 z + 0.4016) + 0.21$</td>
<td>lower part QD</td>
</tr>
<tr>
<td>3</td>
<td>$0.22 - 0.14((x^2 + y^2)^{\frac{1}{2}} - 8.8)$</td>
<td>transitional region</td>
</tr>
<tr>
<td>4</td>
<td>0.151</td>
<td>transition WL-QD</td>
</tr>
<tr>
<td>5</td>
<td>$((0.0003(x^2 + y^2)^2 - 0.0088(x^2 + y^2)^{\frac{3}{2}} + 0.0269 \left(x^2 + y^2\right) - 0.0645(x^2 + y^2)^{\frac{3}{2}} + 1)(-0.1638 z^2 - 0.0317 z + 0.4032) + 0.21$</td>
<td>upper part QD</td>
</tr>
<tr>
<td>6</td>
<td>$0.20 \exp((-z + 1.53)/1.08)$</td>
<td>indium rich region</td>
</tr>
<tr>
<td>7</td>
<td>$(0.20 - 0.10((x^2 + y^2)^{\frac{1}{2}} - 8.8) \exp((-z + 1.53)/1.08)$</td>
<td>transitional region</td>
</tr>
<tr>
<td>8</td>
<td>$0.15 \exp((-z + 1.53)/1.08)$</td>
<td>transitional region</td>
</tr>
<tr>
<td>9</td>
<td>$0.19 \exp((-z - 1.47)/2)$</td>
<td>wetting layer</td>
</tr>
</tbody>
</table>
Height control of quantum dots studied by cross-sectional STM and kinetic Monte-Carlo simulations

In this chapter, two techniques to obtain control over the height of self-assembled quantum dots (QDs) are investigated. After a short motivation, the second section introduces the so-called indium flush. The details of this growth technique are investigated by means of cross-sectional scanning tunneling microscopy (X-STM). In the last section, the relatively new technique of strain engineering of the capping layer is investigated. The ability to control the height of QDs with this technique is studied by X-STM and kinetic Monte-Carlo simulations.

6.1 Motivation

In the last decade the fabrication of self-assembled QDs has been intensively studied. The interest has been, and still is, stimulated by applications of self-assembled QDs in optoelectronic devices. Nowadays, QDs are for instance applied or suggested in QD lasers, single electron transistors, and spin manipulation. From these, and other studies such as those reported in, it is well known that the optical and electronic properties of self-assembled QDs are strongly affected by their size, shape, and material composition. More specifically, height control of QDs allows the accurate tuning of their emission wavelength and $g$-factor. Nowadays, several methods are available to control the height of QDs, among which the use of surfactants, double-capping, the application of an indium flush, and strain engineering of the capping layer. In the following sections the latter two will be investigated.

Section (6.2) of this chapter has been published in *Nanotechnology* 21(21):215705 (2010).
6.2 Indium flush

A method to obtain control over the height of In(Ga)As self-assembled QDs and the wetting layer is the so-called indium flush. This technique is based on a discontinuous capping process. First, a GaAs capping layer with a thickness smaller than the height of the uncapped QDs is deposited. Next, the temperature is raised to desorb the indium that is not covered by the capping layer, thereby lowering the height of the QDs. Although, it is already known that the growth of the second capping layer at elevated temperatures can reduce the height of InGaAs QDs\(^{132}\), raising the temperature during the growth interrupt and subsequently overgrowing at nominal temperature is expected to result in better defined wetting layers and QDs. In this section the size, the shape, the composition, and the photoluminescence (PL) spectra of self-assembled QDs subjected to an indium flush are studied at the atomic-scale by X-STM.

6.2.1 Experimental details

All X-STM measurements were performed with the room temperature STM described in section (2.1.5). The STM was operated in constant current mode on \textit{in situ} cleaved \{110\}-surfaces. Standard electrochemically etched tungsten tips were used. The X-STM measurements were done at high negative bias voltages (\(V \approx -3\) V) and with a tunnel current of \(\approx 40\) nA. At these tunnel conditions the electronic contrast is suppressed, resulting in almost pure topographic imaging of the surface. With the color scale used, InAs (GaAs) appears bright (dark) in the presented X-STM images.

The QD layers were grown by molecular beam epitaxy on a rotated \(n\)-doped GaAs wafer. After the deposition of a 300 nm \(n\)-doped GaAs buffer layer at 590 °C, a superlattice consisting of 25 periods of 2.5 nm AlAs/2.5 nm GaAs was grown to ensure the trapping of defects present in the substrate. Next, the superlattice was covered with 300 nm of \(n\)-doped GaAs and 420 nm of undoped GaAs. A growth interruption of approximately 2 min allowed then the temperature to be lowered back to 590 °C, the nominal growth temperature of the QD layers. Following this, three sequences, each consisting of four QD layers formed by the deposition of 1.98 nm (7 ML) \(\text{In}_{0.5}\text{Ga}_{0.5}\text{As}\), were grown at a rate of 0.05 ML/s. During the whole growth process the As flux was kept constant at a pressure of \(1.26 \times 10^{-5}\) mbar. Within a sequence, three out of the four QD layers were grown with the indium flush technique. This means that these QD layers were first partially capped with a GaAs layer of which the thickness was varied, followed by a rise in temperature to 650 °C. After 30 sec, the temperature was then lowered again to the nominal growth temperature after which the second capping layer was grown. In total, the annealing step takes place over a time window of \(\approx 180\) s. In all sequences, the fourth layer is a conventionally grown QD layer, i.e. without a growth interrupt and indium flush, and serves as a reference layer. The total structure was capped with 200 nm of GaAs.

6.2.2 Wetting layers

The investigation of the indium flush technique as a way to control the QD height is started by an analysis of the wetting layer morphology. Four typical topographic X-STM images of wetting layers grown with a varying thickness of the first capping
layer are depicted in figure 6.1. Even without any statistical analysis it is evident that the height of the wetting layer can be controlled by varying the height of the first capping layer. Furthermore, the segregation of indium atoms along the growth direction appears to terminate abruptly in the case that an indium flush was applied, see figure 6.1a–c. This is a clear indication that most of the surface resident indium is removed during the flush step, preventing any further segregation. To make the analysis more quantitative, the number and the position relative to the start of the wetting layer was counted and marked for $\approx 3000$ indium atoms. A $\approx 400 \text{ nm}$ stretch of each type of wetting layer was analyzed in this manner. In figure 6.2, the result of this statistical analysis is shown. The conventionally grown wetting layer is found to exhibit the expected exponential decay of the indium concentration along the growth direction and the expected segregation length ($\approx 25 \text{ nm}$)\(^{133}\). In contrast, the wetting layers submitted to an indium flush show a stronger decay and shorter segregation lengths. This implies that buried indium segregates out of the wetting layers and leaves the surface during the indium flush step. This additional loss of already buried indium is found to dependent on the thickness of the first capping layer and is the strongest when the first capping layer is the thinnest. The thickness of the wetting layer, i.e. the final InGaAs layer in between the QDs, is found to be 6, 8, 10, 12 bilayers for 2, 3, 4, 6 nm thick first capping layers, respectively. Note, that the statistical analysis presented in figure 6.2 reveals that the wetting layer in the reference layer extends somewhat further than is expected.
Height control of quantum dots studied by X-STM and kinetic Monte-Carlo simulations

from figure 6.1. This is due to local fluctuations in the wetting layer over the ≈ 400 nm stretch of QD layer that was used in the analysis.

It is reported that the critical wetting layer thickness for $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$ QD formation is $\approx 5 \text{ML} \ (1.4 \text{ nm})^{134}$. It is assumed that in the present case all the indium that is deposited after reaching this critical thickness goes into the formation of QDs. When the thickness of the critical layer ($d_{\text{crit}}$) is added to the thickness of the first capping layer ($d_{\text{cap}}$) and the resulting sum is compared with the thickness of the final InGaAs layer in between the QDs that was found experimentally, good agreement is found. This is quantitatively depicted by the dashed blue line, dotted red line, and open red boxes in figure 6.5, that corresponding to $d_{\text{cap}}$, $d_{\text{crit}} + d_{\text{cap}}$, and the experimentally determined average thickness, respectively. This result shows that the indium segregation beyond the position of the indium flush is completely suppressed.

In order to check whether the indium flush method can indeed be used to gain control over the emission spectrum of the wetting layer, a PL experiment was performed specially grown samples. Due to the wafers orientation in relation to the indium and gallium cells during growth, a strong gradient in QD density is present in these samples. This results in inhomogeneity in the PL across the wafer, with either the PL of the QDs or the wetting layer being strongest. The wetting layer PL of three indium flushed samples where the thicknesses of the first capping layer were 2.5, 5.0, and 7.5 nm, respectively, was compared to a reference sample. The PL-spectra, see figure 6.3, clearly show that the wavelength of the emission peak can indeed be tuned, a reduction of the thickness of the first capping layer, corresponding with a reduced
6.2.3 Quantum dots

In order to determine the influence of the indium flush on the structural properties of the QDs, the width and the height of 48 QDs were measured. The width of the observed QDs ranged up to 100 nm, which makes these QDs relatively big. The height of the QDs in the reference layer was found to vary between 7–10 nm. Since, the lateral width of all observed QDs is $> 60$ nm, it is safe to assume that almost none of the QDs are cleaved at their edge and that the observed height variation represents the spread in the height distribution due to a non-uniform growth process. The QD layers were found to be weakly coupled, as one would expect with a 30 nm thick GaAs spacer layer and moderately strained InGaAs QDs$^{136}$. As illustrated in figure 6.4, this results in occasional stacking of the QDs. In this particular sequence the thickness of the first capping layer was varied in the first three QD layers from 2, 3 to 6 nm, respectively. The upper most layer is a reference layer. A quick glance at figure 6.4 reveals that the application of an indium flush reduces the height of the QDs and results in flat top facets. This is in contrast to the QDs in the reference layer that are higher and more lens-like shaped as previously observed for typical InGaAs QDs$^{137}$. The height of all observed QDs as a function of the first capping layer thickness is plotted in figure 6.5. A linear relation is found up to a thickness of $\approx 7$ nm, as indicated by the solid black line. Since, increasing the first capping layer above 7 nm would make the growth procedure
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Figure 6.4: $160 \times 120 \text{nm}^2$ topographic X-STM image of a reference QD and three indium flushed QDs. In the latter case, the thickness of the first capping layer was varied.

Figure 6.5: The QD height (black points) as a function of the thickness of the first capping layer. The black solid line is a linear fit. The red dotted line represents the sum of the first capping layer thickness (blue dashed line) and the critical layer thickness for QD formation ($5 \text{ML}$). The experimentally determined thickness of the final InGaAs layer in between the QDs is given by the red open boxes.
resemble non-interrupted conventional growth, it is expected that the QD height will saturate at this value. This is indicated in figure 6.5 by the horizontal solid black line representing the average height of the QDs in the reference layer. Note that, all the QDs are found to be slightly higher than the experimentally found thickness of the final InGaAs layer in between the QDs (red open boxes). From this, it can be concluded that the surface was not completely flattened during the application of the indium flush and that the QDs stick out a little afterwards. Still, the results presented here show that an indium flush can be used to gain control over the height of In(Ga)As QDs.

In general, the geometry of QDs can be relatively easily extracted from X-STM data. This is not so for the composition profile, which requires tedious FE simulations of the surface relaxation induced by the cleaved QD, see also section (5.3.2). However, extracting the composition profile is worth while. Recently, very strong electrical\textsuperscript{138} and magnetic\textsuperscript{139} tunability of the exciton \( g \)-factor in InGaAs self-assembled QDs grown under similar growth conditions as the current QDs was reported. The origin of the strong electric and magnetic dependence could be identified by performing eight band \( k \cdot p \) simulations that used realistic parameters for the size and composition of the QDs. More specifically, the indium composition profiles that were used are based on the X-STM measurements and the FE calculations presented below.

The various stages involved in the process of extracting the composition profile from the X-STM data are shown in figure 6.6. From the current map, in which the shape of the QDs is not obscured by the surface relaxation (see figure 6.6a), the geometry of the QDs can be readily extracted. Next, a suitable indium composition profile that will serve as the starting point for the FE calculations has to be chosen. From previous studies it is known that a linearly increasing (from bottom to top) or a trumpet-like indium composition profile is typical for InGaAs QDs\textsuperscript{66,130}. Such indium composition profiles are the result of gallium incorporation into the QDs during the initial stage of QD formation, i.e. during wetting layer formation and QD formation. The gallium incorporation reduces the lattice mismatch between the buffer layer and the QDs and thereby lowers the amount of strain present in the system. Upon further QD formation, part of the incorporated gallium atoms will segregate towards the top of the now growing QDs. Since only the indium and the arsenide atoms are being replenished during the growth of the QDs, free gallium atoms are rapidly depleted from the surface. As a result, ever less gallium atoms will be available for incorporation into the QDs, leading to an indium gradient within the QD. For the current case, both a trumpet-like and a linearly increasing indium composition profile were tried in modeling the QDs. Before this can be done, the wetting layers have to be included in the FE model. To account for the indium flush, the wetting layers were terminated at the position of the indium flush. With the model now complete, the next step is running the FE calculations and tuning the parameters of the indium composition profiles until the calculated surface relaxation, see figure 6.6e–f, matches with the actual surface relaxation as measured by X-STM, see figure 6.6d. Both the linearly increasing, \( c_{\text{linear}} = 0.22 + (c_{\text{max}} - 0.22)/h \), and the trumpet-like, \( c_{\text{trumpet}} = 0.22 + (0.22 - c_{\text{max}}) \exp((\sqrt{x^2 + y^2}/0.3) \exp(-z/1.5)) \), indium composition profiles were found to give to good match. The two composition profiles are depicted schematically in figure 6.6b–c. Note that, in both cases the maximum indium concentration, \( c_{\text{max}} \), of the QD in the reference layer is higher than that of the QD in the indium flushed layer (0.35 vs. 0.30). This is agreement with the results presented in the previous section, where the indium flush was found to desorb buried indium from the
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Figure 6.6: a) Current image of two QDs. The top QD belongs to the reference layer while the bottom QD belongs to an indium flushed layer. b-c) Geometrical and composition model used as input for the FE calculations. A linear and a trumpet-like indium composition profiles were assumed. The wetting layer in the reference layer (WL1) was not terminated, while in the indium flushed layer (WL2) it is terminated at the position of the indium flush. d) Topographic X-STM map, and e–f) calculated surface relaxation for the two indium composition profiles.
wetting layers. Here it should be noted that the FE calculates can yield approximately similar concentration profiles that match to the surface relaxation and that the method itself does not provide an answer to which exact composition profile is right. For this, additional methods are needed. In this case, the calculated Zeeman spin-splitting of excitons in the QDs proofed to match nicely with PL measurements for the trumpet-like profile but not for the linear profile.

In order to check whether the indium flush method can be used to gain control over the emission spectrum of the QDs, the same PL experiment as for the wetting layers was performed. In figure 6.7, the macro PL-spectra that were recorded on part of the wafers where the QD PL is favored over that of the wetting layer is shown. As the thickness of the first capping layer is increased, the PL peak is red shifted, as expected for increasing QD height.

6.3 Strain engineering of capping layers

As shown in the previous sections, the technique of indium flush can be used to control the height of QDs. Strain engineering of the capping layer is another, relatively new, method to achieving this is. In this technique, the height of the QDs is controlled by tuning the composition of ternary or quaternary capping layers. By adjusting the ratio in which the different atomic species are present, the degree of lattice (mis)match between the capping layer and the QDs can be tuned. Effectively, this means that the amount of strain can be controlled. As strain is the driving force behind QD decomposition during overgrowth, strain engineering provides a means with which the height of QDs can be controlled.
Nowadays, a large variety of imaging techniques are available to study the morphology of self-assembled QDs in detail, e.g. scanning / transmission electron microscopy\(^{140}\), X-ray diffraction\(^{141}\), atomic force microscopy\(^{142,143}\), atom probe tomography\(^{15,144}\), and cross-sectional scanning tunneling microscopy\(^{1}\). However, all the existing imaging techniques can only provide snapshots of the QDs after the growth is completed. At the moment, only reflection high energy electron diffraction (RHEED) can give realtime information during the growth. But if RHEED provides valuable information about the growth surface, this averaging technique is of little use to study atomic-scale processes such as intermixing or segregation. In this respect, kinetic Monte-Carlo (KMC) simulations of the heteroepitaxial growth process might be of great value and provide further insight in the growth dynamics. However, realistic three-dimensional KMC simulations are computationally challenging\(^{145,146}\) and still need experimental validation.

In this section, KMC results are present using recent developments in computational methods\(^{147}\) that allow simulation on time and length scales never obtained before. The KMC simulations are for the first time compared to an atomically precise QD morphology as obtained by X-STM. The two techniques are used in conjunction to study strain engineering of the capping layer\(^{148,149}\) as a method to control the height of QDs, which is as mentioned before an important parameter which determines the emission wavelength. It is shown that the KMC simulations not only are in good agreement with the X-STM study but also provide valuable details of the growth process that hitherto could not be obtained.

### 6.3.1 Experimental details

All the X-STM measurements presented in this section were performed at 77 K with the low temperature STM described in section (2.1.5). Low temperature ensures long-term stable tunnel conditions and facilitates imaging long stretches of sample without drift. The STM was operated in constant current mode on \textit{in situ} cleaved \{110\}–surfaces. The X-STM measurements were all done at high negative bias voltages and low tunnel currents \(V \approx -3 \, \text{V}, \, I \approx 20 \, \text{pA}\). At these tunnel conditions and with the color scale used, InAs (GaAs)-rich regions appear bright (dark) in the topographic X-STM images.

The material system consists of four InAs / GaAs QD layers grown by molecular beam epitaxy on a \textit{n}-doped GaAs \{001\}-oriented substrate. The growth process is initiated by the deposition of a 350 nm GaAs buffer layer at a temperature of 580°C. The growth sequence of the first QD layer starts by the deposition of 2.7 ML of InAs at 450°C and a growth rate of 0.04 ML s\(^{-1}\). Next, the QD layer is overgrown with a 5 nm thick In\(_x\)Ga\(_{1-x}\)As layer with \(x = 0.00, \, x = 0.05, \, x = 0.10, \, x = 0.15\) for the four consecutive QD layers, respectively. This was done at 450°C and at a growth rate of 0.75 ML s\(^{-1}\). The indium content, \(x\), was calibrated by comparing the reflection high energy electron diffraction (RHEED) oscillations of GaAs and InGaAs / GaAs quantum wells grown under the same conditions as the capping layers of the studied samples. Since the growth rate can be measured in this way with great accuracy, the uncertainty in the nominal indium contents should be very small. The QD layers will be numbered in the sequence as they were grown. On top of the capped QD layer a 50 nm GaAs spacer layer is grown after which the growth sequence for the next QD layer begins. The total structure was capped with 200 nm of GaAs. Finally, an uncapped QD layer was grown on top.
6.3.2 Kinetic Monte-Carlo model

Kinetic Monte-Carlo (KMC) simulations by Peter Smereka (Ann Arbor) model were used to explore the growth of the QD layers. The KMC model is in essence the same as the solid-on-solid (no overhanging atoms) model presented by Orr et al.\textsuperscript{150} and Lam et al.\textsuperscript{145}. These, and the current model, are based on a solid-on-solid bond counting formulation where the elastic effects are incorporated using a ball and spring system. For reasons of simplicity the model will be explained for the two-dimensional case, but can readily be extended to the three-dimensional case. The model assumes a simple cubic crystal, see figure 6.8, in which the atoms are bonded with its nearest (maximal four) and next to nearest neighbors (maximal four). The arrangement of atoms in the crystal is constantly changing through the motion of surface atoms. The parameter governing the motion of the \(i\)th surface atom is the hopping rate \(R_i\), which follows an Arrhenius law:

\[
R_i = R_0 \exp \left( \frac{\Delta E + E_0}{k_b T} \right),
\]

with \(\Delta E\) the change in total energy when moving or adding the atom, \(k_b\) the Boltzmann constant, \(T\) the absolute temperature, and \(E_0\) and \(R_0\) constants that are chosen such that the adatom diffusion rate matches experimental values. The change in energy can be split into two terms:

\[
\Delta E = \Delta E_{\text{chem}} + \Delta W,
\]

where \(\Delta E_{\text{chem}}\) the change in chemical energy and \(\Delta W\) the change in elastic energy. The change in chemical energy arise from local contributions, i.e. bond configurations and bond strengths, and can under the assumption that the bond strengths are the same for nearest and next to nearest neighbors be written as:

\[
\Delta E_{\text{chem}} = - \sum_{j=1}^{N} \gamma_{ijr}
\]
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Figure 6.9: $85 \times 18 \text{nm}^2$ mean filtered X-STM current map of the four consecutive QD layers. Individual indium atoms can be distinguished. The indium fraction, $x$, of the capping layer is increased in the consecutive layers. a) Wetting layer + GaAs capping, b–d) wetting layer + InGaAs capping. Strong variations in the final InGaAs layer are observed in d).

with $N$ the total number of nearest and next to nearest neighbors, and $\gamma_{ij}$ the bond strength between the $i$th atom and the $j$th neighboring atom, see figure 6.8. The elastic interactions are modeled by means of a ball and spring system. This means that each lattice atom is connected to its nearest neighbors by Hookean springs, see figure 6.8, and that the elastic energy is the sum of the energy stored in each spring when the lattice is in mechanical equilibrium. The details of the computational methods to calculated $\Delta E$ and $\Delta W$ are beyond the scope of the current work but can be found elsewhere.\(^{151}\)

6.3.3 Results

The X-STM analysis of the QD layers is started by an investigation of the morphology of the InGaAs layer in between the QDs. In figure 6.9, X-STM current maps of representative stretches of the InGaAs layer as found in all four QD layers are shown. The indium fraction in the $\text{In}_{x} \text{Ga}_{1-x} \text{As}$ capping layer was nominally increased from $x = 0.00$ to $x = 0.15$ in the consecutive QD layers. First, the QD layer where the capping layer consists of a pure GaAs layer is considered. During the initial stage of capping, strain induced by the lattice mismatch between InAs and GaAs drives mass-transport of QD
material (in this case indium) to regions in between the QDs\cite{33,42}. Upon further capping, this indium and the indium that was already present in the wetting layer segregate towards the growth front, resulting in an exponential decaying indium composition profile along the growth direction\cite{133}. A quick glance at the X-STM image of figure 6.9a, shows that this indeed seems to be the case for the first QD layer. The other three QD layers were overgrown with an In$_x$Ga$_{1-x}$As layer ($x > 0$). In these layers, the indium composition profile should therefore resemble a top–hat with an additional exponential decaying indium composition profile due to segregation of the wetting layer. For capping layers with an indium fraction of $x = 0.05$ and $x = 0.10$, the final InGaAs layer in between the QDs is nicely defined, see figure 6.9b–c. However, looking at figure 6.9d, this is evidently different for the fourth capping layer which has the highest indium fraction ($x = 0.15$) of all layers. In contrast to the quasi quantum wells found in the second and third layers that have an uniform thickness of 6.3 nm, here, the thickness is found to vary in the range 4.0–7.5 nm. The first three layers will be analyzed first.

To make the analysis more quantitative, the indium composition profile of each InGaAs layers in between the QDs was deduced from the surface relaxation. This outward relaxation is the result of strain induced by the lattice-mismatch between InAs and GaAs and is simulated by means of FE calculations. For the first layer, the function $a \exp(-z/b)$, representing the segregation of indium from the wetting layer\cite{133}, was used as an input for the FE modeling. In this equation, $z = 0$ nm corresponds with the start of the wetting layer and positive $z$-values represent the growth direction. By adjusting the initial indium fraction, $a$, and the inverse decay constant, $b$, until the calculated outward
relaxation matches the outward relaxation as measured by X-STM, see figure 6.10, the indium composition profile of the wetting layer can be determined. The values that were found to yield the best match are \( a = 0.236 \pm 0.002 \) and \( b = 1.48 \pm 0.02 \) nm. Next, the analysis is extended to the second and third layers. In these layers multiple indium sources contribute to the total amount of indium present in the final InGaAs layer in between the QDs. First, a wetting layer is present prior to capping. Secondly, mass-transport of indium from the QDs to the InGaAs layer occurs during the initial stages of capping. Thirdly, additional indium is deposited during capping (growth flux). To account for this, an exponential decaying indium composition profile, similar to the one found for the case of capping with pure GaAs, was added to a top-hat indium composition profile. The function describing the indium fraction is now given by \( a \exp(-z/b) + x \). The values of \( x \) are taken from the nominal indium contents (\( x = 0.05 \), \( x = 0.10 \)). Since the parameter \( b \) is determined by the temperature and the chemical properties of the individual indium atoms, it is assumed to be the same as in the case of capping with pure GaAs. This only leaves \( a \) for fitting, which is a measure for the amount of indium transferred from the QD to the InGaAs capping layer and the indium already present in the wetting layer. A match between the calculated and the experimentally observed outward relaxation was found for \( a = 0.165 \pm 0.002 \); \( a = 0.105 \pm 0.002 \) nm for the second and third capping layer, respectively. The fact that the value of \( a \) decreases with increasing \( x \), can be explained by better lattice matching between the capping layer and the QD with an increasing indium fraction in the capping layer. As a result the QD will be less strained. Since, strain is the major driving force for mass-transport of indium from the QD to the wetting layer during capping, a reduced strain mismatch will result in a lower indium content in the final InGaAs layer in between the QDs.

The comparison between the outward relaxation profiles from X-STM measurements and the results of the FE calculations are shown in figure 6.10.

The analysis is now extended to the QDs themselves. From AFM measurements the height of the uncapped QDs was determined to be 5.6 nm with a standard deviation of \( \sigma = 0.7 \) nm, see figure 6.11. A total of 113 QDs in approximately 10 \( \mu \)m of QD layer were imaged by X-STM. Just as in the case of the InGaAs layers, the first three QD layers will be treated first, leaving the fourth layer for later. In figure 6.12, topographic X-STM maps of a typical QD as found in the first three QD layers are shown. The
Figure 6.12: 50 × 17 nm² topographic X-STM maps of typical QDs as found in the first three QD layers and the height distribution of the QDs. The indium fraction in the capping layer, $x$, was increased in the consecutive QD layers.

The average height of the QDs as determined by X-STM was found to be 3.9 nm, 4.6 nm, and 5.1 nm ($\sigma = 0.4$ nm) for capping layers with an indium fraction of $x = 0.00$, $x = 0.05$, and $x = 0.10$, respectively. Within the standard deviations, this is a linearly increasing trend. As previously discussed, this result can be explained by the strain reduction with increasing indium fraction in the capping layer. As the strain mismatch is reduced in the consecutive QD layers, the driving force for mass-transport from QD material into the capping layer is also reduced. It was already discussed that the observed composition profile of the InGaAs layers in between the QDs could be explained by this mechanism. Given the height of the uncapped QDs as determined from the AFM measurements, decomposition of the QDs is almost completely suppressed for a capping layer with an indium fraction of $x = 0.10$. Surprisingly, the linear trend of increasing QD height as function of indium fraction in the capping layer is found to break down in the current material system when the indium fraction reaches $x = 0.15$, i.e. in the fourth QD layer. In this layer, the QD height is found to be 3.7 nm, which is even smaller than the QD height in the first layer.

The decrease of the QD height and the variation in the thickness of the InGaAs layer in between the QDs, see figure 6.9d, are an indication that an additional mechanism is involved during the overgrowth of the fourth QD layer. This can indeed be seen in
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Figure 6.13: 880×30 nm² topographic X-STM map of the fourth layer QD layer. The QDs are capped with an In₉.₁₅Ga₀.₈₅As layer. The colored semi-transparent regions at the side mark the overlay of consecutive images. Examples of the four observed peculiarities are marked: 1) Varying thickness of the InGaAs layer in between the QDs, 2) indium depleted regions, 3) reduced QD height, and 4) asymmetrically shaped QDs.

Figure 6.13, which shows a 880 nm long uninterrupted stretch of the fourth QD layer. A couple of striking features are visible. First, as mentioned above, the thickness of the InGaAs layer varies. Long, relatively thick and uniform, stretches are interrupted with variations in thickness and homogeneity close to the QDs. Second, indium depleted regions are observed directly next to the QDs. Third, some of the QDs are asymmetrically shaped. Fourth, the QDs have a smaller height than in the first three QD layers. Since the observed peculiarities might result from several processes in various stages of overgrowth, it is difficult to explain them solely from the X-STM measurements.

KMC simulations are used to further analyze the growth processes. Here, it needs to be stressed that the purpose of the KMC simulations is to indicate trends in the growth processes only. In figure 6.14, a bird’s eye view of the uncapped QDs grown in the KMC simulation is shown. These uncapped QDs are subsequently overgrown with a 10 ML thick InₓGa₁₋ₓAs layer of which the indium fraction, x, was consecutively increased. The results are summarized in figure 6.15, which shows two-dimensional cross-sections (analog to the exposed 110-cleavage plane in X-STM) through the fully three-dimensional KMC data sets. Each rectangle in the figure represents an “atom” and has the height and width of one lattice constant. The cross-sections through the uncapped QDs, see figure 6.15a, show that the QDs have a height of 10 rectangles (≈ 6.0 nm) and are connected by a sub-monolayer of indium. Upon capping of the QDs with a 10 ML pure GaAs layer, see figure 6.15b, indium is transported away from
the QDs and forms a wetting layer with a decaying indium concentration along the growth direction. As a result of this mass-transport, the height of the QDs in this layer is reduced to $\approx 3.6\text{ nm}$. Note that, the QD morphology agrees nicely with the experimentally observed QDs in the first layer. Since the growth front is flat and the QDs are already fully capped, subsequent growth of the GaAs spacer layer has no consequences on the QD morphology. If the indium fraction in the capping layer is set to $x = 0.05$ and $x = 0.10$, see figure 6.15c–d, the KMC simulations show an increase, compared to a pure GaAs capping, of the QD height to $\approx 4.2\text{ nm}$ and $\approx 4.8\text{ nm}$, respectively. Here, the reduction in strain between the QDs and the capping layer due to better lattice matching reduces the mass-transport of indium originally located in the QDs. This trend of increasing QD height with increasing indium fraction in the capping layer is in good agreement with the X-STM measurements and previous results, and again illustrates that strain engineering is an effective way to control the QD height.

If the indium fraction in the capping layer is further increased to $x = 0.15$ and $x = 0.20$, the system enters another regime, see figure 6.15e–f. The height of the QDs is now increased to $\approx 5.4\text{ nm}$ and $\approx 6.0\text{ nm}$, respectively, the latter corresponding to the height of the uncapped QDs. In these two QD layers, the atomic layers in the top of the QDs are not as pure in indium as the bottom part of the QDs. The border between the two regions (marked with a red horizontal line in figure 6.15e–f for an exemplary QD) is well defined, indicating that two independent processes that sequentially play out are involved. The first process is the already discussed mass-transport of indium originally present in the QDs during the initial stage of capping. The second process, occurring during a later stage of capping, is the QD strain driven phase separation of InGaAs into indium rich and gallium rich regions. The indium rich regions preferentially form on top of the QDs where they minimize the total strain of the system. This process has been observed in InAs/GaAs QDs that were capped with an InGaAs layer, and was
Figure 6.15: 140 × 20 nm² cross-sections through the KMC data set (continued on the next page). a) Uncapped QDs. b–f) The indium fraction, \( x \), is increased in the consecutive images which show the situation after growth of the InGaAs capping layer (top panes), and after growth of the pure GaAs spacer layer (bottom panes). e–f) The horizontal red line marks the boundary between the pure InAs region and the region of phase separation. Examples of the three observed peculiarities are marked: 1) variation in the thickness of the InGaAs layer between the QDs (solid red line), 2) indium depleted regions, and 3) asymmetrically shaped QDs.
used to achieve columnar InGaAs/GaAs QDs. The KMC simulations show that the phase separation gets stronger with increasing indium fraction in the capping layer, see for example figure 6.15d–f. Both the X-STM measurements and the KMC simulations reveal that the involved indium atoms come from areas directly around the QDs. As a consequence, these regions are being depleted with indium when the phase separation on top of the QDs kicks in.

Three out of the four peculiarities observed by X-STM in the fourth layer are also present in the KMC simulations where the indium fraction in the capping layer is the highest: 1) large variations in the thickness of the InGaAs layer in between the QDs, 2) indium poor/free regions immediately next to the QDs, and 3) asymmetrically shaped QDs. Exemplary cases of these peculiarities are marked in figure 6.15e–f. In contrast to X-STM, the KMC simulations allow the investigation of the intermediate stages of the growth process. The results show that during the growth of the capping layers the surface becomes unstable, leading to a considerable roughening. The onset of such surface instability and roughening of the surface is well documented for InGaAs quantum wells as a function of the indium concentration and layer thickness. The critical thickness for quantum wells with $x = 0.15$ is $\approx 20$ nm. This is well beyond the 5 nm thick capping layer where the instabilities are observed in the current case. It can be argued that the presence of the InAs QDs locally introduces additional strain in the system which lowers the critical thickness considerably. Furthermore, the fourth QD layer in the sample is subjected to the strain field of the first three QD layers which might further lower the critical thickness, although this contribution is of lesser importance. The observed surface instabilities are manifested most prominently near the QDs, a strong indication that indeed the additional strain introduced by the QDs is responsible. At these sites the thickness of the capping layer is significantly reduced and as a result some of the QDs are not fully capped. The exposed top of these QDs partially erodes upon further capping, giving rise to the asymmetrically shaped QDs. Although, this process leads to a higher degree of QD erosion, it can not reproduce the strong reduction in QD height observed in the X-STM measurements. The phase separation on top of the QDs and the roughening of the surface, both processes that are driven by QD strain, are together responsible for the variation in the thickness of the InGaAs in-between the QDs.

The mentioned surface instability that appears at high In contents is a main factor determining the growth process, and can give rise to peculiar QD structures like those shown in figure 6.16. In this figure a cross-section from the KMC simulations is compared with the X-STM results. Although the matching QD positions are completely coincidental, the agreement between the morphology of the QD layer in the KMC simulation and the actual QD layer is striking. This, and the results presented above, demonstrates the potential of KMC simulation as an excellent tool to investigate the heteroepitaxial growth of nanostructures.

6.4 Summary

It was shown that the height of the wetting layers and self-assembled InGaAs/GaAs QDs can be controlled by the application of an indium flush. The results show that indium not only desorbs from the surface but also segregates out of the wetting layers
and the QDs and leaves the surface during the indium flush. The observed structural properties of the final InGaAs layer in between the QDs correlates very well with their optical properties. The height of the wetting layers and the QDs could be tuned by varying the thickness of the first capping layer. A linear relation between the QD height and the thickness of the first capping layer was found.

The combination of X-STM and KMC simulations was used to investigated the capping of InAs/GaAs QDs with a strained InGaAs layer. FE simulations of the surface relaxation shows that mass-transport from the QD to the capping layer is reduced with increasing indium content in the capping layer and leads to an increase of the QD height. This is reproduced in the KMC simulations. The KMC simulations showed that a 5 nm thick capping layer becomes unstable above a critical indium fraction, resulting in peculiar features in the QD layer: variations in the thickness of the InGaAs layer in between the QDs, indium depleted regions immediately next to the QDs, and asymmetrically shaped QDs. The KMC simulations further show that these features can be explained in terms of mass-transport from the QD to the capping layer, phase separation on top of the QD, and roughening of the surface. The only feature observed by X-STM that could not be reproduced in the KMC simulation is the reduction of the QD height in case of the highest indium content capping layer. To summarize, it was shown that strain engineering of the capping layer can be used to control the QD height. Furthermore, it was shown that KMC simulations are a very valuable asset in understanding the dynamics of QD growth and might in the future be able to predict the outcome of the growth process.
In this chapter, the details and possibilities of droplet epitaxy as an alternative technique to grow self-assembled nanostructures are investigated. In the first section, a brief introduction to droplet epitaxy is given. In the second section, a meticulous cross-section scanning tunneling microscopy (X-STM) study of self-assembled nanostructures grown by droplet epitaxy is presented. This study involves the atomic-scale analysis of strain free GaAs/AlGaAs quantum dots (QDs) and quantum rings (QRs) grown on a (001)-oriented substrate. In the section that follows, the attention is shifted towards the atomic-scale analysis of self-assembled GaAs/AlGaAs nanostructures grown on a (311)A-oriented substrate. As an introduction to the X-STM analysis, the application of quantum wires (QWRs) in a broad contact laser diode is presented. It is shown that QDs can be transformed into QWRs by annealing the sample and that the resulting nanostructures posses unique optical properties that can be exploited in optoelectronic devices.

7.1 Droplet Epitaxy

Traditionally, self-assembled QDs are grown in the Stranski-Krastanov mode. In this growth technique the QD material, of which the lattice constant has to differ from that of the substrate, is deposited in a layer-by-layer fashion. Beyond a critical layer thickness, which depends on the strain and chemical potential, nucleation of islands on the surface starts. In this process, the strain that has been building up in the material due to the lattice mismatch is relaxed and the surface energy minimized. Defect free QDs can be grown in this manner, but the required presence of strain in the material during the growth process is a major complicating factor. For one, strain

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A buffer layer is grown under nominal conditions, followed by a cool down to low temperature and depletion of the group V-elements. Deposition of group III-elements on the surface. Depending on the surface termination, the first few monolayers might form a wetting layer (blue). Further deposition of group III-elements results in the formation of liquid droplets (red) on the surface. The liquid droplets are crystallized into QDs by the application of a group V-element flux. A capping layer is grown at low temperature, followed by high temperature annealing. Further overgrowth can be done at nominal growth conditions.

Figure 7.1: Schematic representation of the various steps involved in droplet epitaxy.

can strongly modify the electronic structure of the materials composing the QD system. Furthermore, strain is the driving force behind QD decomposition, a process in which mass transport of material away from the QD results in lowering of the QD upon capping. In addition, the QD material is mixed with the surrounding matrix, softening the boundary of the QDs. Besides this, strain also plays a determining role in the formation of the wetting layer that usually accompanies the QDs. All these structural imperfections can obscure the intrinsic properties of QDs and hinder the linking of experiment, for example photoluminescence measurements, with a realistic QD model. In this respect, QDs grown by the technique droplet epitaxy can provide a much simpler system. This technique involves the low temperature growth of unstrained liquid group III-elements droplets that are subsequently crystallized into QDs by the incorporation of group V-elements. In figure 7.1, cartoons of the typical steps involved in the process of droplet epitaxy are shown: 1) The process of droplet epitaxy is started with the growth of a buffer layer at normal growth temperature (≈ 500–600°C), after which the temperature is lowered (≈ 150–350°C). After cooling down, the group V-elements that normally constitute an uniform background gas during growth are evacuated from the growth chamber. 2) Next, group III-elements are deposited on the surface. Depending on the type of surface termination, the first monolayers of the deposited group III-
elements can go into formation of a crystalline wetting layer. 3) After the formation of the wetting layer is completed, if occurred at all, any further group III-elements that are deposited on the surface coalescence and form liquid droplets in a Volmer-Weber-like mode. 4) Subsequently, these liquid droplets are crystallized into crystalline QDs by the application of a group V-element flux. Note that, at this point the type of nanostructure can be imposed by tuning the delicate interplay of temperature and pressure. In this way a variety of nanostructures, for example quantum dots, quantum rings, quantum wires, quantum dashes, and nanoholes, can be grown. 5) After crystallization, the newly formed nanostructures are overgrown at low temperature with a capping layer, typically followed by an annealing step to remove defects, improve crystallinity, and recover a flat surface at the growth front. 6) Finally, the nanostructure can be further overgrown at normal growth temperatures with another capping layer.

7.2 GaAs / AlGaAs nanostructures

All the X-STM measurements presented in this section are performed with the room temperature STM described in section (2.1.5). Standard electrochemically etched tungsten tips were used, see section (2.1.6) for the details of the preparation procedure. The STM was operated in constant current mode on in situ cleaved \{110\}-surfaces. The X-STM measurements are all done at a high negative bias voltage \(V \approx -3\) V and with a tunnel current of \(\approx 40\) nA. At these tunnel conditions, and with the color scale used, GaAs (AlAs)-rich regions appear bright (dark) in the topographic X-STM images.

7.2.1 Quantum dots and quantum rings grown on the (001)-substrate

The first material system under consideration consists of QR layers and QD layers grown on a (001)-oriented substrate. After the growth of a 70 nm thick AlGaAs buffer layer on an n-type GaAs substrate at 580°C, the growth sequence of the layers that will contain the nanostructures is started with lowering of the substrate temperature to 200°C. After the cool down the As is evacuated from the growth chamber. This results in an As-stabilized \((4 \times 4)\)-reconstructed surface. Next, 3.75 monolayers (ML) Ga, of which the first 1.75 MLs transforms the As-terminated surface into a two-dimensional GaAs layer\(^{135}\), is deposited at a growth rate of 0.5 ML s\(^{-1}\). The remaining Ga (2 ML) forms liquid Ga-droplets on the surface. These droplets are then crystallized into GaAs QRs or QDs by the application of an As\(_4\) flux \((1 \times 10^{-5} \text{ and } 2 \times 10^{-4} \text{ Torr beam equivalent pressure, respectively})\). Still under As\(_4\) flux, the sample is then annealed at 350°C for 10 minutes. Subsequently, the newly formed nanostructures are capped with 50 nm AlGaAs that is deposited at 350°C, followed by a 5 minutes annealing at 650°C. This annealing is inserted into the growth procedure to ensure that the next layer is grown on a defect free and flat surface. Next, another capping layer of 40 nm is grown at 580°C after which the growth sequence for the next layer is started. In total four buried QR layers and one QD layer were grown in this manner. The total structure is capped with 600 nm GaAs on top of which uncapped QR where grown. A post growth anneal step, which is usually performed to improve the optical properties of the QDs, was not performed on this sample. Both the QDs and QRs will be investigated in this section by means of X-STM.
Atomic-scale analysis of self-assembled nanostructures grown by droplet epitaxy

Figure 7.2: a) 20 × 40 nm² topographic image of the top GaAs/AlGaAs interface. b) 60 × 55 nm² topographic image of the AlGaAs matrix. The position of the first anneal step and the wetting layer is indicated by the black arrow at the top and the right of the image, respectively. The inset c) shows a close-up of the wetting layer. The position of the wetting layer is indicated by the white arrow.

In figure 7.2a–b, the top GaAs/AlGaAs interface and part of the AlGaAs matrix is shown, respectively. Although, no QDs and/or QRs are visible in these images, three interesting features can be observed. First, the GaAs/AlGaAs interface appears very smooth. This implies that high quality flat surfaces are recovered after each growth sequence. Secondly, the position of the first annealing step is clearly visible as a dark layer in the AlGaAs matrix (marked by the top black arrow), signifying a higher AlAs concentration at this point in the sample. This means that a significant portion of the Ga present in the first couple of monolayers is desorbed during the annealing process. Thirdly, a GaAs wetting layer (marked by the black arrow on the right side), is visible as a narrow bright line in the AlGaAs matrix. Closer inspection of the wetting layer, see figure 7.2c, reveals that the thickness of the wetting layer is less than 1 bilayer. This is in agreement with the expected 1.75 ML thick wetting layer when depositing Ga on an As-stabilized c(4 × 4)-reconstructed surface.45,155

First, the QD layer present in the sample will be investigated. In total 15 QDs were imaged. A typical QD is shown in figure 7.3. The QD is found to be bounded by sharply defined interfaces and has a height and width of 13 nm and 28 nm, respectively. AFM measurements on uncapped QDs grown under similar conditions performed by other groups yield similar dimensions135,156,157. Note that, there is an AlAs-rich region on top of the QD (indicated by the white arrow). The formation of this feature can be explained by the difference in mobility of the Al and Ga atoms; the Ga atoms are more mobile and will migrate along the side of the QD during capping while the Al atoms, which are less mobile, are more likely to remain on top of the QD. The driving force behind this migration of incoming adatoms away from the top of the QD is the convex curvature of the growth front at the position of the QDs.158 With the formation
Figure 7.3: 42 × 36 nm² topographic image of a typical GaAs/AlGaAs QD. The AlAs-rich region on top of the QD is indicated with a white arrow. An averaged cross-sectional height profile is taken along the line through the center of the QD and presented in figure 7.4a.

Figure 7.4: (a) Averaged cross-sectional height profile taken along the white line drawn in figure 7.3. b) 2D-fast Fourier transform of figure 7.3. Both periodicities of the (110)-surface yield strong and very localized signals in the FFT-image (red circle: 0.565 ± 0.009 nm, blue circle: 0.40 ± 0.009 nm).

of the AlAs region explained, the next step is to check whether the QDs are strain free, as one would expect with AlAs and GaAs being lattice matched materials. The white line drawn through the center of the QD in figure 7.3 marks the path along which a topographic profile is extracted. This topographic profile is shown in figure 7.4a. Three distinct regions can be observed. From left to right: an AlAs-rich region, the GaAs QD, and the AlGaAs matrix. The apparent height difference between these regions is due to electronic contrast. More importantly, all the regions are flat; there is no outward relaxation of the surface as observed in QDs in lattice-mismatched systems, see e.g. the outward surface relaxation profile of the InAs QDs presented in figure 5.8. To further
Figure 7.5: a) 60 × 30 nm$^2$ topographic image of two QDs. b–c) An atomic grid is overlaid on top of a close-up of the left QD. Al and Ga atoms present in the QD are marked by red and yellow squares, respectively.

illustrate that the GaAs QD is indeed strain free, a 2D-fast Fourier transform (FFT) is done on the topographic image shown in figure 7.3. The result is shown in figure 7.4b. Both periodicities of the (110)-surface yield strong signals in the FFT-image and are very localized. The position and the width of these peaks correspond to corrugations of 0.565 ± 0.009 nm and 0.40 ± 0.009 nm. The small errors bar in these values indicate that there is no variation in lattice constant and that the QDs are indeed strain free.

Whether intermixing of Al is a factor of importance in the formation of GaAs/AlGaAs QDs grown by droplet epitaxy is a question that is frequently raised in the literature. In nearly all the QDs that were imaged in the current work some degree of intermixing is observed. To illustrate this further, two QDs are presented in figure 7.5a. Even without further analysis it is evident that some intermixing of Al has taken place in the left QD. As a matter of fact, the Al intermixing in this particular QD is found to be strongest among all. To make the analysis more quantitative, a grid with atomic dimensions is overlaid on top of a close-up of the left QD, see figure 7.5b–c. On this grid the positions of the Al (dark spots) and Ga atoms are marked with red and yellow squares, respectively. In this way, the Al concentration in this particular QD was found to be ≈ 7%. Note that, the degree of Al intermixing varies from QD to QD, see for example the QD on the right side of figure 7.5a. In this QD the degree of Al intermixing is considerably lower. Therefore, it is conclude that the value of 7% constitutes an upper limit for Al intermixing in these QDs. A closer inspection of the QD geometry reveals a possible source of the Al intermixing. At the bottom interface of the QD in figure 7.6, and to a lesser extend also at the bottom interface of the QDs
shown in figure 7.5a, a GaAs-rich intrusion in the AlGaAs matrix is observed. The fact that these intrusions are always present in QDs that show some degree of intermixing, and the fact that there seems to be a spatial correlation (right above) between an intrusion and the region of strongest intermixing within the QD, is strong evidence that the intrusions are the source of the Al atoms.

The formation of the GaAs-rich intrusions can be explained by the so-called process of local etching\textsuperscript{162}. In this process As atoms diffuse from the crystalline buffer layer into the liquid droplet. As a consequence, the buffer layer directly underneath the droplet liquefies. This liquefaction dissolves the Al atoms as well. This has been suggested by other groups\textsuperscript{163} but never confirmed experimentally. It is assumed that the As atoms diffuse to the side of the droplet and crystallize there\textsuperscript{162}. Given their spatial localization above the intrusions, this seems not to be the case for the Al atoms. Under the current growth conditions, the Al atoms apparently do not have sufficient time to diffuse to the sides of the droplet before crystallization of the entire liquid droplet is completed. This observation is supported by a photoluminescence/AFM study of QRs generated by local etching\textsuperscript{164}. There, the QRs, which have an etched hole in their middle, are formed by the crystallization of the sides of the liquid droplets and subsequent desorption of the remaining Ga. Photoluminescence measurements on the overgrown structures indicate that the QRs consist purely of original droplet material and not of material from the buffer layer.

Concerning the shape of the QDs, it was noticed that the side facets of the imaged QDs are not exactly straight but appear to be somewhat curved. The maximum angle of this curvature is found to be in the range of 34–55° per QD. The upper limit corresponds to the projection of a \{111\}-facet (54.7°) on the (110)-plane. If it is assumed that (1) all the QDs are approximately of equal height and (2) the observed height difference is due to the position of the cleavage plane relative to the center of the QD, the fact that the maximum facet angles constitute a range excludes QD shapes with constant facet angles like rectangular (truncated) pyramids\textsuperscript{66}. Since it has been reported that uncapped AlGaAs/GaAs QDs have \{111\}-facets\textsuperscript{45,153,165}, it is conclude that the shape...
of the QDs is somewhat changed/eroded during capping. The details of the cross-sectional geometry as imaged by X-STM allows mapping of these changes and the construction of a three-dimensional model of the buried QDs. For this one has to go back to figure 7.3, which shows the highest QD that was observed. Since it is the highest, it can be assumed that this QD is cleaved directly through its center. Consequently, the profile of this QD is used to generate a three-dimensional model by fitting a Gaussian function to its boundary, see figure 7.7 (red line), and rotating it around the symmetry axis that lies along the growth direction. Note that, for the purpose of simplicity, the QDs are assumed rotational symmetric. In reality these QDs show a slight elongation along the [-110]-direction. This is the result of a difference in migration lengths of Ga on the (001)-surface in the various crystal directions. However, as a good first approximation these QDs can still be considered round. Next, it is checked whether the profiles of other QDs correspond to profiles obtained by cleaving the three-dimensional model at specific distances from the center. This is illustrated in figure 7.7 for two QDs that are cleaved off-center, see the green and blue points/lines. Although not shown, the same result could be achieved for nearly all observed QDs. From this it is concluded that the observed QDs are Gaussian shaped with approximately equal height but cleaved at different position from the center.

The other type of nanostructure that is present in the current sample are the QRs. Formation of these nanostructures can be achieved by tuning the balance between diffusion of As atoms into, and crystallization at the sides of, the liquid droplet. This can most easily be done by adjusting the intensity of the As$_4$ flux during crystallization of the liquid droplets. To force the growth of QRs instead of QDs the As$_4$ flux has to be lowered; a lower As$_4$ flux allows mass transport to the sides of the droplet before...
crystallization of the liquid droplet is complete\textsuperscript{167}. In figure 7.8a, the uncapped QRs as measured with AFM are shown. The base size of the QRs is found to be much larger than in the case of QDs. Furthermore, the QRs show a strong shape anisotropy; the base size in the [0-11] and [011]-direction are found to be $\approx 50$ nm and $\approx 35$ nm, respectively. As mentioned before, this anisotropy is the result of different migration lengths of Ga on the (001)-surface in the various crystal directions. The height profile of a typical uncapped QR measured along the [0-11]-direction by AFM is presented in figure 7.8b. The results show that the hole in the middle of the QRs does not extend all the way down to the buffer layer. Here it should be noted that the geometry of the AFM tip might prevent imaging of deeper holes. X-STM measurement do not suffer from this particular problem. In figure 7.9, an X-STM image of a buried QR is shown. Of all observed QRs, this one was found to have the deepest hole. Given the AFM results which show comparable dimensions of the hole, this QR is probably cleaved at a position close to its center. However, in the X-STM study only a few QRs were imaged and one can therefore not be sure that a QR that is cleaved directly through its center was imaged. Unfortunately, this prevents a detailed investigation of the geometry and the material composition of the hole. What is know however, is that all the by X-STM observed QRs show no GaAs intrusions in the buffer layer and no intermixing of Al atoms. This suggest that local etching into the buffer does not occur under these growth conditions.

### 7.2.2 Quantum dots and quantum wires grown on the (311)A-substrate

The highest achievable QD density by droplet epitaxy on a GaAs (001)-oriented substrate is $\approx 2 \times 10^{10}$ cm$^{-2}$\textsuperscript{156}. This, in comparison with the Stranski-Krastanov growth method, low upper density puts bounds on the applicability of such QDs in optoelectronic devices. For example, in laser diodes that use QDs as the active medium a much higher QD density is desirable, if not crucial. In this respect, droplet epitaxy on (311)A-oriented substrates is a new and promising technique for creating QDs with densities exceeding $1 \times 10^{11}$ cm$^{-2}$. Furthermore, the anisotropic nature of the (311)A-surface allows the fabrication of quantum wires (QWRs), a highly asymmetric nanostructure
Atomic-scale analysis of self-assembled nanostructures grown by droplet epitaxy

Figure 7.9: $48 \times 23 \text{nm}^2$ topographic image of a QR as recorded by X-STM. The outline of the QR is marked by the dashed transparent line.

Figure 7.10: $2 \times 2 \mu\text{m}^2$ AFM images of the uncapped QDs on the $(311)\text{A}$-surface after 10 minutes annealing at a) $450^\circ \text{C}$ and b) $550^\circ \text{C}$. The high temperature annealing transforms the QDs into QWRs.

Quantum wire laser diode

The process of QWR formation is investigated by atomic force microscopy (AFM). For this purpose two dedicated samples with uncapped QDs were grown. The growth conditions of the QDs are the same as for the X-STM samples and are described in detail in the next section. In figure 7.10, two AFM images of the $(311)\text{A}$-surface after 10 min annealing at a temperature of a) $450^\circ \text{C}$ and b) $550^\circ \text{C}$ are shown. In the former case the QDs shape is retained. The density and height of these uncapped QDs is determined from the AFM image to be $\approx 1 \times 10^{11} \text{cm}^{-2}$ and 2.5 nm, respectively. Upon annealing, the QDs elongate along the [-233]-direction and QWRs are formed. The
reason for this elongation is the strong anisotropic nature of the (311)A-surface where migration in the [-233]-direction is strongly favored\textsuperscript{168}. The migration of constituent QD material is facilitated by the higher annealing temperature. In the current case the QD density is so high that the QDs start to coalesce to form QWRs that are oriented along the [-233]-direction. In a previous study of QWR formation on an (001)-oriented substrate the highest achievable QD density proofed to be too low for QD coalescence and, thus, for QWR formation. As a result quantum dashes were formed instead\textsuperscript{169}. On (311)A-surfaces, however, the shorter migration distance of Ga adatoms makes a higher QD density possible\textsuperscript{163,170}. The average height, width, and length of the current uncapped QWRs is found to be 1.9 nm, 30 nm, > 200 nm, respectively.

The method of forming self-assembled QWRs by elongating and coalescing individual QDs paves the way for the fabrication of QWR structures that can be useful for optoelectronic device applications in strain-free systems. This is illustrated for the current nanostructures by the application of the QWRs in a broad contact laser diode. Before this device is introduced, first the optical properties of the QWRs are investigated. All the photoluminescence spectra presented in the current work are taken at 6 K using the 532 nm line of a frequency-doubled Nd:Y\textsubscript{3}A\textsubscript{15}O\textsubscript{12} laser. Figure 7.11 shows the polarization-resolved photoluminescence spectra of the QWRs taken in the [-233]- and the [01-1]-direction. The spectra show that the QWRs emit at a wavelength around 690 nm with a linewidth of 48 meV. Note that, the emission energy is consistent with the calculated value using a QWR height of 1.9 nm as observed in the AFM and X-STM measurements. The emission from the QWRs is highly polarized along the long axis of the wire, the photoluminescence intensity of the QWRs along the [-233]-direction is large compared to that along the perpendicular [01-1]-direction. Intuitively, this can be understood in a completely classical framework; the electron is restricted to an one-dimensional oscillation with respect to the hole along the axis of the wire. Consequently, radiation from the oscillating dipole is polarized along the direction of the wire. In the current case a polarization anisotropy of 0.18, which is defined as \((I_{[-233]} - I_{[01-1]})/(I_{[-233]} + I_{[01-1]})\), is found. Note that, the polarized direction is perpendicular to the (01-1)-direction. This results in a relative gain in the (-233)-direction and a reduction of losses in the other directions, which are highly desirable features when fabricating lasers that use cleaved \{011\}-surfaces as Fabry-Pérot mirrors.

As demonstration, a broad contact laser diode in which the QWRs serve as the active medium is fabricated. The QWR laser structure is grown on an n-type GaAs (311)A-substrate and contains fivefold-stacked GaAs QWR layers, separated by 16 nm Al\textsubscript{0.3}Ga\textsubscript{0.7}As barriers, as the active core. The core is embedded in a 200 nm Al\textsubscript{0.3}Ga\textsubscript{0.7}As layer for separate confinement. The bottom and top cladding layers consist of 1300 nm n-type Al\textsubscript{0.6}Ga\textsubscript{0.4}As and 1300 nm p-type Al\textsubscript{0.6}Ga\textsubscript{0.4}As with a 100 nm p-type GaAs contact, respectively. After the completion of the entire growth sequence, rapid thermal annealing (750 °C, 4 min) is performed under N\textsubscript{2} ambient. Finally, a broad contact laser diode with a cavity length and width of 1800 µm and 10 µm, respectively, is fabricated. In the cavity is bounded in the long direction by two cleaved \{011\}-surfaces that act as Fabry-Pérot mirrors. Figure 7.12a shows the light output-current characteristics of the QWR laser at 77 K under pulsed operation (0.01% duty cycle, 1 µs pulse width). The threshold current density of the device, \(J_{th}\), is found to be 8.9 kA cm\(^{-2}\). Figure 7.12b, shows electroluminescence (EL) spectra below and above the threshold current density. The subthreshold spontaneous emission has a peak at 730 nm with a linewidth
Atomic-scale analysis of self-assembled nanostructures grown by droplet epitaxy

Figure 7.11: Polarization-resolved photoluminescence spectra of GaAs QWRs measured at 6 K. The photoluminescence intensity along the [-233]- and the [01-1]-direction is plotted. The inset shows a birds-eye view of the uncapped GaAs QWRs.

Figure 7.12: a) Light output–current characteristic of the GaAs/AlGaAs QWR laser diode at 77 K under pulsed operation (0.01% duty cycle, pulse width of 1 µs). b) Electroluminescence spectra below (dotted line) and above (solid line) the threshold current density of $J_{th} = 8.9 \text{kA cm}^{-2}$.

of 47 meV. This peak has, compared to the photoluminescence measurements presented above, been shifted towards longer wavelength (690 nm vs. 730 nm) due to the lower Al composition of the AlGaAs buffer layer. Above the threshold current density, lasing occurs at a wavelength of 722 nm.

Cross-sectional scanning tunneling microscopy

The second X-STM sample under consideration in this chapter consists of a GaAs/AlGaAs QWR layer and a GaAs/AlGaAs QD layer that were grown on a $n$-doped (311)A-oriented GaAs substrate by means of DE. First, a 50 nm GaAs layer is grown at 610°C,
the nominal growth temperature. Next, a 20 nm Al$_{0.35}$Ga$_{0.65}$As buffer layer is grown after which the temperature is lowered to 200 °C. After the cool down the As is evacuated from the growth chamber and 5 ML of Ga are deposited on the surface. This Ga forms liquid droplets. Subsequently, these liquid Ga droplets are crystallized into GaAs QDs by the application of an As$_4$ flux ($2 \times 10^{-6}$ Torr beam equivalent pressure). The newly formed uncapped QDs are then annealed at 550 °C to generate QWRs, see the previous section. Next, the QWRs are capped with a 20 nm AlGaAs layer grown at the annealing temperature. After the completion of this capping layer, an GaAs/AlGaAs multiple quantum well (4×) is grown at the nominal growth temperature. The whole growth sequence is then repeated with an lower annealing and overgrowth temperature of 400 °C, yielding QDs instead of QWRs.

In figure 7.10a, a topographic X-STM image of a typical stretch of QWR layer is shown. One complete QWR (between the two dashed lines) is visible in the image. The length and the variation in height along this QWR is found to be 220 nm and 1.3–1.9 nm, respectively. Although not imaged in their totality, other QWRs are found to span even longer (>250 nm) which is in agreement with the AFM measurement shown in figure 7.10b. The inter-QWR distance in the [-233]-direction is found to be in the order of tens of nanometers. In figure 7.10b–c, two close-up of part of a QWR are shown to illustrate the surface fluctuations present at the bottom GaAs/AlGaAs interface. These fluctuations show up as AlGaAs protrusions in the GaAs QWRs and *vice versa* as GaAs intrusions in the AlGaAs buffer layer. Both are absent at the top interface of the QWRs and at the interfaces of the quantum wells. This indicates that the protrusion / intrusions are formed prior to and / or during the crystallization of the Ga droplets but not during the growth of the capping layer. The formation of these features is attributed to the destabilization of the buffer layer interface by the liquid Ga droplet at low temperature and a subsequent reconfiguration of the surface. A more detailed
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Figure 7.14: a) 35 × 170 nm² topographic X-STM image of the QD layer. An AlAs-rich region emanating from the top of one of the QDs is marked by two transparent lines. b) 16 × 65 nm² topographic image of a typical QD with a smooth and c) rough bottom AlGaAs/GaAs interface.

An explanation of this process will be given further on in this section where the QD layer is analyzed. Despite the substantial interface fluctuations at the bottom of the QWRs, the homogeneity of the contrast, e.g. figure 7.13b–c, indicates that no intermixing of Al with the GaAs QWRs has occurred.

Having investigated the QWRs, the QDs are next. A total of 29 QDs were imaged by X-STM. The average height of the QDs is found to be 2.3 nm with a standard deviation of $\sigma = 0.6$ nm. This is in agreement with the AFM measurements and suggests that there has been little structural change during capping. Low temperature (5 K) photoluminescence measurements on a dedicate sample shows that the QDs emit around 703 nm with a linewidth of 48 meV. This small linewidth indicates high uniformity, a quality that is also reflected by the low $\sigma$ of the QD height distribution as determined from the X-STM images.

In figure 7.14a, a typical stretch of QD layer is shown. Three QDs can be distinguished. A wetting layer connecting the QDs is not observed. In a previous study, where low temperature (6 K) photoluminescence measurement showed no clear peak that could be attributed to the emission of a wetting layer, it was suggested that a wetting layer will not form under the current growth conditions. This is confirmed by the current X-STM measurements. Due to the high QD density approximately half of the observed QDs are found to overlap with other QDs. This illustrated in figure 7.14c, where the right side of a QD overlaps with another. The QDs are found to be bounded
Figure 7.15: a) 10 × 22 nm² topographic X-STM image of a GaAs QD capped with GaAs. The interface is marked by the white transparent line. Note that, the GaAs QD itself is not visible.

by (211)- and (411)-side facets, resulting in a slight elongation of the QDs in the [2-3-3]-direction. Emanating from the top of the QDs are AlAs-rich regions (darker). As a guide to the eye the boundary of one of these regions is marked in figure 7.14a by two transparent lines. These lines are found to roughly follow the [011]-direction. The formation of AlAs-rich regions can be explained by the difference in mobility of the Ga and Al adatoms, analog to the case of the QDs grown on a (001)-substrate. During the growth of the capping layer, Ga adatoms which have a higher mobility than Al adatoms move more readily over the surface. Since they favor the (311)A-surface over the (211)- and (411)-side facets of the QD, and given the limited migration length of Al adatoms, this results in AlAs-rich regions on top of the QDs. The observation that the AlAs-rich regions extend all the way to the GaAs quantum well, and that slight interface irregularities are found at this position, indicates that to some extend the original QD shape is retained at the growth front during capping. Due to the asymmetric QD shape, the lateral position of the QD at the growth front is continuously shifted in the [2-3-3]-direction during overgrowth, resulting in a tilt of the AlAs-rich regions toward the [011]-direction.

In approximately one third of the observed QDs, a GaAs intrusion in the AlGaAs buffer layer that is paired with an AlGaAs protrusion in the GaAs QD is found at the bottom interface, see e.g. figure 7.14c. These paired protrusions/intrusions are better resolved in another sample were the QDs are overgrown with a GaAs capping layer, see figure 7.15. Although the QDs can not be observed anymore in this sample, the view of the interface is much clearer. In both samples the protrusions are always found to form in the [−233]-direction relative to the intrusions and are bounded by an (100)- and (211)-surface. The paired protrusions/intrusions are most likely the result of an interface instability induced by the liquid Ga droplet. It is well known that (311)A-surfaces show temperature instabilities that break up the flat surface into facets that have a lower surface energy. It is suggested that a similar process occurs in the current case, where the (311)A-surface directly underneath the droplet is destabilized by the presence of the liquid Ga and subsequently reconfigures into a
more energetically favorable configuration consisting of (100)- and (211)-facets. In case of the GaAs/AlGaAs QDs grown on an (001)-oriented substrate, see section (7.2.1), the observed GaAs intrusions are attributed to local etching. In that case, As atoms present in the buffer layer, and to a lesser extend also the Al atoms, dissolve into the liquid Ga and recrystallize inside the QD upon the application of an As$_4$ flux. As a result these QDs posses an intrusion at their bottom interface and show some amount of Al intermixing. It has to be stressed here that this is not the case with the current QDs where the homogeneity of the contrast within the QDs, e.g. figure 7.14b–c, indicates that they consist of pure GaAs and that no Al intermixing has occurred.

7.3 Summary

To summarize, in this chapter X-STM measurements on QDs and QRs grown on a (001)-oriented substrate were presented. The X-STM study shows that wetting layers, although not notable, form on an (001)-oriented substrate. The thickness of the wetting layer is found to be less than 1 bilayer. As expected in lattice-matched material systems, the QDs were found to be unstrained. The results show that some degree of Al intermixing with the GaAs QDs occurs during growth. This intermixing is attributed to local etching into the buffer layer directly underneath the liquid droplets. The shape of the QDs is found to be Gaussian. AFM measurements on the QRs show that they have a strong shape anisotropy. The hole in the middle of the QR is found to extend all the way down but not into the buffer layer. No sign of Al intermixing is found in case of the QRs.

It is demonstrated that QWRs can be created by annealing uncapped QDs that were grown on the (311)A-oriented substrate. The QWRs show strongly polarized emission along the direction of the QWRs, a feature that is highly desirable in the fabrication of lasers that use cleaved crystalic surfaces as Fabry-Pérot mirrors. As an application of the studied QWRs to optoelectronic devices, a broad contact laser diode that uses the QWRs as active medium was presented. Lasing under pulsed excitation was observed for the fabricated laser diode.

The atomic-scale X-STM study of the QDs and QWRs grown on the (311)A-oriented substrate reveals that substantial interface fluctuations are present between the nanostructures and the buffer layer. These fluctuations are attributed to the destabilization of the interface by the liquid Ga droplet and subsequent reconfiguration of the surface in energetically more favorable facets. Despite the interface fluctuations, no evidence of Al intermixing is found in both the QWRs and QDs. A wetting layer connecting the QDs is not found. AlAs-rich regions, which are brought on by the difference in mobility of Al and Ga, are found emanating from the top of the QDs.
References


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Summary

Atomic-scale probing of metallic and semiconductor nanostructures

In scanning tunneling microscopy (STM) an atomically sharp metallic tip is brought in close proximity to a (semi) conducting sample to probe the electronic and topographic features of the surface. Three extensions of this technique, namely cross-sectional scanning tunneling microscopy (X-STM), scanning tunneling luminescence microscopy (STL), and spin-polarized scanning tunneling microscopy (SP-STM), are presented in this thesis. In the first technique, X-STM, a sample is cleaved along the (110) natural cleavage plane of a zinc-blende crystal to allow the observation of single dopants and embedded nanostructures such as quantum wells and quantum dots in a plane parallel to the growth direction. In the second technique, STL, the STM-tip is used to locally induces luminescence. The local nature of this technique makes it possible to extend optical probing beyond the diffraction limit. The technique has therefore the potential to provide a wealth of information about light–matter interactions on the atomic-scale. Furthermore, the optical properties of a material system can be linked to its magnetic properties by studying the polarization of the STM-induced luminescence. In this respect, STL and the technique of SP-STM are complementary. In the latter technique a magnetic sensitive STM-tip is used to probe the electromagnetic properties of a surface on the atomic-scale, a highly sought after capability in modern day development of spintronics. Although the techniques of STL and SP-STM have great potential, the downside is that they are notoriously difficult to implement experimentally. This is reflected in the small number of groups that have succeeded in implementing one of the techniques, let alone both simultaneously. This is a pity since the complementary nature of these two techniques opens up a myriad of experiments with which the optical, electronic, and magnetic properties of materials can be simultaneously investigated with atomic-scale resolution. The ultimate goal of this thesis is to combine the two techniques of STL and SP-STM, with the technique of X-STM to study the properties of single dopants and embedded nanostructures. In this thesis the successful implementation of these techniques in a single scanning tunneling microscopy is reported.

It is shown in this thesis that it is possible to relatively easily and cost-effectively implement luminescence detection into a commercially available Omicron low temperature STM. STM-induced luminescence could be collected efficiently from an Au(110)(1 × 3)-reconstructed surface. Furthermore, it was demonstrated that it is possible to simultaneously record the surface topography and the corresponding photon map, both with atomic resolution. The fact that a full luminescence spectrum is recorded at each point at which the luminescence is collected, allows for a spatially resolved spectral analysis. Besides successful STL on a metallic surface, the collection of luminescence from a highly Zn-doped GaAs semiconductor sample was demonstrated. Here, a threshold bias voltage was found for the onset of electroluminescence. No correlation between the shape, the position, and the intensity of the luminescence spectra with the positions of the dopants was found. The results show that the proposed collection system can be used to spectrally collect and analyze the STM-induced luminescence from metallic and semiconductor material systems with atomic-scale resolution.

Spin-polarized tunneling microscopy was demonstrated on a vicinal W(110)-surface covered with a thin iron film. This material system consists of alternating mono- and bilayer magnetic nanowires. Tips having an in-plane direction of magnetization and tips that proofed to have a slanted direction of magnetization were used. Respectively, three and four levels of magnetic contrast were observed with these tips, unambiguously demonstrating SP-STM. The next step
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along the lines of the current work is to extend SP-STM to dilute magnetic semiconductors, e.g. Mn in GaAs. Atomic-scale resolution with magnetic chromium tips has already been observed (not in the thesis) in X-STM measurements on this material system, an important step towards probing the magnetic properties of dilute magnetic semiconductors in the future.

In the last decade the fabrication of quantum dots (QDs) has been intensively studied. The interest has been, and still is, stimulated by applications of self-assembled QDs in optoelectronic devices. Nowadays, QDs are for instance applied or suggested in QD lasers, single electron transistors, and spin manipulation. It is well known that the optical and electronic properties of QDs are strongly affected by their size, shape, and chemical composition. In this thesis the size, shape and chemical composition of QDs and ways to control these properties have been intensively studied for various material systems and growth techniques. To this end, atom probe tomography (APT) and X-STM were employed. The technique of APT is conceptually completely different than X-STM: atoms are evaporated from a high voltage biased specimen by a laser pulse and recorded at a detector. The technique allows the fully three-dimensional characterization of embedded nanostructures, carrying the geometrical and chemical analysis beyond the two-dimensional cleavage plane to which the technique of X-STM is restricted. In this thesis, APT was bench marked against X-STM. It is shown that APT and X-STM complement each other very well. Where X-STM gives only two-dimensional cross-sections, APT provides a fully three-dimensional tomographic reconstruction, and where X-STM has a limited capability to distinguish chemical species, the mass-spectral analysis of APT offers the ability to distinguish different elements from each other. The two techniques were linked by means of computational methods that model surface relaxation. The method followed in this thesis emphasizes structural features of the studied QDs that were not detected or neglected in previous studies but are important in modeling the QDs.

Control over the height of QDs allows the tuning of their emission wavelength and g-factor. Nowadays, several methods are available to achieve this in the Stranski-Krastanov growth mode, among which the use of surfactants, double-capping, indium flush, and strain engineering of the capping layer. In this thesis, the latter two techniques are investigated in detail by X-STM and kinetic Monte-Carlo (KMC) simulations. X-STM studies have, and will continue, to provided a wealth of information giving a better understanding of the growth process. However, the technique only provides a cross-sectional snapshot of the buried QDs after the completion of the growth. In this respect techniques such as APT and KMC simulations can be of great complementary value and provide further insight into the QD morphology and into the details of the growth process. The work presented in this thesis is the first in which a realistic, fully three-dimensional KMC simulation is compared with experimental results. The agreement between the KMC simulations and the experimental X-STM data shows that KMC simulations are a very valuable asset in understanding the dynamics of QD growth and might in the future be able to predict the outcome of the growth process.

In the last part of this thesis, the details and possibilities of droplet epitaxy as an alternative technique to grow self-assembled QDs are reported. Traditionally, QDs are grown in the strain driven Stranski-Krastanov mode. Defect free QDs can be grown with this technique, but the presence of strain in the material during the growth process is a major complicating factor. For one, strain can strongly modify the electronic structure and is the driving force behind QD decomposition and intermixing. The resulting structural imperfections can obscure the intrinsic properties of the QDs and hinder the linking of experiment, e.g. photoluminescence measurements, with a realistic QD model. In this thesis, it is shown that in this respect QDs grown by droplet epitaxy provide a much simpler approach. This technique involves the low temperature growth of unstrained liquid group III-elements droplets that are subsequently crystallized into QDs by the incorporation of group V-elements. It was shown that wetting layers (less than 1 bilayer) form on an (001)-oriented substrate and are absent on an (311)A-oriented substrate. As expected in lattice-matched material systems, the QDs were found to be unstrained. The results show
that some degree of Al intermixing with the GaAs QDs, attributed to local etching, occurs during the growth in case of the (001)-oriented substrate. In case of the (311)A-oriented substrate, substantial interface fluctuations are present between the nanostructures and the buffer layer. These fluctuations are attributed to the destabilization of the interface by the liquid Ga droplet and subsequent reconfiguration of the surface in energetically more favorable facets. It is demonstrated in this thesis that quantum wires (QWRs) can be created by annealing uncapped QDs grown on the (311)A-oriented substrate. The QWRs show strongly polarized emission along the direction of the QWRs, a feature that is highly desirable in the fabrication of lasers that use cleaved crystalic surfaces as Fabry-Pérot mirrors.
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Atomic-scale probing of metallic and semiconductor nanostructures

In scanning tunneling microscopy (STM) wordt een atomair scherpe metalen tip in de nabijheid van een (half)-geleider gebracht om hiermee de elektronische en topografische eigenschappen van een oppervlak te bestuderen. Drie uitbreidingen van deze techniek worden in dit proefschrift gepresenteerd; cross-sectionele scanning tunneling microscopy (X-STM), scanning tunneling luminescentie (STL), en spin-gepolariseerde scanning tunneling microscopy (SP-STM). In de eerste techniek, X-STM, wordt een zinkblende kristal gekliefd langs zijn natuurlijke kliefrichting. Hierdoor is het mogelijk om individuele doterings atomen en ingebetje nanostructuren, zoals quantum putten en quantum punten, te observeren in een dwarsdoorsnede die evenwijdig ligt aan de groeirichting. Met de tweede techniek, STL, kunnen de optische eigenschappen van materialen worden onderzocht op een lengteschaal die kleiner is dan de diffractielimiet van het licht. Met atomaire precisie wordt de STM-tip boven het oppervlak geplaatst en gebruikt om lokaal luminescentie te induceren. De techniek heeft de potentie om een schat aan informatie te leveren over licht–materie interacties op de atomaire schaal. Bovendien kunnen de optische eigenschappen van een materiaal aan de magnetische eigenschappen worden gekoppeld door middel van de polarisatie van de STM-geïnduceerde luminescentie. In dit opzicht zijn STL en de techniek van SP-STM complementair. In de laatste genoemde techniek wordt een magnetisch gevoelige STM-tip gebruikt om de elektromagnetische eigenschappen van een oppervlak op atomaire schaal te bestuderen. Dit is een zeer gewilde functie in de huidige ontwikkeling van spintronica. Hoewel de twee technieken een grote potentie hebben, is het nadeel dat ze experimenteel moeilijk te implementeren zijn. Slechts weinig onderzoeksgroepen zijn erin geslaagd één van deze technieken succesvol te implementeren. Laat staan beide tegelijk. Hierdoor kan helaas geen gebruik gemaakt worden van hun complementaire karakter. Als gevolg hiervan kunnen de optische, elektronische en magnetische eigenschappen van een materiaal niet tegelijkertijd met atomaire resolutie worden onderzocht. Het uiteindelijke doel van de studie zoals beschreven in dit proefschrift is dat de technieken van STL en SP-STM te combineren met de techniek van X-STM om zo de eigenschappen van individuele doterings atomen en ingebetje nanostructuren te bestuderen. In dit proefschrift wordt de succesvolle implementatie van deze technieken in één enkele scanning tunneling microscoop gepresenteerd.

De huidige studie laat zien dat luminescentie detectie relatief eenvoudig en kosteneffectief is te implementeren in een commercieel verkrijgbare Omicron lage temperatuur STM. Met het voorgestelde luminescentie collectie-systeem blijkt het mogelijk om STL-geïnduceerde luminescentie van een Au(110)(1×3)-gereconstrueerd oppervlak op te vangen en te analyseren. Bovendien kan tegelijkertijd de oppervlakte topografie en de bijbehorende fotonkaart met atomaire resolutie worden vastgelegd. Doordat een volledig luminescence spectrum wordt vastgelegd is het mogelijk om naast een ruimtelijke analyse ook een spectrale opgeloste analyse te doen. In dit proefschrift wordt aangetoond dat het ook mogelijk is om luminescentie te induceren en op te vangen van een ballgeleider in de X-STM configuratie. Het materiaal dat hiervoor gebruikt is bestaat uit een zink gedoteerd GaAs. De STL metingen op dit materiaal laten zien dat er voor de generatie van elektroluminescentie er een drempel waarde is in de aangelegde spanning. Een correlatie tussen de vorm, positie en de intensiteit van de luminescentie spectra met de posities van de individuele dotterings atomen is niet gevonden. De resultaten laten zien dat het in dit proefschrift voorgestelde luminescentie collectie-systeem kan worden gebruikt voor het spectrum opvangen, en het met atomaire resolutie analyseren van STM-geïnduceerde luminescentie, op
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zowel metalen als halfgeleiders.

In dit proefschrift wordt SP-STM gedemonstreerd op een W(110)-oppervlak met een trapsgewijks verloop en dat is bedekt met een dunne laag ijzer. Dit specifieke systeem bestaat uit afwisselend enkel en dubbel gelaagde magnetische nanodraden. Voor de metingen zijn tips gebruikt met een magnetisatierrichting die parallel ligt aan het oppervlak. Ook zijn er tips gebruikt met een magnetisatierrichting die een hoek maakt ten opzichte van de tip-as. Met deze twee soorten tips zijn respectievelijk drie en vier verschillende niveaus van magnetisch contrast waargenomen. Dit toont ondubbelzinnig SP-STM aan. De volgende stap langs de lijnen van het huidige werk is om de SP-STM metingen uit te breiden naar magnetische halfgeleiders, bijvoorbeeld met mangaan gedoteerd GaAs. Voorlopige X-STM metingen met een magnetische tip laten zien (niet in dit proefschrift) dat het mogelijk is om dit materiaal af te beelden met atomaire resolutie. Dit is een belangrijke eerste stap op weg naar het bestuderen van de magnetische eigenschappen van magnetische halfgeleiders in de toekomst.

Het fabricatie proces van quantum punten (engels: quantum dots, QD's) is in het laatste decennium intensief bestudeerd. De interesse in deze zelfgeassembleerde nanostructuren wordt gevoed door toepassingen in opto-elektronische apparaten. Zo worden QDs tegenwoordig toegepast in QD lasers, individuele elektron transistors, en spin manipulatie. Van QD's is het bekend dat de optische en elektronische eigenschappen sterk worden beïnvloed door hun grootte, vorm en chemische samenstelling. In dit proefschrift wordt de morfologie van QD's en een aantal verschillende technieken om deze te beïnvloeden in detail bestudeerd. Met zowel de techniek van atom probe tomografie (APT) als X-STM zijn verschillende materialen en groeitechnieken onderzocht. De technieken ATP en X-STM zijn geheel verschillend van aard. Met APT worden atomen door een laser pulsp verdampen van een tip die op een hoog voltage ligt. De atomen worden vervolgens waargenomen met een detector. Deze techniek maakt een volledige driedimensionale karakterisatie van ingebedde nanostructuren mogelijk. Met de vergelijking van de twee technieken wordt in dit proefschrift aangetoond dat APT en X-STM elkaar zeer goed aanvullen. Zo maakt APT het mogelijk om de geometrische en chemische eigenschappen van QD's in drie dimensies te analyseren. Bij X-STM blijft de analyse beperkt tot het tweedimensionale kliefvlak. Wel is in X-STM de resolutie hoger dan in APT, maar heeft de techniek daarnaast een beperkte capaciteit om chemisch onderscheid te maken tussen de verschillende atomen. Met de massaspectrale analyse van APT is het mogelijk om de verschillende elementen en zelfs isotopen te identificeren. De twee technieken worden in dit proefschrift met elkaar verbonden door gebruik te maken van computatiele methoden waarmee de relaxatie van het gekliefde oppervlak kan worden gemodelleerd. De huidige vergelijking benadrukt een aantal structurele eigenschappen van de QD's die niet gedetecteerd of verwaarloosd zijn in voorgaande studies maar die wel belangrijk zijn bij het modelleren van de QD's.

De emissiegolflengte en de g-factor van zelfgeassembleerde QD's kunnen worden afgestemd op een gewenste waarde door de hoogte van de QD's te veranderen. Tegenwoordig zijn er verschillende methoden beschikbaar om dit te realiseren in de Stranski-Krastanov groeimode; bijvoorbeeld het gebruik van oppervlak actieve stoffen, dubbele bekapping, indium flush, en spanning engineering van de bekappingslaag. In dit proefschrift worden de laatste twee technieken nauwgezet onderzocht met behulp van X-STM en Kinetic Monte-Carlo (KMC) simulaties. X-STM heeft in het verleden al een schat aan informatie over het groeiproces geleverd en zal dit in de toekomst ook blijven doen. Helaas verschaf de techniek echter alleen een momentopname van de dwarsdoorsnede van de ingebedde QD's na de voltooiing van de groei. In dit opzicht kunnen KMC simulaties en de eerder genoemde techniek van APT van grote complementaire waarde zijn en verder inzicht bieden in de details van het groeiproces. Het werk dat in dit proefschrift wordt gepresenteerd is de eerste studie waarin een realistisch en volledig driedimensionale KMC simulatie wordt vergeleken met experimentele X-STM metingen van QD's. De overeenkomst tussen de KMC simulaties en de experimentele resultaten laat zien dat de KMC simulaties van grote waarde zijn en in de toekomst wellicht de uitkomst van het groeiproces kunnen voorspellen.
In het laatste gedeelte van dit proefschrift worden de details en de mogelijkheden van druppel-epitaxie als een alternatieve techniek voor het groeien van zelfgeassembleerde QD's besproken. Doorgaans worden QD's gegroeid in de door spanning gedreven Stranski-Krastanov groeimode. Met deze techniek kunnen defectvrije QD's worden gegroeid, maar de aanwezigheid van spanning in het materiaal is echter een complicerende factor. Zo kan de spanning de elektronische structuur sterk beïnvloeden en is het tevens de drijvende kracht achter QD erosie tijdens de groei. De daaruit voortvloeiende structurele tekortkomingen kunnen de intrinsieke eigenschappen van de QD's maskeren. Hierdoor kan de koppeling met een experiment, bijvoorbeeld fotoluminiscence metingen, worden belemmerd. In dit proefschrift wordt aangetoond dat in dit opzicht spanningsvrije QD's die gegroeid worden via druppel-epitaxie een eenvoudiger systeem vormen.

In deze groeitechniek worden eerst de groep III-elementen gedaald op het oppervlak. Deze konden vervolgens samenvloeien in vloeibare druppels. De druppels worden dan gekristalliseerd in QD's door de applicatie van een flux van groep-V elementen. Het blijkt dat met deze groeitechniek de wetting-laag minder dan 2 atoomlagen dik is in het geval van groei op een (001)-georiënteerd substraat en zelfs volledig afwezig is op een (311)A-georiënteerd substraat. Zoals verwacht bij het gebruik van materialen met nagenoeg dezelfde roosterconstante blijken de geobserveerde QD's spanningsvrije te zijn. De resultaten laten zien dat als de QD's op een (001)-georiënteerd substraat worden gegroeid er een zekere mate van aluminium vermenging met de GaAs QD's optreedt. Dit wordt toegeschreven aan het lokaal etsen van het vloeibare gallium in de bufferlaag. In het geval van het (311)A-georiënteerd substraat zijn er grote interface fluctuaties tussen de QD's en de bufferlaag aanwezig. Deze fluctuaties worden toegeschreven aan de destabilisatie van het interface door de vloeibare galliumdruppel en de daarop volgende herconfiguratie van het oppervlakte in energetisch gunstiger facetten. In dit proefschrift wordt laten zien dat naast QD's ook quantumdraden kunnen worden gelabireerd. Dit kan door het verhitten van onbekapte QD's op een (311)A-georiënteerd substraat. De quantumdraden vertonen een sterk gepolariseerde emissie in de lengterichting, een eigenschap die zeer wenselijk is in de fabricage van lasers die gekliefde kristalvlakken gebruiken als Fabry-Perot spiegels.
Dankwoord

In de praktijk komt een dankwoord doorgaans neer op één tot twee pagina's tekst die op het allerklaatste moment aan een proefschrift worden toegevoegd. Deze beschrijving doet echter te kort aan wat een dankwoord werkelijk is. Om te beginnen is het het meest gelezen onderdeel van een proefschrift, een verslag van vier jaar lang opwindend wetenschappelijk onderzoek ten spijt. Ten tweede was er zonder de hulp, de steun, de interesse, en de liefde van de mensen nooit een proefschrift.

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List of publications


List of publications


Papers in progress


Papers published during traineeship (not part of this thesis)


Curriculum vitae

Joris Gerhard Keizer
born 26th of January 1979 in Hengelo, the Netherlands

2008-2012 PhD student at the Eindhoven University of Technology
Photonics and Semiconductor Nanophysics group

2007-1999 Master in Applied Physics, Eindhoven University of Technology
Master project at the Eindhoven University of Technology
Implementation of spin detection in a commercial low temperature
scanning tunneling microscope
Internship at the Catharina Hospital, Eindhoven
Characterization of the physical properties of flexible ureteroscopes
Internship at the Eindhoven University of Technology
Modeling a pinched cascaded arc as a light source

1999-1997 Propaedeutic in Applied Physics, University of Twente, Enschede

1997-1991 High school (VWO), Twents Carmel Lyceum, Oldenzaal

Awards and Honors

Dutch Scanning Probe Microscopy Day 2011, Speaker price
Dutch Scanning Probe Microscopy Day 2010, Poster Price
NEVAC Student Day 2007, Poster Price