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Wijnheijmer, A.P.

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Manipulation and analysis of a single dopant atom in GaAs

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Albertine Pauline Wijnheijmer

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prof.dr. P.M. Koenraad

Copromotoren:
Dr. J.K. Garleff
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Chapter 1

Introduction

One shouldn’t work on semiconductors, that is a filthy mess; who knows if they really exist?

Wolfgang Pauli, 1931

It is impossible to imagine life today without semiconductors. Almost every piece of electronic equipment contains a computer chip, made up of semiconducting material. The functionality of the components on computer chips, e.g. transistors, is realized by adding dopant atoms, either donors or acceptors, into the semiconductor host, in order to introduce free charge carriers. In this respect, the binding energy is an important property, as it has to be sufficiently low that the dopants are easily ionized at room temperature. When ionized, the donors or acceptors introduce free charge carriers into the conduction band (CB) or valence band (VB) respectively.

Over the last few decades, the size of transistors have decreased tremendously, as was predicted by Moore as early as 1965 [1]. Where the channel width of a transistor back in the 1980’s was more than 1 µm, its width in state-of-the-art devices today (2011) is only 22 nm [2], as was published by Intel on May 2, 2011 [3]. The random positioning and discrete nature of dopant atoms becomes apparent at these small scales, leading to statistical variability in e.g. the threshold voltage of the device. Contemporary device simulations therefore take these properties into account [4, 5, 6]. Research devices that are even smaller than commercial devices have reached dimensions where single impurities can dominate the transport properties and where interfaces affect the properties of impurities [7, 8, 9, 10, 11]. Therefore, fundamental research on the atomic scale of the properties of
individual dopants, interactions between neighboring dopants and the influence of interfaces and surfaces is of crucial importance.

Dopants can be used to provide not only free charge carriers, but can also to make semiconductors ferromagnetic. The most important dilute magnetic semiconductor (DMS) is Ga$_{1-x}$Mn$_x$As [12, 13]. Mn acts as an acceptor in GaAs, and also introduces a spin and associated magnetic moment. This material combines magnetic and semiconducting properties and is widely studied for its applications in the field of spintronics, because of its relatively high Curie temperature ($\sim$ 200 K at $x \approx 10\%$ [14, 15, 16]). Although the general properties are largely understood, there are still two competing theoretical models [17, 18, 19, 20]. The models differ in the description of the band structure near the VB edge. Related open issues on the atomic scale are the interaction length between neighboring Mn-ions and understanding of defects that suppress the ferromagnetic coupling.

Nowadays, a wide range of techniques exist that can be used to study these properties. Optical techniques, such as photoluminescence (PL) or photoluminescence excitation (PLE), have an excellent energy resolution in the $\mu$eV regime, but have a limited spatial resolution due to the diffraction of light limit. They are ideal techniques to study optical properties of, for example, quantum dots (QDs), but it is not yet possible to resolve individual dopant atoms in a semiconductor. On the other hand, electron microscopes have outstanding spatial resolution; even atomic resolution can be achieved with transmission electron microscopy (TEM). However, no information about the energy levels can be extracted. Scanning tunneling microscopy (STM) and spectroscopy (STS) combine superb spatial resolution with a reasonable energy resolution. In our system, we routinely achieve atomic resolution, and we typically have an energy resolution of $\sim$ 50 meV. STM and STS are intrinsically surface sensitive. Not only dopants in the surface layer are visible, but dopant atoms up to $\sim$ 2 nm below the surface can be investigated. Therefore STS is the ideal tool to investigate the effect of the surface on dopant atoms.

Just over a decade after the invention of the STM by Binnig and Rohrer in 1981 [21, 22], Zheng et al. were the first to report STM measurements on single Si donors in GaAs in 1994 [23], and this team reported STM measurements on single Zn-acceptors in GaAs in the same year [24, 25]. Since then, various dopants in GaAs have been investigated, e.g. Te [26], Sn [27], Cd [28], Mn [29], and also other host materials, such as InAs [30, 31] and GaP [32]. Not only was the Si donor in GaAs the first to be imaged with STM, it is also one of the most studied donors. The interaction between the Si-atoms and the tip-induced two-dimensional electron gas (2DEG)
or tip-induced quantum dot (TIQD) [33, 34] leads to Friedel oscillations [35]. Feenstra et al. performed STS at 5 K in 2002 [36], and were able to explain most peaks in the spectra. Even such a widely studied material as Si:GaAs can bring new and interesting surprises, as is shown in this thesis. Although the fact that we use much sharper tips than e.g. Feenstra seems only a minor difference at first sight, it has allowed us to unravel new physical phenomena.

The scope of this thesis is as follows. Firstly, the theoretical background and experimental setup are described. The next four chapters are mainly about Si-donors in GaAs, where the most striking results are presented in chapters 4 and 5. These chapters are followed by a detailed analysis (chapter 6), and finally by a discussion of the special situation of Si atoms in the surface layer (chapter 7). Chapter 8 is about a Ga$_{1-x}$Mn$_x$As-based functional device. Chapter 9 is the last chapter about STM, and describes the influence of the microscopic tip properties. The final chapter, chapter 10, deals with a very different system — color centers in diamond — and can be considered as a bonus chapter. Throughout the whole thesis, a consistent use of colors is employed. STM-topography images have a yellow-red color map and d$I$/d$V$ images a yellow-green color map. A list of abbreviations is provided in the appendix.

With this thesis, I will present a number of advances in the fundamental understanding of dopants in III-V semiconductors. Personally, I am glad that some scientists did not listen to Wolfgang Pauli, and pursued the mysteries of the imposing world of semiconductor physics. Let me finish the introduction by yet another quote of Pauli, which puts into words the very essence of this thesis:

God created the solids, the devil their surfaces.

Wolfgang Pauli
Chapter 2

Theory

2.1 Introduction

Most of the experiments presented in this thesis are performed with an STM. In this chapter, the underlying principles of an STM are briefly presented, as well as some phenomena that are important for the interpretation of the data. For a more extended description of an STM, I refer to excellent textbooks, for example reference [37].

2.2 Working principle of an STM

Figure 2.1a shows a schematic of an STM. A sharp conducting tip is brought in close proximity of a (semi-)conducting surface and a voltage is applied between tip and sample. At sufficiently small tip-sample distances (∼ 5 Å) a tunneling current will flow. The tunneling current $I$ is in first approximation exponentially dependent on the tip-sample distance $z_{tip}$ [37]

$$I \propto \exp \left(-2\kappa z_{tip}\right),$$

(2.1)

where the inverse decay length in vacuum ($\kappa$) is typically 1 Å$^{-1}$ [38]. In the constant current mode, the tunneling current is kept constant by adjusting the vertical position by a piezo element in a feedback loop. Scanning laterally over the surface results in a two-dimensional constant current image. We refer to this type of images as topography images, even though they contain both topographic and electronic information. The high sensitivity of an STM originates from the exponential dependence of the tunneling current on the tip-sample distance; a difference in $z_{tip}$ of 1 Å results in a change in the tunneling current of a factor of 10.
2. Theory

[Image of a schematic of an STM (a) and the corresponding energy diagram (b). The onset of the CB and VB are indicated as $E_{CB}$ and $E_{VB}$ respectively. The other symbols are defined in the text.]

### 2.3 Spectroscopy and wave function imaging

The exponential dependence given above is deduced from the modified Bardeen’s formula [39, 40, 41], see figure 2.1b for the corresponding energy diagram

\[
I = \frac{4\pi e}{h} \int_0^{eV} \rho_s (E_{F,s} + E') \rho_t (F_{F,t} - eV + E') |\hat{M}|^2 \, dE'. \tag{2.2}
\]

Here $\rho$ is the local density of states (LDOS) and $E_F$ is the Fermi level, where the subscripts $s$ and $t$ refer to the sample and the tip respectively. The sample voltage is indicated as $V$, with the corresponding energy $E = -eV$. This expression holds for $T = 0K$, where all the states below $E_F$ are occupied and all states above $E_F$ are empty. It is a good approximation for higher temperatures as well, as long as the thermal energy is much smaller than the relevant energy scales in the sample.

In most STM studies, the tip LDOS is assumed to be flat, and furthermore an s wave function is assumed for the tip state, for which the matrix element corresponds to $|\hat{M}|^2 = \exp (-2\kappa z_{tip})$ [40, 41]. This leads to the following expression for the tunneling current

\[
I \propto \int_0^{eV} \rho_s (E_{F,s} + E') \exp (-2\kappa z_{tip}) \, dE'. \tag{2.3}
\]
2.3. Spectroscopy and wave function imaging

Figure 2.2: An example of an $I(V)$ (a) and a $dI/dV$ (b) curve, measured on Mn-doped GaAs. (c-e) Energy diagrams explaining the three regimes in the $dI/dV$ curve.

In chapter 9 we describe in detail that $I \propto \exp(-2\kappa z_{\text{tip}})$ only holds for relatively large tip-sample distances, and we discuss the consequences of the deviations. For the argumentation in this chapter, the deviations are irrelevant.

The derivative of equation 2.3 with respect to $V$ gives a direct relation between $dI/dV$ and the LDOS of the sample (note that $E = -eV$)

$$\frac{dI}{dV}(eV) \propto \rho_s(E_{F,s} + eV) \exp(-2\kappa z_{\text{tip}}).$$

(2.4)

The LDOS of the sample and $dI/dV$ are directly proportional when the tip-sample distance is constant, and the LDOS is energetically resolved. This is used in scanning tunneling spectroscopy (STS).

Figure 2.2a and b show an example of an $I(V)$ and a $dI/dV$ curve respectively, measured on a p-type material (Mn:GaAs). Below $-0.2$ V, $|I|$ and $dI/dV$ increase with increasing $|V|$. This is due to tunneling out of the filled VB states (figure 2.2c). In the region between $-0.2$ V and 1.6 V, hardly any tunneling current flows, because the Fermi level of the tip is
aligned with the semiconductor band gap region (figure 2.2d). The features around 0.8 V and 1.4 V arise due to tunneling into the empty acceptor state, and will be discussed in section 2.6. Both $I$ and $dI/dV$ increase with $V$ for $V > 1.6$ V. This is due to tunneling into the empty CB states (Figure 2.2e).

There are several ways to obtain the $dI/dV$ spectroscopy data. For example, a lock-in technique can be used, where a $dI/dV$ image is measured simultaneously with the topography image using a lock-in amplifier. For this purpose, a modulation signal with a small amplitude and a high frequency is added to the bias voltage, and its response to the tunneling current is measured. The lock-in amplifier combines these two signals, and the output corresponds to the derivative $dI/dV$. However, we use a numerical method. We typically measure an $I(V)$ curve at every pixel on a two-dimensional grid (typically 256 × 256 pixels$^2$). The $I(V)$ curves are numerically differentiated after the actual measurement and in this way, we obtain a three-dimensional data set: $dI/dV (x, y, V)$.

An example of such a three-dimensional data set is shown in figure 2.3a. The yellow-red plane is the stabilization topography and the yellow-green cube is the corresponding spectroscopy data set. There are several ways to present the data:

(I, figure 2.3b) spatial distribution of $dI/dV$ at a certain voltage,
(II, figure 2.3c) voltage dependent $dI/dV$ section along a line,
(III, figure 2.3d) voltage dependent $dI/dV$ curve, averaged over several pixels, and
(IV, figure 2.3e) an equi-$dI/dV$ map. The latter is obtained by defining a $dI/dV$ value, and plotting the corresponding voltage.

A final remark related to this section concerns the $z_{tip}$ dependence in equation 2.4. We are interested in the LDOS, whereas we measure $dI/dV$, which is the product of the LDOS and a term that is dependent on the tip-sample distance. This leads to so-called topography cross-talk. There are methods to circumvent the influence of the tip-sample distance. For example, one can use the normalized conductance $dI/dV/(I/V)$ as defined by Feenstra [42], for which the $z_{tip}$-dependence cancels. However, the normalized conductance does not purely describe the LDOS [42]. Another possibility is to measure $\kappa$ simultaneously with the STS measurement [43], and correct the $dI/dV$ data for the topography cross-talk. This is a very elegant technique, but unfortunately impossible with the available measurement software (Matrix versions 1.0 to 2.2). We therefore choose the set-point such that there is minimal information in the topography image, and take the possible topography cross-talk in consideration during the data analyses.
2.3. Spectroscopy and wave function imaging

Figure 2.3: (a) Three-dimensional d$I$/d$V$ ($x, y, V$) data set (yellow-green), and the stabilization topography (yellow-red). (b-e) Several ways to present the data.
2. Theory

Figure 2.4: GaAs forms a zinc-blende crystal. (a) top view, (b) side view of the bulk and (c) side view of a cleaved surface.

2.4 The \{110\} surface of GaAs

In this thesis, we focus on III-V semiconductors, with a special interest in gallium arsenide (GaAs). We use a cross-sectional technique, exposing one of the \{110\} planes, which are the natural cleavage planes of GaAs.

GaAs has a zinc-blende crystal structure [44]. The (110) plane consists of zig-zag rows along the \([-110]\) direction, with alternating gallium and arsenic atoms (figure 2.4a). Dangling bonds are created at the surface due to the cleavage (figure 2.4b). The system relaxes into a 1×1 surface reconstruction, where the group III elements move into the surface and the group V elements move outward (figure 2.4c) [45, 46]. This is accompanied by a charge transfer and an energy shift; the empty group III surface states move above the CB edge, and the filled group V surface states move below the VB edge [47, 48]. At positive sample bias (empty state imaging, \(V > 0\)), the group III elements are imaged and at negative sample bias (filled state imaging, \(V < 0\)) the group V elements. The fact that the surface states lie outside the band gap leads to an unpinned Fermi level. The consequence of the unpinned Fermi level is described in the next section.

2.5 Tip-induced band bending (TIBB)

Due to the unpinned Fermi level of GaAs\{110\}, the bands in the semiconductor are locally bent by the presence of the metallic STM tip [38, 49, 50]. This phenomenon is called tip-induced band bending (TIBB) and is of crucial importance for the interpretation of the data.

The TIBB is schematically shown in figure 2.5. The curvature of the
2.5. Tip-induced band bending (TIBB)

Figure 2.5: Schematic energy diagram of the tip-induced band bending in n-type GaAs. (a) For \( V > V_{FB} \) the bands bend upward, (b) they are flat at \( V_{FB} \) and (c) bend downward for \( V < V_{FB} \).

Band bending is caused by local charges (ionized donors or acceptors or accumulated electrons or holes), which obey Poisson’s equation

\[
\nabla^2 \Phi = -\frac{\rho}{\epsilon_0 \epsilon_r}, \tag{2.5}
\]

with the potential \( \Phi \), the charge density \( \rho \), the permittivity of vacuum \( \epsilon_0 \) and the dielectric constant \( \epsilon_r \). Typically the electron energy is plotted, which is linked to the potential via

\[
E = -e \Phi. \tag{2.6}
\]

Figure 2.5 shows the three main TIBB situations. At voltages above the flat band voltage \( (V_{FB}) \), the bands bend upward (figure 2.5a). In this case, positive charges are present underneath the tip, either ionized donors for an n-type material or accumulated holes for a p-type material. At \( V_{FB} \) (figure 2.5b), the applied voltage balances the difference in tip work function \( (W) \) and the electron affinity \( (\chi) \), and the bands are flat. At voltages below \( V_{FB} \) (figure 2.5b), the bands bend downward and negative charges are present underneath the tip (accumulated electrons for an n-type material and ionized acceptors for a p-type material).

The TIBB can be calculated by a self-consistent Poisson solver. Feenstra developed a model to calculate the electrostatic potential in three dimensions for a hyperbolic tip near a semiconducting surface [49, 50]. Typically, the extension of the TIBB is only a few nanometer, both in the lateral directions \( x, y \) and in the vertical direction \( z \). An example of a TIBB calculation is shown in figure 2.6. Figure 2.6a shows a schematic of the tip and
2. Theory

![Diagram of tip and sample](image)

Figure 2.6: (a) Schematic of the tip and sample, defining the coordinate system. (b) Lateral extension of the calculated TIBB and (c) extension in the z direction.

sample, and defines the coordinate system. Figure 2.6b shows the lateral extension of the TIBB at \( z = 0 \) nm, and figure 2.6c the extension in the vertical direction at \( r = 0 \) nm. The external voltage for this calculation is 1.5 V, resulting in a maximum TIBB of 250 meV. The rest of the potential drops in the vacuum barrier. There is thus a scaling of roughly a factor of 10 between the external voltage and the TIBB in the sample. We call this scaling factor a lever arm.

The TIBB depends on many parameters, which can be varied in Feenstra’s model. The main parameters are the local doping concentration, tip shape, flat band voltage and tip-sample distance. Some parameters are known or can be determined experimentally, such as the doping concentration and flat band voltage (see chapter 9 for the latter), whereas others have to be estimated, such as the tip shape and tip-sample distance. The latter results in a relatively large error in the TIBB calculation; varying the parameters within realistic limits leads to a variation in the TIBB of a factor of 2. An example of the influence of the choice of parameters is given in chapter 6. This large error might seem problematic. However, it only adds a scaling factor; trends and relative quantities can be investigated accurately.

2.6 Imaging mechanisms

We already described the main features of the \( \frac{dI}{dV} \) spectrum in figure 2.2b. However, we did not yet discuss the peaks around 0.8 V and 1.4 V, which we postponed, because knowledge of the TIBB is required to explain these peaks.
2.6. Imaging mechanisms

There are two imaging mechanisms in STM depending on the polarity: filled state imaging at negative bias, and empty state imaging at positive bias. According to the standard tunneling theory (section 2.3), \( \frac{dI}{dV} \) is proportional to the LDOS in the sample, and the voltage where a peak in \( \frac{dI}{dV} \) appears corresponds directly to the energetic position of the addressed state. This is indeed true for metallic surfaces, where the bands are flat. However, the situation becomes more complicated for semiconducting surfaces, where the bands are bent. The two imaging mechanisms still exist, but the voltage where a peak appears does not directly correspond to the energetic position of the state. We describe the two imaging mechanisms for a p-type material, but the situation is similar for an n-type material.

Filled state imaging

Filled state imaging occurs at negative sample bias, and the electrons tunnel from the sample into the tip. Typically the flat band voltage is between 0.5 V and 1.5 V for tungsten tips on p-type GaAs (see chapter 9, maximum observed range is -0.4 V to 2.0 V). Therefore there is downward TIBB at negative bias. A peak in \( \frac{dI}{dV} \) appears when the acceptor level is aligned with the tip Fermi level \( (E_{F,\text{tip}}) \), which typically occurs at small negative voltages. At this condition, the electron of the filled acceptor \( A^- \) can tunnel into the tip. This is schematically shown in figure 2.7a for two tips that have a different work function \( \Phi_{\text{tip}A} \) and \( \Phi_{\text{tip}B} \) (indicated by the gray arrows), and thus a different flat band voltage. The applied bias voltage is indicated by the black arrows. The difference in flat band voltage has only a minor

Figure 2.7: Schematics for filled state imaging (a) and empty state imaging (b) for two tips, A and B, with different flat band voltages, and thus two different work functions \( \Phi_{\text{tip}A} \) and \( \Phi_{\text{tip}B} \).
2. Theory

effect on the position of the peak voltage.

Empty state imaging

Empty state imaging occurs at positive sample bias, and the electrons tunnel from the tip into the sample. In order to address the acceptor state in empty state imaging, it has to be empty ($A^0$). The transition from filled to empty occurs when the acceptor level is pulled through the Fermi level of the sample ($E_{F,s}$), which happens around the flat band voltage. This is schematically shown in figure 2.7b, again for tip A and tip B. The effect of the difference in flat band voltage is significant. For tip A, the peak appears at small positive voltages ($\sim 0.2\, \text{V}$) and for tip B at much larger positive voltages ($\sim 1.2\, \text{V}$), even though in both cases the same state, at the same energetic position in the band gap, is addressed. Therefore, the flat band voltage is of crucial importance for the interpretation of the $dI/dV$ data, and a procedure to extract the flat band voltage experimentally is given in the next section.

The effect of the tip work function on the position of the peak is much stronger in empty state imaging than in filled state imaging. The reason is that in empty state imaging, the acceptor level aligns with the Fermi level of the sample, whereas in filled state imaging it aligns with the Fermi level of the tip. In empty state imaging, the alignment occurs at a specific TIBB condition. A change in the tip work function changes the TIBB, and the original TIBB condition has to be restored in order to re-establish the alignment. In order to restore the same TIBB, the voltage has to be changed by exactly the same amount as the change in tip work function. There is thus a one to one relation between the change in $\Phi_{\text{tip}}$ and the change in the peak voltage. In filled state imaging, the change in $\Phi_{\text{tip}}$ also changes the TIBBB in the sample, which breaks the alignment of the acceptor level with the tip Fermi level. In this case, however, only the change in TIBB has to be overcome by the bias voltage in order to restore the alignment. This effect is only $\sim 10\%$ of the change in tip work function.

2.7 Extracting the flat band voltage

Loth et al. [51, 43] developed a method to extract the flat band voltage experimentally. This procedure is described in this section. We extended the procedure by including a few effects that Loth et al. neglected. These extensions are described in detail in chapter 9.

The method is based on measuring an $I(z_{\text{tip}})$ spectrum by changing the tip-sample distance ($z_{\text{tip}}$) and measuring the current ($I$). In our case we
2.7. Extracting the flat band voltage

Figure 2.8: (a) Topography image measured at 2.4V where we varied the current set-point. The current was 500 pA in the blue areas, 50 pA in the green areas and 5 pA in the yellow-red area. (b) cross sections through the image shown in (a) and the corresponding current image, averaged over the whole width of the image, showing the changes in the current set-point and the corresponding changes in the tip-sample distance.

change $I$ and measure $\Delta z_{\text{tip}}$, because it turned out to be more reliable. An example of such a measurement is shown in figure 2.8. In approximation, the tunneling current depends exponentially on the tip-sample distance, $I \propto \exp(-2\kappa z_{\text{tip}})$, see equation 2.1, thus

$$\kappa = \ln \left( \frac{I_1}{I_2} \right) / \left( 2(z_{\text{tip},2} - z_{\text{tip},1}) \right).$$  \hspace{1cm} (2.7)

Note that only the difference between $z_{\text{tip},1}$ and $z_{\text{tip},2}$ enters in the equation, thus the absolute tip-sample distance, which is unknown, cancels. $\kappa$ is the inverse decay length, which can be transformed into an effective barrier height $\Phi_B$ using $\kappa = \sqrt{2m_0\Phi_B}/\hbar$. This is indicated by the light red area in figure 2.9. The tunneling barrier is approximated by a trapezium that can be replaced by a rectangular barrier with the average height. The effective barrier height can be translated into the tip work function $\Phi_{\text{tip}}$, using geometrical arguments (see figure 2.9):

$$eV < E_g : \quad \Phi_{\text{tip}} = 2\Phi_B - \chi - E_g - eV + |\text{TIBB}|$$  \hspace{1cm} (2.8a)

$$eV > E_g : \quad \Phi_{\text{tip}} = 2\Phi_B - \chi - E_g + eV - \text{TIBB}$$  \hspace{1cm} (2.8b)

These equations hold for a p-type material, where the Fermi level of the
2. Theory

Figure 2.9: Schematic of the relation between the tip work function and the effective barrier height. See for details references [43, 51].

sample is close to the VB. Similar equations can be derived for an n-type material. We use the bulk values of 4.07 eV and 1.519 eV for the electron affinity $\chi$ and the band gap energy $E_g$ respectively [44, 52, 53].

The relation between the flat band voltage and the tip work function is straightforward. The flat band voltage is $-$ as the name implies $-$ defined as the voltage where the bands are flat. In order to establish this, the applied voltage has to balance the difference between the tip work function and $\chi + E_g$ in the sample

$$V_{FB} = \frac{1}{e} (\chi + E_g - \Phi_{tip}).$$ (2.9)

In chapter 9, we deliberately induce tip modifications, and measure the flat band voltage. We observe that the flat band voltage can change by $> 2$ V. For the example shown in figure 2.8, we find a tip work function of $(3.8 \pm 0.2)$ eV and a flat band voltage of $(1.8 \pm 0.2)$ V.

2.8 Effective mass approach

The effective mass approximation is a powerful approximation, especially for shallow dopants in semiconductors. Only a brief description is given here, more extended descriptions can be found in textbooks such as references [52, 54, 55, 56].

The basic idea is that the total potential can be divided into a periodic part ($\hat{H}_0$, describing the lattice) and a slowly varying part ($V_{imp}$, e.g. the donor potential),
2.8. Effective mass approach

\[ \hat{H}_0 + V_{\text{imp}}(\vec{r}) ] \psi(\vec{r}) = E \psi(\vec{r}). \]  

(2.10)

According to Bloch’s theorem, the wave function in a periodic potential (pure crystal) takes the form

\[ \phi(\vec{r}) = u_{nk}(\vec{k}) \cdot \exp \left( i \vec{k} \cdot \vec{r} \right). \]  

(2.11)

Here \( \vec{k} \) is the wave vector and \( u_{nk} \) is called a Bloch function, and has the same periodicity as the lattice

\[ u_{nk}(\vec{r} + \vec{a}) = u_{nk}(\vec{r}), \]  

(2.12)

with \( \vec{a} \) the lattice constant. The index \( n \) refers to the sub-band. The resulting Hamiltonian for the Bloch-part is

\[ \left[ \frac{\hat{p}^2}{2m_0} + \frac{\hbar}{m_0} \vec{k} \cdot \hat{p} + \frac{\hbar^2 \vec{k}^2}{2m_0} + V(\vec{r}) \right] u_{nk}(\vec{r}) = E_{nk} u_{nk}(\vec{r}). \]  

(2.13)

Here, \( \hat{p} \) is the momentum operator, \( m_0 \) the electron’s rest mass, \( \hbar \) Planck’s constant divided by \( 2\pi \) and \( V \) the potential. This Hamiltonian contains the properties of the host material.

However, we are interested in the properties of the dopant atom, assuming known host properties. We therefore focus on the Hamiltonian for the slowly varying part. Several assumptions and approximation are needed in order to come to the commonly used expressions e.g. for a shallow donor in the effective mass approach. The main approximations and assumptions that we use here are:

(i) only one sub-band is included, for donors it is the CB,
(ii) the potential is slowly varying compared to the periodicity of the lattice, and
(iii) only states and energies around \( k = 0 \) are included, where the CB can be approximated by a parabola.

More involved approximations exist [55], for example, more sub-bands are included to describe acceptors, and states at \( k \neq 0 \) are included for the description of e.g. silicon, which has an indirect band gap. However, for a donor in GaAs, these more involved approximations are not needed and the approximations as given above are sufficient. The wave function can then be written as the product of the envelope function \( \chi(\vec{r}) \) and the Bloch function around \( k = 0 \)

\[ \psi(\vec{r}) = u_{n0}(\vec{r}) \cdot \chi(\vec{r}). \]  

(2.14)
2. Theory

The Hamiltonian for the envelope function is

\[
\left[-\frac{\hbar^2}{2m_0m^*}\nabla^2 - \frac{e^2}{4\pi \epsilon_0 \epsilon_r |\vec{r} - \vec{r}_0|}\right] \chi(\vec{r}) = (E - E_c)\chi(\vec{r}), \quad (2.15)
\]

where we adopted the Coulomb potential around \( \vec{r} = \vec{r}_0 \) for the impurity potential. This Hamiltonian is analogous to the Hamiltonian for a hydrogen atom. The only difference is the effective mass \( m^* \) in the denominator of the first term in the Hamiltonian and the dielectric constant \( \epsilon_r \) in the second term. Both are unit-less. We can therefore use the solutions for a hydrogen atom, with scaled lengths and energies. The following expressions hold for the effective Bohr-radius \( a_B^* \) and the effective Rydberg energy \( E_{Ry}^* \), or binding energy \( E_b \), in units of the Bohr-radius and Rydberg energy of the hydrogen atom

\[
a_B^* = \frac{\epsilon_r}{m^*} a_B = \frac{\epsilon_r}{m^*} 0.53 \text{ Å} \quad (2.16a)
\]

\[
E_{Ry}^* = \frac{m^*}{\epsilon_r^2} E_{Ry} = \frac{m^*}{\epsilon_r^2} 13.6 \text{ eV} \quad (2.16b)
\]

These expressions are surprisingly accurate for many substitutional donors in GaAs. For donors, such as Si, in GaAs we find \( a_B^* = 10.3 \text{ nm} \) and \( E_{Ry}^* = 5.3 \text{ meV} \) \( (\epsilon_r = 13.1 \) and \( m^* = 0.067 \) for the CB), in almost perfect agreement with experimental results. This justifies the approximations and assumptions that were made; the effective Bohr-radius contains many units cells, i.e. the potential is slowly varying, and the effective Rydberg energy is much smaller than the band gap, justifying the use of only one band. For non-Coulombic acceptors, such as Mn in GaAs, which has been studied in this thesis, more involved descriptions are needed, that are for instance based on tight binding calculations [57, 58].
Chapter 3

Experimental techniques

3.1 Introduction

For the experimental investigations we use a commercial Omicron low-temperature STM (LT-STM). We use a cross-sectional technique (cross-sectional STM, X-STM). We cleave the samples in ultra-high vacuum (UHV) and image the cleaved surface. This technique has two main advantages. First, cleaving exposes a clean and atomically flat surface, without the need of heating or sputtering, which could damage, or at least change, the structure. The second advantage is that with X-STM, the cross-section is imaged, which allows a look inside a grown structure.

3.2 UHV system

The surface of the freshly cleaved sample is highly reactive due to the dangling bonds, therefore UHV is needed to suppress surface contamination. Our UHV system consists of three chambers, and the base pressure of the STM chamber is below $10^{-11}$ mbar. This pressure, combined with the additional cryo-pumping at low temperatures, is sufficient to preserve a sample without visible contamination for several weeks.

In order to obtain such low pressures in the STM chamber, additional (ultra) high vacuum chambers are needed: a load lock with a base pressure of $\sim 10^{-8}$ mbar and a preparation chamber with a base pressure of $10^{-11}$ to $10^{-10}$ mbar. The whole setup is schematically shown in figure 3.1, where the different chambers are indicated. During the sample and tip preparation, the turbo pump evacuates the load lock and/or the preparation chamber. During the measurements the turbo pump is switched off to reduce mechanical noise, and the preparation chamber and STM chamber are
Figure 3.1: Schematic image of the UHV system for the LT-STM. The different parts are indicated. See the text for details.
3.3. Sample preparation

The samples and tips are loaded into the load lock, while the preparation chamber and the STM chamber remain at UHV. After the load lock is pumped down to $10^{-8}$ mbar, the samples and tips are transferred to the preparation chamber, where the preparation steps described in the following sections are performed. Afterwards the samples and tips are transferred to the STM chamber. First a tip is loaded in the STM unit and finally a sample is cleaved and loaded in the STM unit. The tip is manually positioned above the sample by piezo steppers, while monitoring the position with a microscope which is attached to a CCD camera. The tip can be placed $\sim 200$ $\mu$m above the surface, with a lateral position control of $\sim 20$ $\mu$m. The approach of the remaining $\sim 200$ $\mu$m is done with an automated approach.

In order to exchange the tip, we unfortunately have to unload the sample. This is a disadvantage of the Omicron LT-STM. During the measurement, the cold sample is in a cold environment, completely shielded from the warm parts of the UHV system, whereas the environment is at room temperature after unloading the sample. Therefore the cold sample acts as a cryo pump and the sample surface gets contaminated. Thus effectively we cannot exchange the tip without losing the sample.

The low temperatures are achieved by a cryostat consisting of two concentric baths: the outer one is usually filled with liquid nitrogen and the inner one with either liquid nitrogen or liquid helium for measurements at 77 K and 5 K respectively. The STM unit is pressed against the cryostat during cool-down. Because the whole STM unit is cooled down, both the sample and the tip are at low temperature during the measurement. A heater is available for variable temperature measurements, although there is no feedback loop for active temperature control. The heating power has to be adjusted manually to reach the desired temperature. We used this heater only for one measurement (chapter 7), where we were able to measure between 5 K and 50 K. After the cool-down the STM is released and hangs in springs. The STM unit is further decoupled from the rest of the UHV setup by eddy current damping, and the whole UHV setup is decoupled from the building by an active damping system.

3.3 Sample preparation

The samples are rectangular pieces, cleaved from a wafer. Typical sizes of the samples are $3.5 \times 8$ mm$^2$. The thickness of a wafer is typically 360 $\mu$m, which is too thick to achieve atomically flat surfaces after cleavage. Therefore the samples are thinned down to a thickness of about 120 $\mu$m by me-
Figure 3.2: On top of the sample gold contacts are deposited (a). A small scratch is made, which acts as the nucleation for the cleavage. After the sample is clamped, the scratch is just above the clamping bars (b).

Mechanical grinding with aluminum oxide powder. Since it is necessary to have good electrical contacts between the sample and the holder, a germanium-nickel-gold or nickel-zinc-gold contact is deposited on top of the sample for respectively n- or p-type samples, see figure 3.2a. Afterwards the sample is annealed (at 300 °C for 90 s, in N₂-atmosphere), during which the germanium or zinc diffuses into the sample converting the Schottky contacts into Ohmic contacts.

Before the samples are clamped in the holder, a small scratch is made. This scratch is the nucleation for the cleavage, which is performed later in the UHV chamber just before the measurement. After clamping, the scratch is just above the metal clamping bars, as shown in figure 3.2b. Thin slices of indium are placed between the sample and the clamping bars. The sample is heated above the melting point of indium and the screws are tightened. The indium provides an even pressure on the sample and a fixed electrical contact.

After loading the holder with the mounted sample into the preparation chamber of the UHV system, the samples are baked at a temperature of 150 °C to 300 °C for half an hour in order to remove any contamination. After the baking process the samples are transferred to the STM chamber and just before the measurement they are cleaved by pushing the sample gently against a ridge until the sample breaks.

3.4 Tip preparation

The tips are electro-chemically etched from polycrystalline tungsten wire, with a diameter of 250 μm. A piece of this wire is placed in a carrier
3.4. Tip preparation

The tip holder consists of a holder and a carrier, which is held in place by a magnet. (b) Schematic of the etching setup.

The top 2 mm of the tungsten wire is put in a 2 molar KOH solution for etching and a platinum-iridium (90% / 10%) spiral acts as a counter electrode, see figure 3.3b. A voltage of 6.3 V is applied over the tip and the spiral, which drives the oxidation. In the etching process the tungsten dissolves:

$$W + 2OH^- + 2H_2O \rightarrow WO_4^{2-} + 3H_2.$$  \hspace{1cm} (3.1)

A glass plate is placed between the tip and the spiral to prevent the $H_2$ bubbles to disturb the flow around the tip. The reaction product $WO_4^{2-}$ drops down along the tungsten wire, shielding the lower part of the wire. For this reason the reaction velocity, and thus the etching process, is the highest at the meniscus. This induces “necking” of the wire at the meniscus and eventually the tip will break at the neck. The current delimiter interrupts the etching process within microseconds after the drop-off, creating very sharp tips.

The carrier is placed into the central part of the holder, and is held in place by a small permanent magnet (figure 3.3a). The complete tip holder is then loaded into the preparation chamber. The tips are baked in the same way as the samples and afterwards they undergo a glowing procedure. A small molybdenum plate is brought into contact with the side of the tip. Then a current of a few ampere is sent through this contact so the tip starts to glow orange, indicating that the temperature is about 900 to 1100 °C. At this temperature the oxide layer will be partially removed. As a next step the tips are treated with an argon bombardment, to mechanically stabilize the tip. The final preparation step is characterization of the tip.
3. Experimental techniques

by measuring the field emission current. We approach the tip with a metal sphere, until the distance between the tip apex and the metal sphere is a few millimeters. A few hundred volts is applied over the metal sphere and the tip, so a field emission current of 1 up to 50 nA is reached. The procedure is repeated a few times to check the reproducibility. Field emission is only possible when the tip is sharp and the reproducibility and the stability of the field emission current are measures for the stability of the tip. At this point the tip is ready to be placed into the STM unit.
Chapter 4

Rings of ionization

4.1 Introduction

In this chapter we report on the manipulation of single electrons on a single donor in a dynamic manner, without a structural modification. This process is a pure ionization process, and this opens the possibility to study donor-donor interactions and to measure the binding energy of individual donors.

We will demonstrate this effect on the well known system Si:GaAs, which has been studied by several groups [23, 33, 35, 36, 59]. General observations are Friedel oscillations (charge density oscillations) at negative bias [35] and positively ionized donors at high positive voltages [23]. The additional positive charge causes the bands to drop and results in an enhanced tunnel current, which is visualized by STM as a protrusion in the topography images. Our system behaves similarly at voltages far from 0 V, and we use this to identify the observed features to be Si donors. However, we observe an extra feature. At relatively low positive voltages we observe sharp circular features around the donors, that we ascribe to the ionization of the donor due to the TIBB. In Si doped GaAs with a doping concentration of $\sim 10^{18} \text{ cm}^{-3}$ we find that the lateral extension of the TIBB is of the same order as the radius of the tip apex [49]. For studying the ionization process, the lateral extension of the TIBB needs to be in the order of a few nanometer and therefore ultra sharp tips are needed.

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4. Rings of ionization

Figure 4.1: (a) constant current topography image at 1.25 V and 20 pA. Three donors are surrounded by a disk of enhanced topographic height. The atomic corrugation is not disturbed by the disks. (b) Cross-sections through another donor at different voltages. At the edge of the disk a jump in the topographic height is seen, indicated by the arrows.

4.2 Ionization of single donors by the STM tip

Figure 4.1a shows a constant current topography image at 1.25 V and 20 pA. The donors are identified by their topographic contrast at negative voltages, where Friedel oscillations appear [33, 35], as well as by their spectroscopic behavior at positive and negative voltages (see chapter 6). Contrary to former measurements on Si donors in GaAs, a bright disk around the donor is visible, and the atomic corrugation is not distorted by the disk. The size of the disk depends on the applied voltage, as shown in figure 4.1b. The section through the donor shows that the edge of the disk appears as an instantaneous step, indicated by the arrows in figure 4.1b, with a width of < 0.5 Å, indicating that the disk is not related to LDOS effects. We will show that the step in the topography images is due to ionization of the donor.

We start our discussion with the description of the ionization mechanism, which is schematically shown in figure 4.2. When the tip is laterally far away from the donor (figure 4.2a), the bands on top of the donors are not influenced by the tip and are flat (figure 4.2b). We perform our measurements at 5K, and therefore the thermal energy is much smaller than the ionization energy and the donors are neutral. If the tip is close to the
4.3 Dependence of the ionization on radial distance

donor, there is TIBB at the position of the donor (figure 4.2c). At a posi-
tive sample bias, the bands bend upward and the donor level is lifted as
well (figure 4.2d). At a critical distance, the TIBB is such that the donor
level aligns with the onset of the CB in the bulk, and the donor ionizes.
The Coulomb field of the ionized donor causes the bands at the surface
to drop, therefore the amount of states available for tunneling enhances
(figure 4.2e). This results in an instantaneous enhancement of the tunnel
current, leading to a retraction of the tip in the constant current mode, as
seen in figure 4.1b. A similar effect was reported for the comparable system
of Mn acceptors in InAs by Marczinowski et al. [60].

The ionization process depends on the TIBB at the position of the
donor, which can be manipulated in three different manners. (i) Changing
the radial distance between the tip and the donor, simply by moving the tip
laterally. (ii) Increasing the applied voltage, which enhances the TIBB. At
sufficiently low voltage the donor is neutral, and above a threshold voltage
it is ionized. (iii) Reducing the tip sample distance, which also enhances
the TIBB. All three methods have been experimentally explored in detail
and quantitatively agree with our calculations, as described in the next
sections.

4.3 Dependence of the ionization on radial dis-
tance

The ionization by laterally approaching the donor can be seen in constant
current topography images. The edge of the disk in figure 4.1a represents
the ionization event, and the donor is ionized inside the disk, and neutral
outside the disk. The disk diameter depends on the depth of the donor
below the surface [61], which we discuss in chapter 5.

4.4 Dependence of the ionization on the sample
voltage

The proposed ionization mechanism predicts larger disks for higher volt-
ages, as the extension and amount of the TIBB is larger for higher voltages.
This is experimentally investigated and confirmed by voltage dependent to-
pography images and STS. Figure 4.3a shows the stabilization topography
image of the STS data set shown in figure 4.3b to d. In the differential
conductance images, the edge of the disk appears as a ring. Figure 4.3b
and 4.3c show such a ring measured at 0.31 V and 0.49 V respectively. The
Figure 4.2: Schematic representation of the ionization mechanism. When the tip is laterally far away from the donor (a), the bands on top of the donors are flat (b) and the donor is neutral ($D^0$). As the tip approaches the donor with a positive sample bias (c), the bands are lifted due to the TIBB (d). When the donor level aligns with the CB in the bulk, the electron escapes and the donor ionizes ($D^+$). (e) The Coulomb field of the ionized donor increases the number of states available for tunneling, indicated by the red areas, and therefore the tip retracts when operated in the constant current mode.
4.4. Dependence of the ionization on the sample voltage

Figure 4.3: (a) Topography image of a donor at a voltage of 1.5 V and a current of 3.15 nA. (b) and (c) Spatially resolved $dI/dV$ maps at the indicated voltages. Higher differential conductivity is seen as a ring around the donor center, the ring diameter increases with voltage. The black line indicates the position of the $dI/dV$ section in (d). The hyperbola in (d) shows the evolution of the ring with $V$. The white line is a TIBB contour at 0.155 eV. (e) Calculated TIBB as a function of voltage and position.
4. Rings of ionization

Images confirm that the diameter increases with voltage. Image (d) shows a cross-section through the spectroscopy map along the black line in image (b). The hyperbola of higher differential conductivity corresponds to the diameter of the ring as a function of voltage. According to the proposed mechanism the donor ionizes at a certain TIBB, therefore we expect the ring to follow a line with constant TIBB.

We calculate the TIBB in 3D using the procedure described in reference [49]. The resulting TIBB as a function of distance to the center of the tip and voltage is shown in figure 4.3e. To extract the flat band voltage, which is an essential parameter in the calculations, we measured the effective barrier height [43], see for details chapter 9. For this data set we found a flat band condition of \(-1.1 \pm 0.1\) V. For other measurements obtained with a different tip, we find other flat band conditions, and we observe the onset of the hyperbola at different voltages, consistent with the difference in flat band condition. For the measurement shown in figure 4.3 the ring follows a calculated TIBB contour of 155 meV.

4.5 Dependence of the ionization on the tip-sample distance

As a next step we changed the TIBB on top of the donor by varying the tip-sample distance. The experimental result is shown in figure 4.4. The disk diameter was extracted from topography images, where the current set-point was varied between 5 pA and 3 nA, while the bias voltage remained constant at 0.4 V. The resulting variation of the tip sample distance is almost 3 Å in our experiment. Again, we performed TIBB calculations to quantitatively compare them with the experimental disk diameters. In order to make this analysis, the absolute distance between tip and sample \((z_{\text{tip}})\) has to be known. However, in STM only the relative change, \(\Delta z_{\text{tip}}\), is known accurately. We assumed a typical tip sample distance of 5 Å at 20 pA and 0.4 V [38, 62, 63]. Varying this value leads to a horizontal shift of the data points in figure 4.4g with respect to the calculated lines. We find that the data points follow a TIBB contour of 145 meV. We measured the voltage dependence of this very same donor with the same tip (figure 4.4h), which shows a very similar TIBB value of 150 meV. Important to note is that we used the same set of parameters in both calculations. The good agreement between both approaches supports the proposed ionization mechanism.
Figure 4.4: (a-g) Dependence of the ring radius on the tip-sample distance. The images are 8 nm × 8 nm. The TIBB contours (red lines) are added to the experimental data points (black dots). (h) Voltage dependence of the same donor as in (a) to (g), measured with the same tip.
4. Rings of ionization

4.6 Conclusion

We have shown that the charge state of individual donors can be precisely controlled by the STM tip in a dynamic manner. The dependence of the ring diameter on the voltage and the current set-point proves that the donor state can be ionized by moving the tip laterally, enhancing the voltage or reducing the tip sample distance. Manipulating the charge of individual donors opens new possibilities, e.g. studying donor-donor interactions and measuring the binding energy of individual donors.
Chapter 5

Enhanced binding energy of dopants below the \{110\} GaAs surface

5.1 Introduction

The binding energy $E_b$ is one of the crucial properties of dopant atoms in semiconductors. The dopants should have a sufficiently low $E_b$, such that they act as donors and acceptors, which can easily be ionized at room temperature to provide free carriers in the CB or VB respectively. Even though it can still be a challenge to find good doping elements especially for new semiconductor materials, e.g. a shallow acceptor for gallium nitride [44] and magnetic impurities [64], appropriate bulk dopants have been found for the commonly used materials such as Si and GaAs. Having large binding energies, deep level defects were a problem because they act as traps that reduce the carrier density. Therefore the binding energy is of crucial importance to characterize a dopant atom. The binding energy in nanoscale devices has become a matter of research in the recent years. Experimental efforts have been taken to measure $E_b$ of dopants as a function of the device dimensions [8, 9, 11, 65] revealing a slight increase for nanoscale devices. In these experiments, the precise positions of the dopants with respect to the interfaces were not known.

Figure 5.1: Donor binding energy as a function of depth below the surface in the effective mass approach. Including the effect of image charges due to the vacuum (solid gray) causes an increase compared to the case where image charges are neglected (dashed black). Nevertheless the overall effect is a reduction towards the surface.

Effective mass theory of Coulombic impurities predicts a reduction of $E_b$ close to a barrier [66], shown by the dashed black line in figure 5.1. However, for low dimensional systems with a higher dielectric constant than the surrounding material, an enhancement is expected. This is due to the effect of image charges (also called dielectric confinement), as was shown by the tight binding method for quantum rods [67] and by density functional theory (DFT) calculations for nanocrystals [68]. However in case of the semi-infinite semiconductor-vacuum interface, the image charges cause a minor effect (figure 5.1, solid gray), and the calculations show the expected reduction of the binding energy towards the surface. Contrary, DFT calculations that include the surface reconstruction, predict a deep state for Si donors in the first layer of GaAs(110), corresponding to $E_b \approx 0.5\,\text{eV}$ [46], which was attributed to the dangling bond of the surface donor. These calculations are only done for Si donors in the surface layer and not for subsurface layers.

In this chapter we present a method to measure the binding energy of individual dopants close to a semiconductor surface. We investigated

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1Calculations performed by prof.dr. Peter Maksym and dr. Mervyn Roy, department of Physics and Astronomy, University of Leicester
two technically important systems: the Si donor and the Mn acceptor in GaAs. For Si donors, we measure the threshold gate voltage $V_{th}$ that is needed to ionize the individual donors with the STM tip [69]. From $V_{th}$ we can estimate the binding energy and show that it gradually increases towards the surface. In case of Mn acceptors, we use the empty state wave function as a landmark, and also in this system we find an enhancement of the binding energy towards the surface.

5.2 Enhanced binding energy of Si donors

In this section we focus on Si donors underneath the GaAs{110} surface, because their properties and contrast in STM and scanning tunneling spectroscopy (STS) are well understood [23, 35, 36]. Furthermore Si in GaAs is the model hydrogenic donor. In chapter 4, we showed that we can ionize the individual donors by the electric field induced by the STM tip (i.e. TIBB). In this chapter we use the ionization rings to measure the binding energy for donors in different depths below the surface.

The ionization process has been characterized quantitatively with respect to the sample voltage and tip sample distance in chapter 4 [69], and was also observed for Mn acceptors in InAs [60]. It was shown that each donor ionizes at a specific TIBB of $\sim 150$ meV, which varies from donor to donor. We extracted the voltage dependent diameter of the rings surrounding the donors. The result in figure 5.2b shows that the ring diameter increases with voltage. The error bars reflect the spectroscopic resolution. When the sample voltage is smaller than the threshold voltage $V_{th}$, the TIBB is not sufficient to ionize the donor even when the tip is located directly on top of the donor.

In order to experimentally investigate the depth dependence of the binding energy, we first determined the depth of each donor below the surface. Typically we can image dopants up to ten monolayers below the surface ($\sim 2$ nm, 2 Å per layer) in topography, and in spectroscopy we can image dopants that are even a bit deeper below the surface. For the depth identification we use the height amplitude and the odd-even symmetry [23]. It is assumed that the height contrast of the donor decreases monotonically with increasing depth below the surface. We can determine whether the donor is in an even or an odd layer below the surface by looking at the symmetry with respect to the GaAs lattice. Si donors in GaAs replace a Ga atom and therefore a donor in an odd layer is located underneath a surface Ga atom, e.g. atomic layer (AL) 3, and a donor in an even layer is located in between two Ga surface atoms, e.g. AL 4, see figure 5.3a. At positive polarity, the
5. Enhanced binding energy of dopants below the \{110\} GaAs surface

Figure 5.2: (a) $dI/dV$-map at 0.24 V, obtained on the \{110\} surface of Si:GaAs showing the rings of ionization around the Si donors. The numbers in brackets refer to the layer in which the donor is situated, counting the surface layer as 1. (b) Voltage dependence of the ring radius. The lines are added to guide the eye. (c) The onset of tunneling into the bulk CB (green dots) and $V_{th}$ (open red dots) for $D_1$ to $D_5$, where the horizontal axis represents the depth of the donor below the surface.
5.2. Enhanced binding energy of Si donors

Ga sub-lattice is imaged (section 2.4), thus donors in an odd layer have an even symmetry with respect to the Ga sub-lattice and dopants in an even layer have odd symmetry. Note that we count the surface layer as 1. In this way, we can order all the dopants according to their depth below the surface with monolayer precision. An example is given in figure 5.3b.

Applying this method to the donors in our measurements shown in figures 5.2 and 5.4, we find that donors deeper below the surface have a lower $V_{th}$. This is clearly seen in the $dI/dV$-maps taken at different voltages shown in figure 5.4a to 5.4c. The rings of ionization for the donors in layer 5 and 6 (figure 5.4a) appear already at 0.09 V, but a much higher voltage, up to $\sim$ 1 V, is needed to ionize the donors closer to the surface (figure 5.4c). The same dependence of $V_{th}$ on depth is experimentally observed in figure 5.2c, and $V_{th}$ from both data sets are listed in figure 5.5a. $V_{th}$ differs between figures 5.4 and 5.2 by $\sim$1 V for donors at the same depths due to differences in the flat band condition. Note that the onset of tunneling into the bulk CB (green dots in figure 5.2c) is at a constant voltage for all donors.

We interpret our data in the following way. As the TIBB decays monotonically into the bulk, its effect is always stronger for donors closer to the surface than for donors deeper in the material. We therefore expect that a donor close to the surface ionizes at a lower TIBB, i.e. a lower sample
5. Enhanced binding energy of dopants below the \{110\} GaAs surface

Figure 5.4: (a) to (c) Voltage dependent dI/dV-maps, measured with a different tip than the data set shown in figure 5.2. All three images are measured on the same area of the sample. The image size is $48 \times 48$ nm$^2$. The layer in which the donor is situated is indicated, counting the surface layer as 1. The rings of ionization clearly appear at lower voltages for donors deeper below the surface. (d) to (f) Schematic energy diagram including the TIBB in the homogeneous approach.
Figure 5.5: (a) $V_{th}$ relative to the flat band voltage ($V_{FB}$), (b) the corresponding TIBB at the donor position and (c) the estimated binding energy (see text for details). The squares and stars refer to the measurement shown in figure 5.4 and figure 5.2 respectively. The solid lines are added to guide the eye.
5. Enhanced binding energy of dopants below the \{110\} GaAs surface

voltage, than a donor that is located deeper below the surface. As we observe the opposite in our experiment, the binding energy must be enhanced for donors close to the surface. In a homogeneous model, where the donor level is rigidly shifted with the bands, the binding energy would correspond to the TIBB at the donor position (figure 5.4d to f). A large fraction of the externally applied voltage drops across the vacuum barrier; a sample voltage of \(\sim 1\) V corresponds to a TIBB of \(\sim 150\) meV as is shown in figure 5.5a and b [49]. The scatter of the data points in figure 5.5 is due to the Coulomb interaction of the randomly distributed donors, giving rise to local fluctuations of the potential. In the next paragraph we discuss how to derive the binding energy from the TIBB.

Due to the ultra sharp tips that we use [69], the TIBB extends in the bulk less than the bulk Bohr radius of Si in GaAs of 10.3 nm. Instead of a rigid shift of the donor level, the TIBB “squeezes” the Coulomb potential of the donor, as shown in figure 5.6a. The red dotted line represents the TIBB and the solid black line depicts the bare Coulomb potential. The superposition of the TIBB and the Coulomb potential is represented by the blue dash-dotted line, and is shown in 3D in the inset. The donor potential is squeezed by the TIBB, and therefore its energy level is shifted upward, see figure 5.6b. When this shift equals the binding energy and the state becomes resonant with the conduction band in the bulk, the donor ionizes. The magnitude of this shift can be estimated by the overlap between the wave function of the donor and the TIBB: \(\Delta E = \int \Psi \cdot \text{TIBB} \cdot \Psi^* d^3r\) [70]. The TIBB calculation contains a number of assumptions (e.g. tip shape, tip-sample distance) resulting in an uncertainty in the order of a factor of 2. The bigger challenge is to find the correct \(\Psi\). As a first guess, we use the 1s wave function of the bulk donor and modify the Bohr radius according to our measurements. The extension of the LDOS of the donors as observed in our STS data is indicated by the dashed blue line in figure 5.2b. It decreases by a factor of \(\sim 2\) for donors closer to the surface, corroborating the enhanced binding energy. The donor LDOS as measured in the STS is a projection of the real 3D wave function – where the real wave function as well as the details of the projection are not known [71]. Thus the measured extension does not directly equal the Bohr radius, but we assume that the extension of the 3D wave function scales similarly as the contrast we observe experimentally, and thus reduces by a factor of \(\sim 2\) for donors near the surface. The deepest donors that are visible, ionize at a low TIBB, as expected for a bulk like donor, see figure. 5.5b. We therefore assume that those donors have the bulk Bohr radius of 10.3 nm. We scale the Bohr radius by a factor of up to 2 for donors closer to the surface to extract an
5.2. Enhanced binding energy of Si donors

![Graph showing the comparison of bare Coulomb potential, TIBB, and their superposition.](a)

**Figure 5.6:** (a) Comparison of a bare Coulomb potential (solid black line) with the TIBB (red dotted line), where the tip is located on top of the donor. The blue dash-dotted line represents the superposition of the Coulomb potential and the TIBB, which is shown in 3D in the inset. (b) There is an additional lever arm between the TIBB and the binding energy.
5. Enhanced binding energy of dopants below the \{110\} GaAs surface

**estimate** of the binding energy as a function of depth below the surface.

The result is plotted in figure 5.5c. Keeping the discussed limitations of our approach in mind, we find that the estimated binding energy increases from a bulk-like value for donors located 1.2 nm below the surface (6 atomic layers) to \(\sim 40\) meV for the donors close to the surface. Note that the samples are doped two orders of magnitude above the metal-insulator transition. This explains the observed \(E_b\) of \(\sim 1\) meV for the deeply buried donors, which is smaller than the bulk value of 5.6 meV for isolated donors [44, 52].

The enhanced binding energy towards to surface is surprising. DFT calculations predict \(E_b \approx 0.5\) eV [46] for a Si atom in the surface layer of GaAs(110). This was attributed to the half filled dangling bond. Therefore this calculation does not explain the observed gradual increase. Effective mass theory of Coulomb impurities near a vacuum barrier predicts a reduction of the binding energy, see figure 5.1, and thus does not describe donors close to surface particularly well. Including the effect of image charges (solid red line) increases the binding energy compared to the situation where image charges are neglected (dashed black line). However, for a semi-infinite semiconductor, the overall effect is a reduction of the binding energy towards the surface. There are indications that the effective mass theory fails close to the surface. DFT calculations show that the dielectric constant is reduced near the surface [72]. Moreover, the broken symmetry and buckling distort the lattice at the surface, inducing a strain field, which decays on a roughly similar length scale as the enhanced binding energy [73, 74]. This might invalidate single-band effective mass theory and require a multi-band theory. Furthermore, for distances smaller than the Bohr-radius, the donor might couple with the surface states, or with the vacuum barrier. These effects are expected to affect the binding energy for donors close to the surface [65, 75]. We can only speculate whether these are the true reasons for the enhanced binding energy or that other effects are involved.

Clearly, the effective mass theory fails for donors close to a vacuum barrier. Other methods, such as tight binding methods or DFT calculations, are not applicable either, due to the large Bohr-radius of 10.3 nm for Si in GaAs. State-of-the-art tight binding calculations can cope with a few thousand atoms, corresponding to a cube with \(\sim 4\) nm edges [57], and for a DFT calculation, this volume is even one order of magnitude smaller. Calculating a donor in GaAs requires therefore too much computer power, and is nowadays not possible with existing numerical simulations.
5.3. Enhanced binding energy of Mn acceptors

For the Mn acceptor in GaAs, we also find an enhanced binding energy, which is described in this section. We perform our STM measurements at 5 K on Mn:GaAs samples with a doping concentration of $10^{18}$ cm$^{-3}$, grown by molecular beam epitaxy (MBE).

Figure 5.7a shows an $I(V)$ spectroscopy image at 1.65 V, showing in total seven Mn acceptors in different depths below the surface. The typical bow-tie shape is clearly visible [29]. The depth of the Mn atoms was determined following reference [76] and is indicated in the image in AL below the surface, counting the surface layer as 1. The contrast of the deeply buried acceptors (AL 13 and 14) is very weak (note the non-linear scale bar); the contrast is much stronger for Mn atoms closer to the surface and we observe the known breaking of the symmetry towards the surface [77].

The Mn acceptors induce several peaks in the $dI/dV$ spectroscopy curves. In the analysis of the Mn binding energy, we focus on the peaks around $+1.5$ V, see figure 5.7b. We first discuss the energetic position of the peaks, and towards the end of this section we discuss the presence of three peaks, instead of one peak. These peaks arise from tunneling into the empty state Mn wave function (section 2.6). In order to address the empty state wave function, we have to meet two requirements. First we have to be in the empty state imaging mode, i.e. $V > 0$ V. Secondly the Mn acceptor has to be neutral. The transition between a negatively charged acceptor
5. Enhanced binding energy of dopants below the {110} GaAs surface

Figure 5.8: The peak position for acceptors deeper below the surface (b) is located at a voltage further away from the flat band voltage, and thus at a larger total downward TIBB, compared to acceptors close to the surface (a). Nevertheless, the TIBB at the acceptor position is smaller for acceptors deeper below the surface.

to a neutral acceptor occurs when the acceptor level is pulled through the Fermi level in the sample, which happens around the flat band voltage. We thus expect to observe the empty state Mn peaks around $V_{FB}$.

For the measurements shown in this section, we determined $V_{FB}$ to be $(2.5 \pm 0.5) \text{V}$ by measuring $z_{tip}(I)$ (see section 2.7 and chapter 9), which is $\sim 1 \text{V}$ above the Mn induced peaks. We thus observe the empty state peaks at downward TIBB, which leads to the conclusion that the binding energy must be enhanced. The schematic energy diagram in figure 5.8 shows that

$$E_b = \Delta E_{F-VB} - \text{TIBB},$$

where $\Delta E_{F-VB}$ corresponds to the energy difference between the Fermi level and the VB in the bulk. This is an unknown parameter, which adds a constant offset to our data. We choose $\Delta E_{F-VB} = 25 \text{meV}$, such that the binding energies approach the bulk value of 113meV for the deepest Mn atoms. Note that there is downward TIBB, thus TIBB < 0.

The peak positions are extracted experimentally by fitting the d$I$/d$V$ curves with Gaussians [78], where we use the negative differential conductivity as a landmark to order and count the peaks, and are shown in figure 5.9a. The peaks of Mn atoms close to the surface appear at a higher voltage, i.e. closer to $V_{FB}$ and thus at a smaller downward TIBB compared to the Mn atoms deeper below the surface. However, figure 5.8 shows that the TIBB at the acceptor position at the peak voltage is smaller for acceptors deeper below the surface, indicating a monotonic increase of the
binding energy towards the surface. By calculating the TIBB in 3D at the peak voltages, we extract the peak position relative to the VB, i.e. the binding energy, for all the acceptors in the measurement and the result is shown in figure 5.9b [78].

The enhanced binding energy of Mn atoms towards the surface is confirmed by an additional, more independent measurement, where the dependence of the peak position on the tip-sample distance was determined. We performed spectroscopy on the same area of the sample with the same tip, with three different current set-points of 2.5 nA, 250 pA and 25 pA. Effectively we change the tip-sample distance by 2 times 1 Å, while keeping the other parameters the same. By changing the tip-sample distance, we change the TIBB. Due to the change in TIBB, the peak positions shift, and from the sign of the shift we can prove whether there is upward or downward TIBB at the peak voltage, independent of the determination of the flat band voltage.

We performed these measurements on a MBE-grown Mn:GaAs sample, with a Mn doping concentration of $10^{19}$ cm$^{-3}$. An $I(V)$ spectroscopy image at 1.17 V is shown in figure 5.10a. Several Mn dopants are visible and their depth below the surface in AL is indicated. Close to three Mn atoms in layer 5, indicated by AL 5*, there are deeply buried Mn atoms present, indicated as Mn (deep). They hybridize with their neighboring Mn dopant, and therefore we focus our analysis on the other mananases, which are located in AL 2, 3, 4 and 5.

Figure 5.10b shows $dI/dV$ spectra of the Mn atom in AL 2 for the three different current set-points. We averaged the spectra within a box of 10 $\times$ 7 pixels (2.3 nm $\times$ 1.6 nm). Clearly, the peak positions depend strongly on the
5. Enhanced binding energy of dopants below the \{110\} GaAs surface

Figure 5.10: (a) $I(V)$ spectroscopy image (15 nm × 14 nm) at 1.17 V showing several Mn atoms. The depth below the surface in AL is indicated. The set-point of the stabilization topography was 2.0 V and 2.5 nA. (b) Spectra of the Mn in layer 2. The Mn-induced peaks in the band gap shift when changing the current set-point. (c) to (e) Schematic explaining the voltage shift of the peaks with $z_{tip}$. When increasing $z_{tip}$, the TIBB is reduced, and thus the alignment is broken (c) and (d). In order to restore the alignment, the voltage has to be reduced in case there is downward TIBB (e).
5.3. Enhanced binding energy of Mn acceptors

As described above, the peaks appear when the acceptor level is aligned with the Fermi level in the sample (figure 5.10c). When we increase the tip-sample distance by reducing the current set-point, we also reduce the TIBB. We therefore break the alignment (figure 5.10d). In order to restore the alignment, we have to increase the TIBB by lowering the voltage, if we assume downward TIBB (figure 5.10d and e). Thus, the observation that the peaks shift to a lower voltage when reducing the current set-point, proves that there is downward TIBB at the peak voltage.

We extract the peak voltage by fitting the curves with Gaussians. We define peak 1 as the smaller peak and peak 2 as the larger peak. For most Mn dopants, peak 1 appears at a lower voltage than peak 2. The resulting peak positions are plotted in figure 5.11a and b. We calculate the TIBB to transform the peak voltage to the binding energy, analogous to the procedure described above. The flat band voltage was determined by fitting the curves with Gaussians.
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to be 1.7 ± 0.5 V by $I(z_{\text{tip}})$ measurements. We used a tip radius of 3.5 nm and a tip-sample distance of 4 Å for the measurement at 2.5 nA, 5 Å for the measurement at 250 pA and 6 Å for the one at 25 pA. The resulting binding energies are plotted in figure 5.11c and d. The data points for the three set-points almost coincide, as is expected because we take the change in tip-sample distance into account in the TIBB calculations. These measurements thus confirm the enhanced binding energy towards the surface, and we find a similar enhancement as found in figure 5.9.

We observe three peaks in figure 5.7, corresponding to three bound Mn levels. Only two peaks are resolved in figure 5.10, probably due to a slightly worse resolution. Tight binding calculations [58] predict three bound Mn states in the band gap. These are due to different spin orientations of the Mn atom and the bound hole. There are three spin components: the spin of the Mn atom is $M = 5/2$, the spin of the VB orbital momentum is $l = 1$, and the hole spin is $s = 1/2$. The following Hamiltonian applies

$$ H = \Delta \left( \vec{l} \cdot \vec{s} \right) + \epsilon \left( \vec{M} \cdot \vec{s} \right). \quad (5.2) $$

Here $\Delta$ is the spin orbit coupling and $\epsilon$ is the exchange interaction. In reference [58], the exchange interaction is assumed to be much larger than the spin orbit interaction ($\epsilon \gg \Delta$). Therefore, the spin couples first to the Mn spin, and we define $\vec{G} = \vec{M} + \vec{s}$, thus $G = \{2, 3\}$. There are 21 states with $G = 3$, which are unbound and form a broad resonance in the VB [58]. The states with $G = 2$ couple with $\vec{l}$ and form bound states in the gap. We define the total spin vector $\vec{F} = \vec{G} + \vec{l}$, thus $F = \{1, 2, 3\}$ for $G = 2$. The states with $F = 1$ form the three-fold degenerate ground state, the $F = 2$ state is 5-fold degenerate and the $F = 3$ state 7-fold degenerate. A scenario where the spin-orbit interaction is assumed to be much stronger than the exchange interaction leads to a similar result, with bound $F = 1, 2, 3$ states and unbound $F = 4$ states.

The experimentally observed splitting of $\sim 5$ meV for the deepest — bulk-like — Mn atoms (figure 5.9b) is much smaller than the theoretically predicted 40 meV splitting due to the exchange interaction [58]. We furthermore observe an increase of the splitting towards the surface. We therefore interpret the experimental peaks as the three-fold degenerate ground states with $F = 1$, which are split due to for example strain close to the surface.

The solid line with the triangles in figure 5.9b corresponds to the binding energy as calculated by tight binding methods performed by a different group [57]. We only added the theoretical data points for the deepest level. The theoretically predicted binding energy can be divided into two regimes: a regime where it increases gradually and a steep increase for the
last few atomic layers of the crystal. They attribute the gradual increase to modifications in the dispersion relation and strain, due to the lattice relaxations that are involved in the surface reconstruction (i.e. buckling). The onset of the steep increase in the binding energy occurs when the wave function of the Mn atom starts to interact with the vacuum or the surface states, according to the authors of reference [57]. They stress that the exact value of the binding energy depends on phenomenologically chosen model parameters. We do observe the gradual increase of the binding energy toward the surface, however the steep increase is absent.

5.4 Conclusion

In summary we have presented a method for estimating the binding energy as a function of depth below the surface. In case of Si-GaAs we find an enhancement of the binding energy, with an estimated value of \( \sim 40 \text{ meV} \), in contrast to the predicted reduction within the effective mass model. We conclude that the effective mass approach fails for Si in GaAs which is a model hydrogenic donor in bulk GaAs and we expect the same failure for all hydrogenic donors close to a semiconductor surface.

Also for the Mn acceptor in GaAs we find an enhancement of the binding energy towards the surface. We find an increase from the bulk value of 113 meV to \( \sim 170 \text{ meV} \) for the Mn in layer 2. In this case tight binding calculations support the observed enhancement.

The enhanced binding energy can have implications for devices. Current device simulations [6] take the random distribution of the dopant atoms into account to calculate the microscopic potential, but adopt \( E_b \) as determined in the bulk [44]. The enhanced binding energy close to the surface leads to freezing out of the carriers. Also the observed reverse order of the ionization, which starts with dopants that are located \( \sim 1.5 \text{ nm} \) below the surface and propagates towards the surface, modifies the operation of a nanoscale device.
Chapter 6

A comprehensive study of single Si dopants in GaAs by scanning tunneling microscopy

6.1 Introduction

In the previous chapters, we introduced the rings of ionization, and discussed some of the main properties. In this chapter, we discuss these STM and STS measurements in more detail. We explain all spectroscopic features in the STS data. These measurements reveal that a second electron can be bound to the donor, show the influence of the tip shape on the ring shape, and show the Coulomb interaction between neighboring donors. We present a comprehensive overview of STS on single silicon dopants in gallium arsenide.

6.2 Defect identification

Figure 6.1 shows a series of topography images of Si:GaAs, all measured at the same area of the sample. There are several types of defects, labeled a to d. Defect a is identified as a SiGa subsurface donor: we observe the typical Friedel oscillations at large negative voltages and bright protrusions
6. A comprehensive study of single Si dopants in GaAs by scanning tunneling microscopy

Figure 6.1: (a-e) Typical STM topography images of Si:GaAs\{110\}, all measured at the same area of the sample at the indicated voltages. (f) Schematic explaining the difference in step height at the edge of the disk for the donors in different depths below the surface.
6.3 Detailed STS analysis

We performed STS on our sample, and a topography image of the same area is shown in the top left panel of figure 6.2. The depth of the Si donors is indicated in atomic layers, counting the surface layer as 1. On a grid of 256 × 256 pixels within the dotted square, we took \( I(V) \) spectra. The numerical derivative gives the LDOS when a constant tip-sample distance is assumed (\( dI/dV \propto LDOS \cdot \exp(-2\kappa z_{\text{tip}}) \), see chapter 2). We thus obtain the LDOS as a function of \( x \), \( y \) and \( V \). Typically we use 200 to 300 voltage steps between -1.5 V and +1.5 V. The resolution after applying a Gaussian filter in the voltage direction is better than 100 mV. Several lateral \( dI/dV \) images at the indicated voltages are shown in figure 6.2. Below \( \sim -1.1 \) V there are Friedel-like oscillations [35]. In the voltage region between -1.1 V and 0.2 V, the donors in different depths appear at different voltages, as explained in chapter 5, and show an increasing ring diameter with voltage. They disappear when the extension has reached a few nanometer, and
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Figure 6.2: A series of spatially resolved $dI/dV$ images at the indicated voltages. The images are 40 nm × 40 nm. The topography image (top left, 1.25 V 20 pA) is slightly larger: 47 nm × 47 nm. The set-point of the STS measurement was 1.5 V and 3.15 nA (the stabilization topography is not shown).
6.3. Detailed STS analysis

Figure 6.3: (a) Typical d$I$/d$V$ curve on the bare surface (solid black), on a Si donor (dash-dotted red) and the difference between the two (dashed blue). (b-d) Sections through the d$I$/d$V$ data set on top of the donors marked Si$_b$-Si$_d$ in figure 6.2. The left hand side ($r = 0$ nm) is on top of the donor’s center. A spectrum on the bare surface is subtracted in order to suppress the signal from tunneling into the bands.

...appear again at the onset of tunneling into the CB at $\sim 0.2$ V.

We discuss all these features using cross-sections through the d$I$/d$V$ data set. Figure 6.3b-d shows three d$I$/d$V$ cross-sections taken on top of the donors marked by Si$_b$-Si$_d$ in figure 6.2. We applied an azimuthal average and $r$ is the distance to the donor center. The color scale represents d$I$/d$V$. We subtracted a spectrum obtained on the bare GaAs surface in order to suppress the signal from tunneling into the conduction and valence band. Therefore there is no significant signal in the images far away from the donor ($r \approx 10$ nm). Closer to the donor center, several features are visible. These features are highlighted, color coded and numbered in figure 6.4 and explained in the next paragraphs.
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Figure 6.4: (a) All features in the section shown in figure 6.3c are highlighted, numbered and color coded. Schematic of the ionization process (1), filled state wave function (2) and the empty state wave function (4). The black dotted line is added to guide the eye and the white dashed line marks the onset of the CB.

(1) Ionization curve (red)

One of the most striking features is the hyperbolic signature of the ring of ionization (red, 1), whose diameter increases with voltage. The donor ionizes when its level is aligned with the Fermi level in the sample, and therefore the ionization ring follows a TIBB contour, as explained in chapter 4. We calculate the TIBB quantitatively using the code developed by Feenstra [49]. There are several input parameters. Some are well known, such as the (average) doping concentration, temperature, band gap and the dielectric constant. Others are relatively unknown and are estimated: tip shape (radius of curvature at the tip apex and the opening angle of the shank), tip-sample distance and flat band condition. By varying these parameters within realistic limits, we can obtain a perfect agreement between theory and experiment. However, the fit is not unique. We test this by varying the parameters to extreme limits. A typical tip-sample distance $z_{tip}$ is 5 Å. The measurement shown in figure 6.2 was measured with a set-
6.3. Detailed STS analysis

Figure 6.5: Experimental ionization curve (black dots) and calculated TIBB contour (gray line) for three different parameter sets.

point of 1.5 V and 3.15 nA, which is a higher current set-point than typically used. We therefore assume that 7 Å is the upper limit and as a lower limit we choose 3 Å. We calculate the TIBB for these three values for \( z_{\text{tip}} \) and optimize the other parameters to fit the experimental data points\(^1\). The result is shown in figure 6.5. In all graphs the fit is similarly good, though the parameters are different and the total TIBB differs by a factor of 2 between the extreme cases. The message here is that even though we can only extract the TIBB with a \( \sim 30\% \) uncertainty, we can compare the relative values within one data set (i.e. measured with the same tip) with a much higher accuracy, as we did to measure the binding energy as a function of depth below the surface we reported earlier (chapter 5 and reference [61]).

(2) Wave function filled state (orange)

The next feature we address is the bottom part of the parabolic feature (orange, 2). This contrast reflects tunneling of electrons from the filled state donor wave function. In order to address the filled state wave function, we have to meet two requirements. First, we have to be in the filled state imaging mode, i.e. \( V < 0 \), and secondly the donor should be filled. The change from a filled to an empty donor state occurs when the donor level is aligned with the sample Fermi level [82]. Thus the tunneling conditions for the filled state donor wave function are the same as for the ring of

\[^1\text{The following parameters are not varied:} \]

Full opening angle tip shank: 19°
Doping concentration: \( 2 \cdot 10^{18} \text{ cm}^{-3} \)
Flat band condition: -1.1 V
A comprehensive study of single Si dopants in GaAs by scanning tunneling microscopy

Figure 6.6: The extension of the filled state wave function is larger for donors deeper below the cross-sectional surface.

ionization and the orange and red features lie on the same TIBB contour, see figure 6.5.

There is a gap between the red (1) and orange (2) feature. The ionization causes a change in the tunneling scheme, and does not induce a traceable feature in the dI/dV spectrum. Other tunneling channels are required, e.g. tunneling into the CB, in order to visualize the ionization. Therefore, the red feature appears only when injection into the CB occurs, and the onset of the CB is indicated by the white dashed line. The orange feature represents the wave function and therefore its extension corresponds to the projection of the Bohr radius. We observe that the extension of the wave function increases with increasing depth below the surface, see figure 6.6. The y-axis corresponds to the dI/dV signal, integrated over a small voltage window around the orange feature, normalized by the amplitude at r = 0 nm. Note that this is the projection of the wave function, and therefore its width does not directly correspond to the Bohr radius. Nevertheless, the smaller diameter for Si atoms closer to the surface corroborates the enhanced binding energy [61]. The extension is a factor of ~ 3 smaller for donors close to the surface compared to the deeply buried donors. Using the particle in a box approach as a first order approach, a reduction of the Bohr radius by a factor of ~ 3 corresponds to an enhanced binding energy of a factor of ~ 9. In chapter 5, we found similar ratio; we found an enhancement to ~ 40 meV for donors close to the surface, compared to
the bulk binding energy of 5 meV.

(3) Wave function second electron (brown)

The donors in layer 1 and 3 have a sharp feature around -1 V, highlighted in brown (3) in figure 6.4. We suggest that this is the filled state wave function for a second electron that can bind to a hydrogenic donor. For a bulk Si atom in GaAs with a binding energy of 5.6 meV, the binding energy of the second electron is only 0.3 meV (5.55% of the normal $D^0 \rightarrow D^+$ binding energy [83]). Donors close to the surface have an enhanced binding energy [61], and therefore we expect that the binding energy of the second electron is enhanced as well. This second ring should follow a contour line of the TIBB with a lower value. We extracted the position of both rings for the two donors in layer 1 in figure 6.2 (labeled $Si_a$ and $Si_b$). The result plus the calculated TIBB lines is shown in figure 6.7. Both are surface donors measured within the same data set, so they should follow the same TIBB contour. We observe that they are slightly different. Also the exact shape of the second ring (brown feature) differs for both donors; the second ring of $Si_a$ is somewhat flatter than the second ring of $Si_b$. This is probably due to the local environment, which can change both the local TIBB (local doping concentration), and the binding energy of the donor itself. On average we

Figure 6.7: Donors close to the surface have a second ring around -1 V. The black dots are the experimental data points and the lines are TIBB contours at the indicted energies in meV.
indeed see that the second ring follows a TIBB contour line with a lower value than the contour line that follows the first ring. The difference in the TIBB between the first and second ring is approximately a factor of 10, whereas a factor of 18 is expected, because the binding energy of the second electron is 5.55% of binding energy of the first ring [83]. We can explain this difference qualitatively as follows. The TIBB contours do not directly equal the binding energy as we explained in chapter 5 [61], see figure 6.8. The extension of the TIBB is of the same order as the width of the Coulomb potential. Therefore the donor level is not rigidly shifted with the bands. Instead the Coulomb potential is squeezed by the TIBB, which pushes the donor level upward (thick blue line figure 6.8). When this shift equals the binding energy, and the donor level becomes resonant with the CB, the donor ionizes. This mechanism adds a lever arm to the TIBB: a TIBB of $\sim 150\text{meV}$ is needed in order to ionize a donor with a binding energy of $\sim 40\text{meV}$. This lever arm depends on the overlap between the TIBB and the wave function. We expect the wave function of the second electron to be larger than the wave function of the first electron, which is also confirmed by our measurements. The overlap between the wave function and the TIBB is therefore smaller for the second electron, resulting in a larger lever arm, and therefore the difference between the TIBB contour and the binding energy is larger as well. This is in qualitative agreement with our observation that the ratio between the TIBB that is needed to ionize the first and the second ring is smaller than 18. Note that we only observe a second ring for donors close to the surface, which have an enhanced binding energy. For donors deeper below the surface, which have the bulk binding energy, we only observe a single ring. For bulk donors, the binding energy of the second electron is expected to be $\sim 0.3\text{meV}$, which is smaller than the thermal
6.3. Detailed STS analysis

Figure 6.9: (a) Zoom of the $dI/dV$ section through Si$_c$ (layer 3) with the calculated contours of the filled and empty state wave function. (b) Schematic of the voltage condition for tunneling into the empty state wave function.

Energy at 5 K of 0.43 meV. We therefore do not expect to observe a second ring for deeply buried donors.

(4) Wave function empty state (green)

The empty state wave function is also present in our measurements, highlighted in green (4) in figure 6.4. A zoom of this state, where we enhanced the contrast, is shown in figure 6.9a, where the downward curvature is clearly visible. In order to address the empty state wave function, the Fermi level of the tip has to align with the donor level (section 2.6). This occurs at small positive voltages, and is schematically shown in figure 6.9b. From this schematic it is clear that the voltage condition for tunneling into the empty state wave function is

$$eV = TIBB - E^*.$$  \hspace{1cm} (6.1)

Here $TIBB > E^* > 0$, so $eV > 0$. Experimentally we observe that the empty state wave function appears at a lower voltage for increasing $r$. When the tip is laterally removed from the donor, the TIBB at the donor center is smaller, thus a lower voltage is needed to align the Fermi level of the tip with the donor level (equation 6.1). We can calculate this voltage using the TIBB calculations [49] and assuming a certain energy $E^*$. Note
that this is an iterative process, as the TIBB depends on the voltage, and the voltage condition depends on the TIBB.

For a donor in layer 3 (Si$_c$), the best result is obtained for $E^* = 95$ meV and is shown in figure 6.9a. The TIBB contour at 95 meV is added as well, which nicely follows the filled state wave function as expected. Note that the extra lever arm that we discussed above, also holds for the empty state wave function. The donor level does not rigidly follow the bands, and therefore the level as drawn in figure 6.9b, is deeper than it would be in the rigid band model. We therefore find an apparent binding energy ($E^* = 95$ meV) that is higher than the real binding energy $E_b$.

(5) and (6) Surface states (blue and cyan)

The last two features in figure 6.4 are highlighted in blue and cyan (5 and 6). We observe features around 0.2 V and 1.0 V in the spectrum obtained on the bare surface (figure 6.3a). They correspond to tunneling into the C$_3$ and C$_4$ surface states [47, 48, 84]. Theoretically these states are located 0.5 V and 1.0 V above the onset of the conduction band. Due to the Coulomb potential of the positively ionized donor, these features are shifted to lower voltages inside the ring. Subtracting a spectrum obtained on the bare surface as we did in figures 6.3b-d, induces a peak, followed by a negative contrast, inside the ring around 0.2 V and 1.0 V.

6.4 Influence of the tip on the ring

In the results presented so far, we observe an almost perfectly circular disk or ring, which is almost exactly centered around the donor. The rings in for example reference [60] show deviations from a circular ring, and the center of the ring does not coincide with the acceptor’s position. The donor or acceptor contrast itself is measured by the last atom of the tip. The ring’s shape and position are defined by the overall shape of the tip on a scale of several nm. The overall tip shape does not have to be circular symmetric and the last atom through which the tunneling current flows does not have to be located at the middle of the tip apex. The effect of the tip properties is nicely visible in figure 6.10. Both images are measured at the same location and at the same tunneling conditions. Between the measurements there was a tip modification and a few atoms dropped from the tip on the sample. This modification occurred on a different area of the sample, and after the modification we went back to the original area. Due to this change in the tip, either the shape, the work function or both, the disks change from almost perfect circles to egg-shaped rings.
6.5 Donor-donor interaction

The Coulomb interaction is also present in our measurements, visible as the reduced diameter of the rings where they overlap, see e.g. the zoom of the d$I$/d$V$ image at 0.16 V (bottom right image of figure 6.2). An extended discussion of the donor-donor interaction is given in reference [85], and we only describe it qualitatively here. When a donor is ionized, it adds an additional attractive potential to a neighboring donor. A higher voltage is thus needed to ionize this second donor, which is visible as a reduced ring diameter. The rings are only reduced in diameter where they overlap, because the donors are neutral outside the rings and a neutral donor does not influence a neighboring donor.

We study this in more detail using the measurement shown in figure 6.11. Three donors are present in this measurement, indicated by Si$_a$, Si$_b$ and Si$_c$. Si$_a$ is a surface donor, which has a second ring as described above. The Coulomb interaction is visible by the reduced diameter is figure 6.11a, where the ring of Si$_b$ and second ring of Si$_c$ overlap. Note that Si$_c$ is neutral between its small and large ring. Still the diameter of Si$_b$ is reduced where they overlap. Technically, the diameter of Si$_b$ is enlarged outside the second ring of Si$_c$, because Si$_c$ is negatively charged in that region.
6. A comprehensive study of single Si dopants in GaAs by scanning tunneling microscopy

Figure 6.11: (a) Lateral dI/dV image at 0.43 V and (b) dI/dV cross-section showing the Coulomb interaction. The schematic in (c) shows the charge state of the three donors in this measurement.
6.6 Summary

Figure 6.11b shows a $dI/dV$ section along the line in (a), and reveals a discontinuity where the hyperbolas of $\text{Si}_b$ and $\text{Si}_c$ cross, better visible in the zoom. This again reflects the Coulomb interaction: the attractive potential of the first donor shifts the ionization hyperbola of the second donor to higher voltages and vice versa. We have to keep in mind that $\text{Si}_c$ can have three charge states, due to the second electron that can bind to it. We come to the following charging diagram, see figure 6.11b and c. Both donors are ionized ($\text{Si}_b^+\text{Si}_c^+$) in the region where the ring of $\text{Si}_b$ and the small ring of $\text{Si}_c$ overlap and on the bare surface, outside all rings, $\text{Si}_b$ is neutral, whereas $\text{Si}_c$ is negatively charged ($\text{Si}_b^0\text{Si}_c^-$). $\text{Si}_c$ is only neutral in the region between its small and large ring. The different charge states of the three donors in our measurement are indicated in figure 6.11b and c.

6.6 Summary

We have performed spatially resolved scanning tunneling spectroscopy on Si doped GaAs. Analysis of the spectra and the images lead to a full understanding of all the features in the measurements. Several observations are worth noting. We showed that we can ionize single Si donors by the STM tip, and we can visualize this ionization process. Our model reproduces the observed dependence of the ionization process on the applied voltage. In a previous chapter we showed that we can extract the binding energy from the ionization threshold, and we showed that it is enhanced for donors close to the surface. This result is corroborated in this chapter by the reduced extension of the wave function towards the surface, and by the energetic position of the empty state wave function. Furthermore we suggest that a second electron can be bound to donors close to the surface, which is a result of their enhanced binding energies. All the analyses fit together, and this leads to a comprehensive study of STM and STS on Si-doped GaAs.
Chapter 7

Bistable behavior of Si atoms in the GaAs\{110\} surface

7.1 Introduction

In the previous chapters we have discussed subsurface Si donors. Si atoms in the surface layer behave very differently, which is the focus of this chapter. The surface dopants are bistable; they behave similarly as subsurface donors at large positive and negative voltages, whereas they turn into a negatively charged configuration at voltages close to 0 V. All surface Si atoms (i.e. Si atoms located in the topmost layer of the crystal) are bistable, and all bistable defects are surface Si atoms. The switch between the two configuration is abrupt, although the time between two switching events is long, on the order of seconds to minutes. We investigate several dependencies of the switching, and provide arguments that more than electrostatics is involved, most likely a lattice relaxation of the Si atom.

7.2 In a nutshell

Figure 7.1 summarizes this behavior. The STM image in figure 7.1b shows a surface Si atom, imaged at a low positive sample voltage of 0.5 V and 0.5 nA. The fast scan direction is from right to left, and the slow scan direction is...
7. Bistable behavior of Si atoms in the GaAs\{110\} surface

Figure 7.1: Si atoms in the GaAs\{110\} surface switch between a substitutional donor Si\textsuperscript{+} (a) and a negatively charged interstitial-like Si\textsuperscript{−} (c). (b) STM topography at the critical voltage for switching showing both configurations. The slow scanning direction is parallel to the horizontal axis. (d) Schematic potential landscape of the bistable system. (e) Switching rate versus temperature measured at 25 pA.

from top to bottom. The Si atom has two distinct appearances: it is either dark or bright with an ionization disk. We interpret the white state as a substitutional donor configuration (figure 7.1a), and the dark state as an interstitial-like configuration (figure 7.1c), which will be substantiated later. Two bistable configurations suggest a potential landscape with two minima, separated by an energy barrier $E_{barr}$ (figure 7.1d). Figure 7.1e shows the switching rate $\tau^{-1}$ versus temperature $T$ between 5 K and 20 K. $\tau^{-1}$ is constant below 20 K, suggesting a non-thermal behavior, whereas it increases with $T$ above 20 K, suggesting a thermally excited process. In the next sections we elaborate the experimental results, and discuss the possible models.
7.3 Experimental results

7.3.1 General observations: voltage dependence

Our STM measurements were performed on the \{110\} cleavage surface of Si-doped GaAs with an average doping level of $\sim 10^{18}$ cm$^{-3}$. The observations presented here were similarly measured on samples with a lower Si doping concentration of $\sim 10^{17}$ cm$^{-3}$. We present the results measured on the highly doped material, because it allows better statistics.

We identify the dopants in our measurements based on their well known contrast at voltages far from 0 V [36] (see section 5.2 for their depth identification). Si$_2$, Si$_3$ and Si$_4$ in figure 7.2a-c are subsurface Si$_{Ga}$ donors, Si$_1$ and Si$_6$ are Si$_{Ga}$ atoms in the surface layer, and Si$_5$ is a Si$_{As}$ acceptor. As expected for a highly doped sample, $\sim 20\%$ of the Si atoms were incorporated as Si$_{As}$ acceptors [45, 80, 81]. All Si atoms in the surface layer are bistable; they resemble Si$_{Ga}$ donors at voltages far from 0 V, but turn into a negatively charged defect at low positive voltages. STM and STS at voltages far from 0 V identified the donor configuration as a substitutional Si atom in the surface layer of GaAs$\{110\}$. The donor configuration has an ionization ring, and its binding energy follows the gradual enhancement of $E_b$ towards the surface.

Figure 7.3 shows examples of both types of subsurface impurities; a Si$_{As}$ acceptor is labeled A$^-$, and a Si$_{Ga}$ donor is labeled D$^+$. A Si$_{Ga}$ impurity that is embedded in the surface layer can switch between the donor configuration and the acceptor configuration, and is therefore labeled Si$^+$, Si$^0$ or Si$^-$, depending on its configuration. The subsequent images in figure 7.3a to d show the three possible charge states of this impurity. Figure 7.3a shows the positively ionized surface donor Si$^+$ at a sample voltage of 2 V, and figure 7.3b shows the neutral surface donor Si$^0$ at a sample voltage of 1.1 V. At a critical voltage $V_{crit}$ = 0.9 V (figure 7.3c), the Si$_{Ga}$ in the surface switches between the donor and the acceptor configuration. This happens while the tip is at random positions. Note that the atomic corrugation is not distorted due to the switch, proving that the switch is not related to a tip modification. At a sample voltage of 0.7 V, clearly below $V_{crit}$, the Si$_{Ga}$ atom in the surface is found in the negatively charged Si$^-$ configuration, see figure 7.3d. The charge states of the different configurations of the surface Si atoms are demonstrated by the line profiles along the [001]-direction (horizontal axes) in figure 7.3e. The red dashed line depicts the cross-section through the ionized donor Si$^+$, the blue dash-dotted line through the neutral donor Si$^0$, and the black solid line through the negatively charged configuration Si$^-$. The green dotted line profile through
Figure 7.2: (a - c) STM topographies of Si-doped GaAs(110) measured at 5 K and 20 pA. The applied voltage is given in the image. \(\text{Si}_2\), \(\text{Si}_3\) and \(\text{Si}_4\) show the normal donor contrast, \(\text{Si}_1\) and \(\text{Si}_6\) switch to a black contrast at low voltage, and \(\text{Si}_5\) is an acceptor, \(\text{Si}_{\text{As}}\). (d) Cross-sections of the Si atom in the donor \(\text{Si}^+\) state (red dotted line) and in the acceptor state \(\text{Si}^-\) (black line).
Figure 7.3: (a-d) Topography images at different voltages showing an ionized subsurface donor D$^+$ and a subsurface acceptor A$^-$. The surface Si atom can have three charge states: (a) positively ionized Si$^+$, (b) neutral Si$^0$, (c) switching between neutral and negatively charged and (d) negatively charged Si$^-$. (e) Cross-sections through the defects.
the negatively charged Si\textsubscript{As} acceptor A\textsuperscript{−} reflects the shape of the Coulomb potential. Comparing the contrasts of the Si\textsuperscript{−} defect with the defects that carry a single negative charge, A\textsuperscript{−}, or a single positive charge, Si\textsuperscript{+}, we see that the Si\textsuperscript{−} contrast resembles the A\textsuperscript{−} contrast, although the amplitude of the topographic contrast is different. The amplitudes differ from each other, because the line sections plotted in figure 7.3e reflect impurities in different depths, that are furthermore measured at different voltages. In figure 7.2d we compare line sections before and after the switch, thus the profiles are measured on the same dopant, and at the same voltage. The black line depicts the negatively charged Si\textsuperscript{−}, the red dashed line depicts the ionized donor Si\textsuperscript{+}. Both lines show the profile of a Coulomb potential with the same amplitude (within 20%). From the inverted contrast we conclude that Si\textsuperscript{−} carries one negative elementary charge.

In the previous paragraph, we distinguished three charge states, even though we identified only two configurations. The reason is that the donor configuration has two possible charge states. We thus identify two mechanisms that can charge the charge state: ionization and switching. The ionization is discussed in the previous chapters, and is a fast (≪ 1 ms), purely electrostatic process. The second manipulation – switching – involves a change in the configuration, and is a much slower process where seconds to minutes are involved. The surface Si atoms switch between a donor configuration (where ionization is observed from Si\textsuperscript{0} to Si\textsuperscript{+}) and a negatively charged configuration Si\textsuperscript{−}. Moreover, in chapter 6 we showed that a second electron can be bound to donors close to the surface, including Si atoms in the surface layer that are in the donor configuration. In this case, the Si atom is also negatively charged, but its configuration is qualitatively different than the dark state discussed in the current chapter. The second electron in the negatively charged donor configuration (second ring, chapter 6) is hydrogenic, and extends over a few nanometer. Contrary, the negative charge in the dark configuration discussed in this chapter, is localized on the Si atom, probably on its dangling bond. This is the crucial argument that more than purely charging and discharging is involved, possibly a lattice relaxation.

7.3.2 Dependence on the current set-point

In this section we address the dependence of the switching on the current set-point. The \( I \) dependent measurements shown in figure 7.4 are conducted with the same tip on the same ensemble of donors as the voltage dependent investigation shown in figure 7.2, and yield the same \( V_{\text{crit}} \). Varying \( I \) clearly affects the timescale of the switching. We define \( \tau^{-1} \) as the
7.3. Experimental results

Figure 7.4: Current dependent topography images of the same area of the sample as figure 7.2. The timescale of the switching is large at low $I$ (a, b), and decreases at higher $I$ (c, d). The arrows indicate the fast scanning direction.
number of switching events per second. At a low current of 20 pA, shown in figure 7.4a, the donor switches only once during the measurement. At a 10 times higher current of 0.2 nA (figure 7.4b), the donor switches a few times. This corresponds to 0.071 Hz < $\tau_{0.2 \text{nA}}^{-1} < 1$ Hz. At a current of 2 nA, the switching rate increases even more: 0.25 Hz < $\tau_{2 \text{nA}}^{-1} < 4$ Hz. Due to the high switching rate, the Si atom switches in almost every line resulting in the rather ragged image at the donor. Note the difference between the forward and the backward scan shown in figure 7.4c and d respectively. In both cases the Si atom starts negatively charged and switches to the donor configuration during the scan line. This demonstrates that the negatively charged configuration is favorable in the undisturbed situation when the Si atom is not affected by the tip, whereas the donor configuration is favorable only with the tip nearby. For a more quantitative analysis, we compare the switching at 25 pA and a 250 pA. Averaging all data in the low temperature regime below 20 K (see section 7.3.4) yields $\tau_{25 \text{pA}}^{-1} = 0.040 \pm 0.085$ Hz, and $\tau_{250 \text{pA}}^{-1} = 0.42 \pm 0.19$ Hz. The roughly constant ratio of $\tau^{-1}/I \approx 2.5 \cdot 10^{-10}$ switching events per electron suggests an inelastic process. This efficiency is $\sim$6 orders of magnitude smaller than reported for other inelastic processes as e.g. scanning tunneling luminescence [86].

A process that is driven by inelastic excitations typically has the highest switching rate when the tip is located on top of the center of the impurity, see e.g. reference [87]. This is not the case in our system. The switch from black to white typically does occur with the tip close to the center of the Si atom, but the switch from white to black does not. This happens somewhere in the scan line, when the tip is away from the donor. However, we observe an enhancement of the switching rate for both transitions. The enhancement in the switching rate for the Si$^+$ to Si$^-$ transition (white to black), is visible only indirectly. It is evident because the Si atom starts in the black configuration in almost every scan line in figure 7.4c and d, whereas it stays white for the rest of the image in figure 7.4a.

### 7.3.3 Pinning

A straightforward way to measure $\tau^{-1}$ would be to place the tip on the Si atom, and record the switching events as ‘random telegraph noise’ in the tunneling current. Time traces of e.g. the switching motion of atomic pairs on the Pt decorated Ge(001) surface [88] were measured this way. When we tried this, no switching occurred at all. In order to understand this behavior, we varied the frame size as shown in the sequence of images on an individual Si atom shown in figure 7.5. The images are plotted in their original frame size. For large images (figure 7.5a-c), the Si atom switches as
7.3. Experimental results

Figure 7.5: Topography images of a Si atom in the first layer of GaAs\{110\} at 5 K. Scanning large frames (a-c), it switches from white to black as \( V \) is lowered below \( V_{\text{crit}} \). At small scan sizes (d-f), it stays white even far below \( V_{\text{crit}} \). Images are plotted in the original frame size. Up and down refer to the slow scanning direction.

.described above. It is in its white configuration for \( V > V_{\text{crit}} \) (a), switches during the scan when \( V \approx V_{\text{crit}} \) (b), and it is in its black configuration for \( V < V_{\text{crit}} \) (c). For frame sizes below \((9\text{ nm})^2\) (d-f), it switches from black to white during the first scan (d) and stays white (e). Even when applying a sample voltage far below \( V_{\text{crit}} \), the Si atom remains in its white configuration (f). We also tried applying a negative sample voltage down to \( -0.7 \text{ V} \) or retracting the tip >100 nm from the surface for 15 minutes, but the Si atom stayed white. Only after increasing the scan area, i.e. removing the tip laterally, the Si atom turns black again. The critical distance for unpinning was experimentally found to be on the order of the tip radius. This explains why switching has not been observed in previous STM studies. We use ultra sharp tips with a radius of a few nanometers, whereas in previous STM studies blunter tips were used [69]. We confirmed experimentally that when a blunter tip is used, the Si atom is pinned in its white configuration for much large frame sizes, and switching can not be observed.
7. Bistable behavior of Si atoms in the GaAs\{110\} surface

Figure 7.6: Critical voltage $V_{\text{crit}}$ versus temperature.

7.3.4 Temperature dependence

Next we investigate the temperature dependence of the switching dynamics. In order to investigate purely the influence of the temperature, we need to stay on the same area of the sample and image the same Si atoms. Otherwise different properties of different Si atoms might mask the influence of the temperature. This requires simultaneous removal of drift while heating up the STM. We succeeded in characterizing the switching behavior of three individual Si atoms as a function of voltage and current for several temperatures between 5 K and 50 K in steps of $\sim 8$ K. Due to the pinning discussed in the previous paragraph, we have to measure an image at each temperature, at various voltages and current set-points, and extract the switching rate from the STM images.

We investigated the dependence on the temperature of both $\tau^{-1}$ and $V_{\text{crit}}$. $V_{\text{crit}}$ is defined as the voltage where the most switching events occur. We furthermore measure $\tau^{-1}$ and $V_{\text{crit}}$ at two current set-points, 25 pA and 250 pA, because the switching rate depends on $I$ as described above.

The resulting $V_{\text{crit}}$ as a function of temperature is plotted in figure 7.6. $V_{\text{crit}}$ remains constant for $T < 40$ K, within the uncertainty of the measurement of $\sim 100$ mV. The critical voltage drastically decreases above $\sim 40$ K. This trend is confirmed by independent measurements at 77 K, where $V_{\text{crit}} = 0.2$ V was found. Furthermore no significant difference is observed between $V_{\text{crit}}$ measured at $I = 25$ pA and 250 pA, which is consistent with the current
dependent measurements at 5 K shown in figure 7.4.

Figure 7.7 shows the experimentally measured switching rates \( \tau^{-1} \) as a function of temperature and as a function of inverse temperature on a log scale for a current set-point of 25 pA and 250 pA. Figure 7.7a and b show the results for two individual donors at these two set-points, and figure 7.7c shows the result of all three donors together. For temperatures below \( \sim 20 \text{K} \) we find a constant switching rate, whereas \( \tau^{-1} \) increases with \( T \) above \( \sim 20 \text{K} \). We therefore fit the data with the expression for a thermally excited process, with an additional temperature-independent term \( \tau_{0}^{-1} \) [89]

\[
\tau^{-1} = \tau_{0}^{-1} + \nu \cdot e^{-E_{\text{barr}}/kT}.
\] (7.1)

Here \( \nu \) corresponds to the attempt frequency and \( E_{\text{barr}} \) to the energy barrier between the two configurations. The solid lines in figure 7.7 correspond to the fit results. The contribution of the two terms is clear in the plots of \( \tau^{-1} \) versus the inverse temperature, as is indicated by the dashed lines. The regime where \( \log(\tau^{-1}) \) decreases linearly with \( T^{-1} \) corresponds to the thermally activated term, and the regime where \( \tau^{-1} \) is constant to the temperature-independent term. This demonstrates the crucial impact of a non-thermal contribution.

The parameters \( \tau_{0}^{-1} \), \( \nu \) and \( E_{\text{barr}} \) derived from these fits are summarized in table 7.1. The results are shown separately for the individual Si atoms at both current set-points. There is a clear dependence of \( \tau_{0}^{-1} \) on the current set-points, and therefore the value averaged over all three donors is given. Such a clear trend does not exist for the other parameters, and therefore we only show the individual results. The resulting barrier height is similar to the barrier extracted for a roughly comparable process studied by Heinrich et al. [89], whereas the attempt frequency is low compared to the literature. For example, a frequency in the THz regime is expected for phonons, and the impinging electrons have a frequency of tens of MHz to GHz. Experimentally a frequency of \( \sim 10^6 \text{Hz} \) was observed by Heinrich et al. [89] for hopping CO molecules on Cu(111), which they could not explain. We observe a frequency of \( \sim 100 \text{Hz} \), which is even a few orders of magnitude lower. This suggests that a more complicated mechanism is involved than e.g. purely the excitation of phonons.

Prior to further interpretation, we briefly summarize the experimental results. The charge states \( -\text{Si}^- \) for the black state and \( \text{Si}^+ \) for the white state are derived from topography images, where both configurations show a Coulombic contrast, but inverted with respect to each other. The black configuration is favorable on the bare surface when the Si atom is not
7. Bistable behavior of Si atoms in the GaAs\{110\} surface

Figure 7.7: Switching rate $\tau^{-1}$ versus temperature $T$ (left column) and versus $1/T$ (right column) for the individual donors at 25 pA (a) and 250 pA (b) and for all three donors (c). The solid lines are fits with $\tau^{-1} = \tau_0^{-1} + \nu \cdot e^{-E_{bar}/kT}$. The contribution of the two terms is clear in the plots of $\tau^{-1}$ versus $1/T$. 

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7.4. Discussion

Our model is based on density functional theory (DFT) calculations of SiGa in the top layer of GaAs(110) [46] and on the formation and dynamics of DX− centers in bulk Si:GaAs [90, 91]. Both bare a strong resemblance and can be related to the observed switching. DFT predicts a mid-gap state for Si atoms in the GaAs(110) surface $\sim 0.5$ eV below the conduction band, which is attributed to the half-filled dangling bond. This calculation is only performed for the neutral situation, whereas the negatively charged situation might have a lower energy. This is the case for the DX− center in GaAs [91], which is the second ingredient in our interpretation. This defect has been studied extensively for a number of donor species in different III-V semiconductor hosts. DX− centers are donors that are relaxed to an

Table 7.1: Results from fitting $\tau^{-1} = \tau_0^{-1} + \nu \cdot e^{-E_{barr}/kT}$ to the experimental data of switching rate versus temperature. Influenced by the tip, and the white state is favorable with the tip close to the Si atom. The time scale is much larger than the time scale involved in the ionization process, which proves that more is involved than purely charging and discharging of the Si atom. The critical voltage, which determines whether the positive or the negative charge state of the Si impurity is found, indicates that electrostatics play a crucial role for the underlying potential landscape. The dependence of $V_{crit}$ on the temperature indicates that switching takes place between metastable states. The constant switching rate below 20 K proves that a non-thermal process is involved, whereas the increasing switching rate with current suggests that inelastic tunneling processes are involved in switching the Si atom.

<table>
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<th>$E_{barr}$ (meV)</th>
<th>$\tau_0^{-1}$ (Hz)</th>
<th>$\nu$ (Hz)</th>
<th>$E_{barr}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Si}_1^{25\text{pA}}$</td>
<td>0.02 ± 0.14</td>
<td>206 ± 194</td>
<td>17.03 ± 3.8</td>
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<tr>
<td>$\text{Si}_1^{250\text{pA}}$</td>
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<td>11.0 ± 9.5</td>
<td>5.1 ± 3.4</td>
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<tr>
<td>$\text{Si}_2^{25\text{pA}}$</td>
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<td>59 ± 28</td>
<td>12.8 ± 1.9</td>
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<tr>
<td>$\text{Si}_2^{250\text{pA}}$</td>
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<td>81 ± 141</td>
<td>14.2 ± 7.0</td>
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<tr>
<td>$\text{Si}_3^{25\text{pA}}$</td>
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<td>109 ± 44</td>
<td>14.1 ± 1.6</td>
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<tr>
<td>$\text{Si}_3^{250\text{pA}}$</td>
<td>0.39 ± 0.04</td>
<td>22.1 ± 3.5</td>
<td>8.95 ± 0.63</td>
</tr>
<tr>
<td>all, 25 pA</td>
<td>0.040 ± 0.085</td>
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<tr>
<td>all, 250 pA</td>
<td>0.42 ± 0.19</td>
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</table>
interstitial position, e.g. under hydrostatic pressure. In this configuration, a bond with a neighboring As atom is broken, creating two saturated internal dangling bonds. These defects are deep states and are only stable when a second electron is bound to it, i.e. when they are negatively charged.

We propose the following model, schematically shown in figure 7.8. We identify the white donor state as a configuration where the dangling bond is empty, which would be the case for the original Ga atom on the clean GaAs surface (figure 7.8a). This is due to buckling, which is accompanied by a charge transfer between the Ga and the As atoms, resulting in an empty Ga dangling bond and a filled As dangling bond [47, 48]. Because a Si replaces a Ga atom, an empty dangling bond can be expected, and in this configuration a shallow hydrogenic donor is created (figure 7.8b and c), which can be neutral or ionized. On the bare surface, where the dark state is favorable, the dangling bond is completely filled \((-2e)\), thus the total charge is \(-e\) (figure 7.8d). This is similar to the DX\(^-\) center in bulk GaAs, which also has a filled dangling bond, and is only stable when negatively charged.

There are several indications that a lattice relaxation, i.e. a movement of the Si atom, is involved in the switch. Previous STM experiments on GaAs\{110\} showed that the STM tip can influence buckling [92]. The authors propose that buckling is suppressed for small tip-sample distances, and a “truncated-bulk” situation is obtained, i.e. the surface atoms reside at their bulk positions, as expected for an unrelaxed surface. Furthermore, the DFT calculations in reference [46] show that the buckling is reduced near a surface Si atom, compared to the clean GaAs surface. And finally,
we observe of two qualitatively different configurations that both carry a single negative charge. The first is the donor configuration, where a second electron is bound to it (second ring, see chapter 6) and the second is the DX$^-$-like configuration discussed in this chapter. This strongly suggests that more than electrostatics is involved, probably a lattice relaxation.

Next we discuss the mechanism underlying the switching. Based on the fit to the experimental $T$-dependence (figure 7.7), we conclude that the process is thermally activated for $T > 20$ K, but non-thermal processes dominate for $T < 20$ K. We explore quantum tunneling and inelastic processes as two possible non-thermal processes.

In case of pure quantum tunneling, where the Si atom tunnels between two bonding configurations, no dependence on $I$ is expected, whereas a constant ratio between $\tau^{-1}$ and $I$ is expected for an inelastic process. The strong dependence of $\tau^{-1}$ on the tunneling current therefore points to an inelastic process. Note that the rate for both the transition from Si$^-$ to Si$^0$/+ and the transition from Si$^0$/+ to Si$^-$ depend on the tunnel current, i.e. both the excitation and the relaxation depend on $I$. Moreover, the Si atom switches when the tip is at random positions, not necessarily located close to the Si center. This holds especially for the Si$^0$/+ to Si$^-$ transition. For an inelastic process, the transition preferentially occurs when the tip is located on top of the atom. However, in case of the excitation of phonons, which are less localized than the Si atom itself, this restriction is relaxed. Furthermore, the extended wave function of Si$^0$ (figure 7.8b) can facilitate a less localized excitation or relaxation.

Experimentally, we observe a high $V_{\text{crit}}$ at low $T$, and a low $V_{\text{crit}}$ at high $T$ (see figure 7.6). We explain this as follows. We assume that the external voltage adjusts the relative positions of the potential minima corresponding to the Si$^0$/+ and the Si$^-$ configurations, as is schematically shown in the insets in figure 7.6 and in more detail in figure 7.9. Rigidly shifting the curves with respect to each other affects the barrier height $E_{\text{barr}}$ between the minima. We estimate that the voltage needed to align both parabolas is 0.2 V (figure 7.9b), based on the observation of $V_{\text{crit}} = 0.2$ V at 77 K. Below 0.2 V, Si$^-$ is favorable (figure 7.9a), and above 0.2 V Si$^+$ is favorable (figure 7.9c, d). In the range $0.2 \text{ V} < V < 1.0 \text{ V}$ the system is meta-stable; the white configuration is favorable, but the barrier between the minima is large. At high $T$, the large barrier can be crossed (thermally excited, similar to thermionic excitation over a Schottky barrier), and therefore the system goes to the Si$^+$ state as soon as the parabolas align at 0.2 V, thus $V_{\text{crit}} = 0.2$ V. At low $T$ however, the large barrier cannot be crossed thermally, and the system switches only when the barrier is sufficiently reduced by
7. Bistable behavior of Si atoms in the GaAs\{110\} surface

<table>
<thead>
<tr>
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<th>High T</th>
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<tr>
<td>(a)</td>
<td>V&lt;0.2V</td>
<td>• Si$^-$</td>
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<td>(b)</td>
<td>V~0.2V</td>
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<tr>
<td>(c)</td>
<td>0.2&lt;V&lt;1V</td>
<td>meta stable • large frame: Si$^-$ • small frame: Si$^+$ (pinning)</td>
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<td></td>
<td><img src="c" alt="Schematic" /></td>
</tr>
<tr>
<td>(d)</td>
<td>V~1V</td>
<td>• large frame: switching: Si$^-$→Si$^+$ • $V_{\text{crit}} = 1.0V$ • small $E_{\text{barr}}$ • small frame: Si$^+$</td>
</tr>
<tr>
<td></td>
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Figure 7.9: Schematic of our model. For $V < 0.2V$, the black Si$^-$ configuration is favorable (a), for $0.2V < V < 1.0V$, the system is metastable for low $T$ (b, c) and for $V > 1.0V$ the white Si$^+$ configuration is favorable (d).
increasing the voltage to 1.0 V, thus $V_{\text{crit}} = 1.0$ V. This reduced barrier can either be crossed by quantum tunneling, or by inelastic excitations, or by a combination of both effects.

This concept of a meta-stable situation for $0.2 \, \text{V} < V < 1.0 \, \text{V}$ can furthermore explain the observed pinning at low $T$. At low $T$, the Si$^-$ atom cannot cross the barrier up to 1 V, even though the donor-like configuration is favorable above 0.2 V. This is similar to the persistent photo-conductivity at low temperatures observed for DX$^-$ centers [91]. The region where the tip influences the energy landscape is of the order of the tip-radius. For frame sizes larger than the tip radius, the potential landscape is modified only for a short period when the tip is located near the Si atom, and when the tip moves further along the scan line, the original potential landscape is restored, favoring and the black configuration. Therefore for large frame sizes, the black configuration is observed, even though the white configuration is favorable for short period in time. In case of scanning small frames however, the tip is always close to the donor, giving the system sufficient time to cross the large barrier. Once the Si atom has switched to Si$^{0/+}$, it will remain in this configuration.

The argumentation above leads to the following concept. Clearly inelastic processes are involved in the switching, which is proven by the dependence on the current set-point, and possibly quantum tunneling is involved as well. The measured temperature dependence is very similar to the expected behavior for crossing a barrier with quantum tunneling. However, we cannot disentangle the contributions from inelastic processes and quantum tunneling. Based on the low attempt frequency, we propose a two-step process. DX$^-$ centers in GaAs also follow a two-step process [91, 93], where the DX$^-$ center is first excited into a neutral DX$^0$ configuration, which is meta-stable. The DX$^0$ configuration can then either be further ionized into a substitutional donor configuration, or capture an electron from the CB and relax back into the DX$^-$ configuration. Another example where a two-step process occurs, is the system of H atoms moving on Si(001) [87]. In this case, the barrier between two locations of the H atom is large. However, the system can be inelastically excited, which reduces the barrier significantly, and increases the tunnel probability through the remaining barrier. In our case, something similar could occur. The two-step process could be the subsequent capture of two electrons, similar to the DX$^-$ center. Another possibility is that the system is inelastically excited, which reduces the remaining tunnel barrier, e.g. the excitation of a vibrational mode of the buckled surface atoms, which facilitates the geometrical motion of the Si atom by quantum tunneling. For all these two-step processes, we expect
7. Bistable behavior of Si atoms in the GaAs\{110\} surface

a low attempt frequency.

7.5 Conclusions

We found that Si atoms in the surface layer of GaAs\{110\} switch between a donor-like Si$^{0/+}$ configuration and a negatively charged Si$^-$ configuration at a critical voltage. Si$^-$ is identified as a Si atom on an interstitial site similar to the DX$^-$ center in bulk-GaAs. The bulk-like donor Si$^{0/+}$ is restored if the dangling bond at the Si site is depleted.

The switching rate depends on the feedback current and on the temperature. A constant switching rate below 20K proves the existence of a non-thermal process. This process involves inelastic excitations, possibly in combination with quantum tunneling.

Our results emphasize the importance of the surface on the properties of dopants. In many studies, the impurities are described by their bulk properties. Typically the surface is only taken into account by assuming minor modifications. By now there are more and more indications of the significant impact of the surface, for example our own work on the enhanced binding energy (chapter 5) and the switching discussed in this chapter. Also other groups report on the impact of the surface, for example Lee et al. report that Mn atoms in the GaAs surface are insensitive to the TIBB, in contrast to subsurface impurities [94].
Chapter 8

Nanoscale potential fluctuations in (GaMn)As/GaAs heterostructures

From individual ions to charge clusters and electrostatic quantum dots

8.1 Introduction

The dilute p-type semiconductor gallium manganese arsenide, (GaMn)As, has been the focus of considerable research effort due to its potential for applications in spintronics. The free holes provided by the substitutional manganese acceptors in this material are responsible not only for its high electrical conductivity but also for its ferromagnetic properties [12, 13, 15, 18, 19, 95]. The Curie temperature, $T_c$, of the as-grown crystal is relatively low but can be significantly enhanced up to temperatures of $\sim 185$K by thermal annealing [14, 15, 16]. This is due to the removal by out-diffusion of interstitial manganese ions, Mn$_i^{2+}$ [14, 16, 96, 97], which form in Ga$_{1-x}$Mn$_x$As for $x > \sim 2\%$ and act as doubly ionized donors [98], thus compensating the free holes and lowering $T_c$.

Recent experiments have demonstrated how controlled thermal annealing can be used to diffuse Mn$_i^{2+}$ ions from a capping layer of (GaMn)As into

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8. Nanoscale potential fluctuations in (GaMn)As/GaAs heterostructures

Figure 8.1: (a) Schematic diagram of our p-i-n diode. (b) Mn\textsubscript{i} ions diffuse out of the GaMnAs layer upon annealing, creating electrostatic quantum dots in the quantum well plane. (c) Current-voltage dependence at $T = 4\,\text{K}$ for as-grown device (blue) and the device annealed for 14 h at 200 °C (red).

the underlying GaAs layer of a heterostructure. This leads to the formation of quantum dots in which electrons are spatially confined on a length scale of $\sim 10\,\text{nm}$ by the attractive Coulomb potential of nanoscale clusters of these ions [99, 100]. Magneto-tunneling spectroscopy measurements have shown that these potential minima are approximately parabolic and circularly symmetric and give rise to simple harmonic-like electron eigenstates.

In this chapter, we use a combination of cross-sectional STM and STS at 5 K to probe directly the nature of the fluctuations of the electrostatic potential induced by the diffused Mn\textsubscript{i}\textsuperscript{2+} ions. Scanning the tip across the heterostructure reveals a pronounced decrease of the energy gap at the GaAs-(GaMn)As interface. Analysis of the images and spectra allows us to link the deep minima of the potential landscape to individual clusters, formed close to the (GaMn)As-GaAs interface. There are $\sim 7$ Mn\textsubscript{i} ions in each cluster, with a total charge of $\sim 13$ elementary charges, confirming that the ions are doubly charged. Our experiments demonstrate the power and future potential of STM and STS techniques in elucidating the effect of individual dopants on the properties of functional devices.
8.2 Device structure

Figure 8.1a shows a schematic diagram of the double barrier p-i-n resonant tunneling diode structure employed in our experiments. Our samples were grown by MBE on a (100) n-GaAs substrate. The layer composition, in order of growth: a 300 nm thick layer of n$^{+}$-GaAs, Si-doped to $2 \times 10^{18} \text{ cm}^{-3}$, a 100 nm buffer layer of n-GaAs doped to $2 \times 10^{17} \text{ cm}^{-3}$, an undoped central intrinsic region comprising a 20 nm GaAs layer, a 5 nm AlAs tunnel barrier, a 6 nm GaAs quantum well (QW), a 5 nm AlAs tunnel barrier and a 10 nm GaAs layer, and, finally, a 50 nm capping layer of p$^{+}$-(GaMn)As with 5% Mn. The top (GaMn)As spacer layer was grown at 230°C, the 300 nm n$^{+}$-GaAs layer at 580°C, and the others at 620°C. For a narrow range of annealing conditions, the random clustering of Mn$^{2+}$ ions that have diffused into an undoped GaAs spacer layer between the (GaMn)As and the GaAs QW modifies the electrostatic potential, giving rise to a small number of potential energy minima within the quantum well plane, see figure 8.1b.

The effect of thermal annealing on the low temperature current-voltage characteristics of the diode is illustrated in figure 8.1c. Annealing at a temperature $T_A = 200°C$ for 14 hours leads to an increase by several orders of magnitude of the tunnel current flowing through the device at applied voltages below the flat-band condition. We attribute this behavior to the diffusion of Mn$^{2+}$ ions into the nominally undoped GaAs layer (i-GaAs) between the (GaMn)As layer and the upper AlAs barrier. This lowers the local effective barrier height for the electrons tunneling into the quantum well from the n-doped layer below. For these STM and STS measurements, we have employed a higher $T_A$ than that used in reference [100], with the aim of increasing the density of the diffused Mn$^{2+}$ ions, thus making it easier for our STM measurements to detect the diffused ions and their effect on the potential profile.

8.3 Topography results

The large area (160 nm × 55 nm) cross-sectional STM topography scan in figure 8.2a reveals clearly the interface between the (GaMn)As capping layer and the undoped GaAs spacer layer directly below it, and also the two AlAs barriers which appear as two dark, horizontal bands in the scan. Of particular interest is the wavy pattern in the GaAs layer directly under the lower AlAs barrier. This pattern was absent in the topography images of the as-grown sample, see figure 8.2b. The wavy pattern provides visual information about the modulation of the electrostatic potential and can
8. Nanoscale potential fluctuations in (GaMn)As/GaAs heterostructures

Figure 8.2: (a) Large area (160 nm × 55 nm) cross-sectional STM topography scan of the annealed sample, measured at -3.5 V and 25 pA. (b) Topography scan of the as-grown sample, measured at -3 V and 25 pA. (c, d) Band structure perpendicular to the cleaved surface, parallel to the STM tip.

be interpreted using the schematic energy diagrams in parts c and d of figure 8.2, which show the band structure perpendicular to the cleaved surface, parallel to the tip. When a negative sample voltage is applied, the bands bend downward [49]. At the n-side of the structure (figure 8.2d) the conduction band is pulled below the Fermi level of the sample (E$_{F,s}$) due to this band bending, creating a 2DEG at the semiconductor-vacuum interface. The 2DEG is not created at the p-side of the structure, see figure 8.2c. We interpret the wavy edge between the yellow and orange regions at the bottom of figure 8.2a as representing the spatial variation of the edge of the Fermi sea in the electron accumulation layer adjacent to the barrier.

8.4 Spectroscopy results

The bias condition for the formation of the 2DEG is also revealed in our STS measurements. Figure 8.3a shows a cross section through the dI/dV data set, perpendicular to the interface, averaged over the full width of the image. This plot closely resembles the band diagram and layer composition
8.4. Spectroscopy results

Figure 8.3: (a) Cross section through a spectroscopy map, parallel to the white dashed line in (b). The white dashed line in (a) indicates the onset of the 2DEG. The color scale in a is log(dI/dV). (c) Cross-section through the topography image in (b), showing the cross-talk with the topography. The arrows in (c) indicate the positions where the spectra shown in figure 8.4 are taken.
of our device. The parabolic feature at the bottom right-hand side of the image, highlighted by the white dashed line, gives the bias condition for the onset of the 2DEG. The onset voltage increases toward the substrate as expected; the Fermi level is closer to the CB at the n-side of the structure, so a smaller negative voltage is needed to create the 2DEG. Note that the creation of the 2DEG is an effect of tip-induced band bending, and therefore it appears at a negative voltage, even though the 2DEG itself is related to the CB.

A cross-section through the topography (figure 8.3c) shows a significant change in tip-sample distance ($\Delta z$) during the measurement, even though the surface is atomically flat. This is caused by electronic effects. In a first approximation, the tip-sample distance, $z_{\text{tip}}$, enters exponentially in the differential conductance, $\frac{dI}{dV} \propto \rho \exp(-2\kappa z_{\text{tip}})$. Here $\kappa \sim 1\,\text{Å}^{-1}$ is the inverse decay length in the vacuum [37, 41] and $\rho$ is the LDOS. Ideally we want to measure at a constant tip-sample distance, because changes in $\Delta z$ lead to so-called topography cross-talk, which manifests itself in two ways in our data. The first is the apparent change in the band gap in the intrinsic region and second is the alignment of the AlAs barriers.

The band gap appears to be significantly smaller on the p-side (left) than at the n-side (right), with a smooth transition in the intrinsic part of the p-i-n structure, indicated by arrow 2 and 3. Figure 8.3c shows that the tip is $\sim 0.75\,\text{Å}$ further away from the sample at $y = 40\,\text{nm}$ than at $y = 0\,\text{nm}$. We thus underestimate the LDOS where the tip is further away from the sample, which leads to an apparent band gap widening at the n-side of the structure.

The second consequence of the topography cross-talk is the apparent alignment of the AlAs barriers. The onset of tunneling into the CB appears at a lower voltage in the AlAs barriers than in the surrounding GaAs. We observe this consistently in all our measurements. The AlAs barriers appear dark in the topography image (figure 8.3b), which means that the tip is closer to the sample on top of the barriers. This leads to an overestimation of the LDOS on top of the AlAs barriers and thus an apparent reduction of the band gap.

Our spectroscopy data show both the $\Gamma$ and the $X$ minima in the CB of the AlAs barrier (see figure 8.4). Spectra measured on top of GaAs (black) show only one step, whereas we observe two steps in spectra measured on the AlAs layers (gray). We attribute the first step to the onset of tunneling into the $X$ minimum, and the second step to the onset of tunneling into the $\Gamma$ minimum. This reflects the well-known transition from a direct band gap in GaAs to an indirect band gap in AlAs [53].
8.5 Potential fluctuations

Figure 8.4: $dI/dV$ spectra on the GaAs (black) and the AlAs barrier (gray). Both the onset of tunneling into the $X$ and the $\Gamma$ minimum are visible in the AlAs barriers.

The cross section in figure 8.3a also shows the band gap narrowing at the (GaMn)As-GaAs interface as the tip is moved over the (GaMn)As, indicated by arrows 1 and 2. The image reveals a step both in the CB and in the VB, so we observe both a change in the band gap and a shift of the Fermi level. Part of the 280 meV change in the band gap is due to an apparent band gap widening on the i-GaAs layer, caused by TIBB [49, 101]. The screening length in i-GaAs is much longer than that in the heavily p-doped (GaMn)As layer, leading to a larger TIBB. Using the code in reference [49], we estimate the difference in TIBB to be 100-200 meV. The large error is due to the uncertainty in the input parameters in the TIBB calculation. The remaining change corresponds to the real band gap narrowing due to the heavy p-type doping and is therefore estimated to be $130 \pm 50$ meV, reflecting the merging of substitutional Mn acceptor states with the valence band of (GaMn)As [15] (the acceptor level for isolated Mn acceptor is 113 meV above the valence band). This is in qualitative agreement with reference [102].

8.5 Potential fluctuations

We now consider the lateral fluctuations of the edge of the 2DEG (i.e. the wavy bright pattern) shown in figure 8.2a. The edge of the 2DEG in the $xy$-plane represents the position where the Fermi level of the sample crosses the conduction band at the surface and is therefore a constant po-
8. Nanoscale potential fluctuations in (GaMn)As/GaAs heterostructures

Figure 8.5: (a) Simulated curves at three distances, $d$, from the (GaMn)As-GaAs interface with a scaled $x$ axis, showing the scaling of the fluctuations with $l = 2d$. (b) Typical $dI/dV$ spectrum at the p-side. (c) 3D representation of the onset of the CB. (d-f) Onsets of the VB for the as-grown and the annealed samples. The black dashed lines indicate the (GaMn)As-GaAs interface, the white dashed lines indicate the GaAs-AlAs interface of the first barrier. (g, h) Numerical simulations of the potential fluctuations near the (GaMn)As-GaAs interface for as-grown (no Mn$_i$ diffusion) and annealed samples respectively. (i) Line sections through the experimental data in (e) at three different distances $d$ from the (GaMn)As-GaAs interface (dots) and the corresponding fits (lines). The blue balls indicate the charged clusters. A 50 mV offset is added to the black line for clarity.
8.5. Potential fluctuations

tential contour. The lateral fluctuations in the onset of this bright pattern are thus a clear indication of the presence of lateral potential fluctuations. We can compare the characteristic length scale of these fluctuations with simulations of the local electrostatic potential fluctuations induced by the downward diffusion of \( \text{Mn}^{2+} \) ions [99]. The correlation length of the electrostatic potential across the \( xz \) plane increases with increasing \( y \), i.e. with increasing distance to the plane of charges at \( y = 0 \), because fluctuations with high spatial frequencies tend to be exponentially filtered out, according to Laplace’s equation. Figure 8.5a presents numerical simulations of the electrostatic potential fluctuations for different distances \( d \) in a normalized length scale \( x/d \). The characteristic size of the potential fluctuations \( l \) can be estimated as \( l \approx 2d \), indicated by the scale bars. The \( l = 2d \) approximation also works for the wavy pattern in figure 8.2b; the length scale is \( \sim 80 \text{ nm} \) at \( d = 36 \text{ nm} \).

In order to investigate the spatial distribution of the potential fluctuations and trace them to particular \( \text{Mn}^{2+} \) nanoclusters, we performed cross-sectional STS with high lateral resolution on the (GaMn)As-GaAs-AlAs region of the annealed and as-grown samples. A typical \( dI/dV \) curve is shown in figure 8.5b. We extract the onset of the CB and VB as a function of the lateral position from these data sets, by defining a critical \( dI/dV \) value, \( \epsilon \), as shown in figure 8.5b. The onset of the CB is schematically shown in 3D in figure 8.5c. A similar way of presenting STS data was used in reference [103], and we now elaborate this technique by applying it on a functional device. At positive sample voltages the fluctuations in the CB tend to be screened by the free holes. We therefore focus on the onset of the VB, measured at a negative bias.

The experimentally determined onsets of the VB for the as-grown and the annealed sample are shown in figure 8.5d-f. The gray scale and the contour lines correspond to the bias onset (in volts) of the VB. The images show the i-GaAs layer between the (GaMn)As layer and the first AlAs barrier. The bright area at the top is the (GaMn)As layer, the dark area at the bottom is the first AlAs barrier, the black dashed line indicates the (GaMn)As-GaAs interface, and the white dashed line indicates the GaAs-AlAs interface. For the as-grown sample, the contour lines show fluctuations in the \( x \)-direction on the length scale of a few nanometers. On a longer length scale (a few tens of nanometers), they are straight and parallel to the interfaces. However, for the annealed sample, we find significant potential fluctuations close to the (GaMn)As-GaAs interface. The fluctuations are short ranged, \( < 5 \text{ nm} \), and become more spread out toward the AlAs barriers, becoming shallower and longer, \( > 15 \text{ nm} \).
Parts g and h of figure 8.5 show the corresponding simulated potentials\(^1\) (for details see reference [99]). In the as-grown sample, almost all of the interstitials reside in the (GaMn)As layer where their potential is heavily screened by the high density of free holes. This inhibits formation of the local potential fluctuations, and therefore the contour lines tend to be straight and parallel to the interface (figure 8.5d, g). Annealing causes the interstitials to diffuse toward the undoped GaAs-AlAs layers. Diffusion of the Mn\(_i\) into GaAs following the model presented in reference [14] predicts that most of the Mn\(_i\) ions will be located within a few nanometers of the (GaMn)As-GaAs interface. This interface has an effective width of \(\sim 2\) nm (figure 8.2a and 8.5d-f, \(y = 0\) corresponds to the estimated position of (GaMn)As-GaAs interface) due to the necessary conditions for growing low temperature (GaMn)As. This leads to the significant uncertainty of \(d\) for \(d < 5\) nm. For \(d > 10\) nm the precise form of the vertical distribution of Mn\(_{i}^{2+}\) does not play a significant role in the resulting landscape of the electrostatic potential fluctuations [99]. In the simulations presented in parts a, g, and h of figure 8.5 we assume a delta-layer of Mn\(_i^{2+}\) at the (GaMn)As-GaAs interface, with randomly formed clusters of Mn\(_i\). We assume perfect screening inside the (GaMn)As layer in the simulation. This is in qualitative agreement with the experimental data of figure 8.5e, f, which indicate very little propagation of electrostatic potential fluctuations at \(y < 0\), toward the bulk of the (GaMn)As layer.

Simulations both for the as-grown sample and for the annealed sample agree qualitatively with the experimental images: there are strong, short ranged fluctuations near the interface, that become shallower and longer ranged with increasing \(y\). The length scale of the potential fluctuations in the simulation corresponds to the length scale in the experiments, and we again find the characteristic scale of \(l \approx 2d\), seen in the line sections shown in figure 8.5i. The sections are taken parallel to the interface (area 2), at three distances from the (GaMn)As-GaAs interface: 4.0 nm (black), 6.0 nm (red), and 8.0 nm (blue). Scale bars of length \(2d\) are added.

### 8.6 Number of charges per cluster

The nanoscale fluctuations of the measured electrostatic equipotential lines in figure 8.5i can be fitted with the Coulomb potential generated by two charged clusters (labeled 1 and 2), each extending over \(\sim 10\) nm, with \(N_i\) elementary charges in each cluster. We apply a 2D plane fit, where we fit

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\(^1\)The simulations are performed by prof.dr. Laurence Eaves and dr. Oleg Makarovsky, School of Physics and Astronomy, University of Nottingham
8.6. Number of charges per cluster

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Table 8.1: Overview of the fit results.

all $37 \times 200$ pixels of the experimentally extracted onset of the VB map at once. We model the nanoclusters as point charges, see figure 8.6c. We include two clusters ($i = 1, 2$) with $N_i$ charges in each cluster, located at $(x_{0,i}, y_{0,i})$. We include image charges due to the metallic screening in the (GaMn)As layer (the term with $r^+$ in equation 8.1a). In order remove the potential landscape due to the p-i-n structure, we subtracted a line-section far away from the cluster. The resulting potential is:

$$
V = V_0 - e \frac{1}{4\pi \varepsilon_0 \varepsilon_r} \sum_{i=1,2} \left( \frac{N_i}{r^+} - \frac{N_i}{r^-} \right),
$$

(8.1a)

where $r^\pm = \sqrt{(x-x_{0,i})^2 + (y \pm y_{0,i})^2 + z_0^2}$. (8.1b)

Here $x_{0,i}$ is the position of the cluster along the interface, and $z_0$ is the depth of the cluster below the cross-sectional surface. Both $x_{0,i}$ and $y_{0,i}$ can be obtained from the STM scan within a few Å. The main fitting parameter for each nanocluster is thus the effective charge $+N_i \cdot e$. We adopted $\varepsilon_r = 13.1$ as in bulk GaAs. There are indications that an effective $\varepsilon_r$ with a lower value should be used, due to the effect of image charges in the vacuum barrier [69, 85, 94]. However, the presence of the metallic tip induces image charges as well, and increases the effective $\varepsilon_r$. We therefore used the bulk value as a zeroth order approximation.

We focus on the intrinsic region between the (GaMn)As layer and the first AlAs barrier. We exclude a layer with a thickness of 3nm directly beneath the (GaMn)As layer, because the approximation of the individual defects by a cluster fails for shorter distances to the cluster. Figure 8.6 and table 8.1 summarize the fit results. Note that we kept $z_0$ fixed and we fit the data for three values of $z_0$.

We find $N_1 = 13 \pm 2$ elementary charges and $N_2 = 12 \pm 2$ charges, consistent with the degree of clustering deduced from the modeling of the
Figure 8.6: (a) Onset of the VB after correction for the p-i-n structure. $y = 0$ nm corresponds to the (GaMn)As-GaAs interface. (b) Coulomb fit. (c) Schematic of the two clusters (blue balls) and their image charges (orange balls). (d-i) Line sections through the experimentally found onset of the VB (black dots) and the fit (red lines) at the indicated distances $y = d$. 
8.7 Internal structure of the clusters

We now address the origin of the fluctuations on the atomic level, i.e. the individual defects in the charged clusters. We compare the fluctuations in the onset of the VB (area 2, figure 8.5f) with the corresponding topographies, which are shown in parts a and b of figure 8.7. The contour line at $-1.0 \text{ V}$ is copied into both topographs in blue. The dip in the onset of the VB encloses about seven individual defects in cluster 1, marked by the black stars. Figure 8.7c and d show a zoom of cluster 1 and 2. Figure 8.7c is a topography image and figure 8.7d is a spectroscopy map at $0.68 \text{ V}$. In the topography image not all the defects are resolved individually, especially in cluster 2. The spectroscopy image reveals two Mn$_i$ in the center of cluster 2. Other defects might be present, though we can exclude arsenic anti-sites, which have a well known contrast in STM [104].

The defects are bright at positive sample voltages (a) and are almost
invisible at negative sample voltages (b). Similar defects are observed in the as-grown sample (figure 8.7e, f, marked by the black stars). In the as-grown sample, these defects do not form clusters and they are located deeper inside the (GaMn)As layer, further away from the (GaMn)As-GaAs interface. In close vicinity to these clusters in the annealed sample, the onset of the VB is pushed to lower voltages. This indicates that the defects are positively charged. The previously obtained value of $13 \pm 2$ charges in cluster 1 agrees very well with seven doubly ionized defects; thus the doubly charged interstitial manganese donor ($\text{Mn}^{2+}_i$) is the most likely candidate for these defects. The clusters form randomly, confirmed by our simulations, which assume random diffusion. The interstitials are efficiently screened by the free holes in the (GaMn)As layer, thus the Coulomb repulsion is much smaller than the thermal energy at the annealing temperature and the activation energy [14, 99]. Therefore the formation of the clusters is not prohibited by Coulomb repulsion. Note that the contrast that we identify as $\text{Mn}^i$ is bright and circularly symmetric at positive sample voltages (see insets in parts e and f of figure 8.7), as is expected for a donor, in contrast to reference [105]. The contrast attributed to $\text{Mn}^i$ in reference [105] is later identified as substitutional Mn in the first subsurface layer [76].

For cluster 2 it is not possible to count the individual $\text{Mn}^i$ atoms as we did for cluster 1. However, the probability of forming a cluster with a total charge of twelve elementary charges consisting of six doubly ionized $\text{Mn}^i$ ions is much larger than a cluster consisting of twelve singly charged defects. We therefore conclude that the clusters mainly consist of $\text{Mn}^{2+}_i$. In addition we expect the $\text{Mn}^i$ to be doubly ionized in the intrinsic region.

### 8.8 Ionization ring

Figure 8.8a shows a series of $dI/dV$ images of area 2 (the same area as in figure 8.5f, and 8.7a-d). Surrounding cluster 1, we observe a ring whose diameter increases with voltage. Figure 8.8b shows a cross section through this ring along the dashed black line in figure 8.8a. These rings are ionization rings and are well understood for single impurities [60, 69], see chapters 4, 5 and 6. The charge state of the defect is different inside the ring than outside the ring, and an increasing diameter with voltage indicates that the defect is donor-like. However, the observation of a donor-like ring in a p-type material is unexpected, because the ring appears when the defect level is pulled through the Fermi level by the tip-induced band bending [49]. This suggests that the potential minimum in the CB in the vicinity of the $\text{Mn}^{2+}_i$ nanocluster is very deep, $\sim 1$ eV. This estimate is supported by a
8.8. Ionization ring

Figure 8.8: (a) Series of dI/dV images at the indicated voltages of area 2 (figure 8.5f and 8.7), showing a ring of ionization at the GaMnAs-GaAs interface. (b) Cross-section along the black dashed line in a. (c, d) There are strong short ranged fluctuations in the onset of the bands in the annealed sample (c) indicated by the arrow, which are not present in the as-grown sample (d). The sections are taken at the (GaMn)As-GaAs interface and the color scale is log(dI/dV).
cross-sectional scan at the (GaMn)As-GaAs interface, parallel to the interface (figure 8.8c), which reveals a local minimum in the CB, with a depth of \( \sim 0.8 \) eV, approximately half of the band gap of GaAs. We attribute these fluctuations to clusters of charged defects. The numerical simulations of the potential due to diffusing Mn\(_i\) also indicate the presence of potential minima of this depth [99]. We do not observe these deep minima in the as-grown sample as shown in figure 8.8d. We expect only the weakly bound Mn\(_i\) to move during annealing, because we used a low annealing temperature of only 200 °C [14]. This is another indication that the charged clusters consist of charged Mn\(_i\), and confirms our identification of the bright defects in figure 8.7e as Mn\(_i\).

8.9 Summary

In summary we have performed detailed cross-sectional STM and STS measurements on double barrier p-i-n resonant tunneling diode structures in which the p-layer is (GaMn)As containing 5% Mn. We compare our measured images and spectra with numerical simulations and previous experimental observations of the effect of interstitial Mn diffusion on the electronic properties of (GaMn)As/GaAs p-i-n diodes. We extract the onset of the VB, and our measurements confirm the formation of nanoscale electrostatic potential fluctuations in the annealed devices. The deep minima of these fluctuations can strongly confine electrons in QD-like states. These measurements allow us to trace the origin of a particular electrostatic potential minimum to nanoscale clusters containing a small number (approximately seven) of charged defects. We provide evidence that these charged defects are doubly ionized Mn interstitial ions. Our results provide direct microscopic evidence to demonstrate that the electronic properties of semiconductor devices can be manipulated on the nanoscale by moving individual charged impurities. These results provide a fundamental advance in our general understanding of the effect of a charged impurity distribution on the formation of nanoscale electrostatic potentials and the way in which this affects the characteristics of nanoelectronic semiconductor devices. We also demonstrate a technological capability to probe this effect and to trace it down to individual elementary charges.
Chapter 9

The influence of the tip work function on scanning tunneling microscopy and spectroscopy on Zinc doped GaAs

9.1 Introduction

In the previous chapters, we have regularly used the experimentally determined flat band conditions and tip work functions. This method was explained in section 2.7, and was developed by Loth et al. [43, 51]. In this chapter we elaborate this method, by including some effects that were neglected in the previous studies by Loth et al. We apply this extended method to a measurement of Zn acceptors in GaAs, where we investigate the influence of the tip work function on the Zn signatures in STM and STS. We deliberately change the tip work function and experimentally extract the flat band condition. We observe two qualitatively different situations in the STS data, depending on the tip work function. Hardly any Zinc-induced peaks in the dI/dV spectra are visible in the first case, whereas in the second case strong peaks are present at the Zn atoms, which are followed by negative differential conductivity.

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Shallow and deep acceptors in III-V semiconductors have been the subject of many STM studies in recent years. Both shallow and deep acceptors have a by now familiar anisotropic shape, which was first reported for the shallow acceptor Zn in GaAs in 1994 [24, 25] and for the deep acceptor Mn in GaAs in 2004 [29]. Since then, many authors have studied these acceptors with STM [27, 28, 30, 31, 32, 43, 76, 77, 78, 106, 107]. All the STM studies report that the anisotropic contrasts appear at small positive sample voltages, but the specific voltage differs between 0.6 V [29] and up to 3 V [24, 25]. Furthermore, it is commonly accepted by now that the anisotropic contrast appears at different voltages from tip to tip on the same sample. It is generally believed that the anisotropic shape is visible when tunneling into the conduction band is suppressed. Several models have been proposed in the past to explain the triangular shape of the shallow acceptors (see e.g. figure 9.1c and e) or the bow-tie like shape for deep acceptors. For example, the authors in reference [27] suggest that the triangle appears due to tunneling into the empty valence band (VB) states, implying that tunneling into the conduction band (CB) is completely suppressed. Reference [43] states that the triangles are only visible when there is a depletion layer underneath the tip, and propose a model that involves resonant tunneling through evanescent gap states [106]. Other authors suggest that the triangle appears due to tunneling into the excited state of the acceptor [107]. In case of the deep acceptor Mn in both InAs and GaAs, it has been shown that the wave function is imaged [30, 31, 32, 77, 78], where mixing between spherical harmonic functions with s and d character are responsible for the bow-tie shape. Furthermore it was shown recently that the symmetry is lifted for acceptors close to the surface due to surface induced strain [77].

We start the chapter by presenting our STM results. We then describe the method of extracting the flat band voltage experimentally in detail, which is necessary for the analyses and interpretation of our results given in the final section of the chapter.

### 9.2 Results

We performed our cross-sectional STM and STS measurements on Zn-doped GaAs, with an average doping concentration of \(2 \cdot 10^{19} \text{cm}^{-3}\). The measurements were performed at 5K.

Figure 9.1 shows a series of STM topography images, measured at different sample voltages and with two different tips. We see the same behavior in the STM images as is presented in references [27, 28, 43, 107]. At a
Figure 9.1: Series of topography images of Zn:GaAs at different voltages. (a) to (c) are measured with the same tip and (d) and (e) are measured with a different tip. External voltage, current set-point and flat band voltage $V_{FB}$ are indicated. The images are 25nm × 25nm. The typical triangular contrast appears at low positive voltages. This $V_{FB}$ strongly depends on the flat band voltage.
9. The influence of the tip work function on scanning tunneling microscopy and spectroscopy on Zinc doped GaAs

high positive sample voltage (figure 9.1a) the Zn atoms appear as dark depressions, at lower positive voltages (figure 9.1b) bright features start to appear, but the depressions are still visible, and at an even lower voltage (figure 9.1c), the typical triangular features appear. This behavior is similar for all the positive bias STM images of Zn-GaAs. The triangles appear at a well defined voltage, as can be seen in figure 9.1b and c. The voltage difference between the two images is only 50 mV, but in figure 9.1b there are still dark depressions visible near the tip of the triangle, that are gone in figure 9.1c. Important to note is that the triangles remain visible when reducing the sample voltage. Therefore we define \( V_\triangle \) as the highest voltage where the bright triangles can be observed without any visible depressions in topography images. Although the behavior is similar in all the measurements, \( V_\triangle \) differs for different tips. This is clearly visible in figure 9.1c and e, which were measured with different tips. In both images the triangles are clearly visible, but they are measured at voltages that differ by 0.35 V.

9.3 Extracting the flat band voltage

In order to understand the origin of the differences in \( V_\triangle \), we deliberately induce tip modifications, measure \( V_\triangle \) and determine the tip work function \( \Phi_{tip} \) for each tip. For the determination of \( \Phi_{tip} \) we follow the procedure as described in section 2.7 and improve it for our measurement. A short recap of the method is that by measuring \( I(z_{tip}) \), or in our case \( z_{tip}(I) \), the inverse decay length \( \kappa \) is obtained. This can be translated into the effective barrier height \( \phi_B \), from which the tip work function can be extracted (see section 2.7 for a more extended description).

In our analysis we include two effects that Loth et al. [43, 51] neglected, which turn out to have a significant effect. The first is the effect of the image charges due to the tunneling electron. Secondly, we use a more advanced approximation for the dependence of the tunneling current on the tip-sample distance than the commonly used approximation \( I \propto \exp(-2\kappa z_{tip}) \).

We first discuss the effect of the image charges due to the tunneling electron. The reduction of the tunneling barrier due to image charges has been studied extensively in the literature [108, 109, 110]. We consider a semi-infinite metal (the tip) on top of a semi-infinite semiconductor slab with a dielectric constant \( \epsilon_r \), separated by a vacuum barrier with a width \( z_{tip} \). The potential due to the image charges is then given by equation 9.1 [108, 109, 110]
9.3. Extracting the flat band voltage

\[ \Phi_i = -\frac{e^2}{8\pi\epsilon_0} \left[ \frac{1}{2z} + \sum_{n=1}^{\infty} \left( \frac{\frac{1}{2}a^n}{z_{\text{tip}}n + z} + \frac{\frac{1}{2}a^n}{z_{\text{tip}}n - z} + \frac{a^n}{z_{\text{tip}}n} \right) \right] \]

(9.1)

where \( a = \frac{\epsilon_r - 1}{\epsilon_r + 1} \). This barrier is shown on scale in figure 9.2a for various tip-sample distances \( z_{\text{tip}} \), where we use an electron affinity of the sample \( \chi \) of 4 eV, a tip work function \( \Phi_{\text{tip}} \) of 3.9 eV and a sample voltage of 1.6 V. The CB, VB and Fermi level of the tip \( (E_{F,\text{tip}}) \) are indicated. The image charges clearly cause a strong reduction of the effective tunneling barrier. The smaller the tip-sample distance, the bigger the effect. For \( z_{\text{tip}} \lesssim 2.5 \, \text{Å} \), the barrier even becomes negative. In figure 9.2b the corresponding reduction in \( \kappa \) is plotted, where we calculated \( \kappa \) at the maximum of the barrier \( \kappa \equiv \sqrt{2m_0\Phi_B/\hbar} \) (WKB approach, see for example reference [54]). The dash-dotted black line corresponds to the original rectangular barrier and the dashed cyan line corresponds to the barrier including the image charge potential.

The second effect is a bit more subtle. The key element is that the approximation of the tunneling current in STM analyses by \( I \propto \exp(-2\kappa z_{\text{tip}}) \) is not accurate for \( z_{\text{tip}} \lesssim 5 \, \text{Å} \). This effect is described in detail in for example reference [37]. The full expression for tunneling through a rectangular barrier is given by [54]

\[ I \propto \frac{4\tilde{k}_t\tilde{k}_s\kappa^2}{\kappa^2 \left( \tilde{k}_t^2 + \tilde{k}_s^2 \right) + \left( \tilde{k}_t^2 + \kappa^2 \right) \left( \tilde{k}_s^2 + \kappa^2 \right) \sinh^2(\kappa z_{\text{tip}})} \]

(9.2)

Here \( \tilde{k}_{t,s} \) are the wave vectors in the tip and the sample respectively, divided by their effective masses. \( \kappa \) is the inverse decay length, defined by \( \kappa \equiv \sqrt{2m_0\Phi_B/\hbar} \) and \( \Phi_B \) is the barrier. This expression indeed goes to \( I \propto \exp(-2\kappa z_{\text{tip}}) \) for \( z_{\text{tip}} \gg \kappa^{-1} \).

Next we address the issue that the barrier including the image charge potential is not square, whereas equation 9.2 holds for a rectangular barrier. Reference [37] approximates the net barrier by a rectangular barrier with a height equal to the maximum of the net barrier. This is plotted as the dotted blue line in figure 9.2b. In our work we calculate the transmission for the real barrier using transfer matrices [54]. We start with a rectangular or trapezoidal barrier with height \( \Phi_0 \) (here \( \Phi_0 = 3.9 \, \text{eV} \)). We then calculate the image potential for a certain \( z_{\text{tip}} \). We divide the net barrier into \( N \) square barriers, see inset II and III in figure 9.2b. We typically use \( N = 10^4 \), as the results are converged at this value of \( N \). Using the
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Figure 9.2: (a) Reduction of the tunneling barrier due to the effect of image charges. The barriers are shown on scale. Various parameters are indicated. (b) Comparison between the decay length $\kappa$ as found with various approximations. See the text for details.
9.3. Extracting the flat band voltage

transfer matrices we calculate the transmission and we repeat the procedure for all the tip-sample distances. We thus end up with the transmission versus $z_{\text{tip}}$. Ideally we want to fit these curves to the experimental $I(z_{\text{tip}})$ curves to find the original rectangular barrier $\Phi_0$, because $\Phi_0$ is needed to extract the tip work function. In practice this is nearly impossible due to the numerical calculations, thus we reverse the method. We therefore extract the value of $\kappa$ that an experimentalist would find from the calculated transmission curve. We do this by locally fitting the transmission curve with $\exp(-2\kappa_{\text{app}}z_{\text{tip}})$ \(^1\). In reference [37] this is called the apparent barrier height, or apparent decay length $\kappa_{\text{app}}$.

The barrier including the image charges goes to $-\infty$ at the edges. The image charge potential is a classical approach, and we are dealing with very short length scales in the Å regime. The WKB approach fails for rapidly varying potentials. Therefore an atomistic view would be the proper way to describe this problem, but in such an approach it is nearly impossible to link an experimental decay length to a tip work function. Therefore we stay in the classical approach, and we investigate two possibilities to deal with the singularities in the potential at the edges. The first is to fully include this in the transmission calculation. The result is the solid red line in figure 9.2b. The second possibility is to include only the positive part of the barrier. The result of this approach is the long-dashed green line in figure 9.2b.

We now discuss the summary given in figure 9.2b in more detail. The reduction in the barrier due to the image charges is shown by the difference between the dash-dotted black and the dashed cyan line. These are lines resulting from the simple calculation, neglecting all above described difficulties: $\kappa = \sqrt{2m_0\Phi_{B,\text{max}}/\hbar}$. The dotted blue line is the approximation as described in reference [37]. The barrier is approximated by a rectangular barrier, with a reduced height due to the image charges. The last two lines, the solid red and the long dashed green, result from the full transmission calculation for the image potential. For the red line the negative part of the barrier is included, whereas we only include the positive part for the long-dashed green line. The calculations for these two lines include the most effects, and will thus be the closest to reality. Note that the exact shape of the solid red, dotted blue and long-dashed green lines depend on the values of $\tilde{k}_t$ and $\tilde{k}_s$, which are not very well known. They depend on the kinetic energies and on the effective masses of the electron in the tip and the sample. Especially the kinetic energy and the effective mass in

\[^1\]We use $\kappa_{\text{app}} = -\frac{1}{2} \frac{\text{d}}{\text{d}z_{\text{tip}}} (\ln (I(z_{\text{tip}})))$, instead of actually fitting the curve. See for more details for example reference [37].
tungsten tip are relatively unknown. In the example shown here we use $\tilde{k}_t = 0.5 \text{ Å}^{-1}$ and $\tilde{k}_s = 0.6 \text{ Å}^{-1}$.

Figure 9.3 compares simulated $\kappa$ versus $z_{\text{tip}}$ curves where we varied the parameters. We show the result for the transfer matrix method where the negative part of the barrier is included (solid red, figure 9.2b, subset II) and where this part is neglected (long-dashed green, figure 9.2b, subset III). The dash-dotted black line corresponds to the original rectangular barrier. The left column displays the results for $\tilde{k}_t = 0.01 \text{ Å}^{-1}$ and the right column for $\tilde{k}_t = 0.5 \text{ Å}^{-1}$. The rows correspond to different sample voltages as indicated. The main difference between the voltages is the wave vector in the sample, which is given by $\tilde{k}_s = \sqrt{2m_0m^*E_{\text{kin}}/(\hbar m^*)}$. For 2V, the electron tunnels into the CB, so the CB effective mass has to be used. The kinetic energy is given by the difference between the Fermi level of the tip and the onset of the CB, which is 0.5 eV for a sample voltage of 2 V. This gives $\tilde{k}_s = 1.39 \text{ Å}^{-1}$. For a positive voltage close to the conduction band, the kinetic energy is much smaller, 0.1 eV for a sample voltage of 1.6 V, leading to $\tilde{k}_s = 0.62 \text{ Å}^{-1}$. At negative voltages the VB effective mass has to be used, and the kinetic energy is given by the full VB of 6.5 eV [47, 48]. This leads to $\tilde{k}_s = 1.94 \text{ Å}^{-1}$. We see that for large positive and negative voltages the behavior is the same: $\kappa$ drops for small $z_{\text{tip}}$ and there is a plateau for large $z_{\text{tip}}$. The influence of the choice of $\tilde{k}_t$ is small. However for small positive voltages, close to the onset of the CB, the choice of $\tilde{k}_t$ is significant and depending on this choice, there is a local maximum in the long-dashed green curve.

If we now turn to our experimental $\kappa(z_{\text{tip}})$ data (figure 9.4), we find a qualitative agreement. Note that the x-axis displays $\Delta z_{\text{tip}}$, because we do not know the absolute tip-sample distance. It is clear that the image charges play a role in the experiments: $\kappa$ drops for small $z_{\text{tip}}$, whereas for large $z_{\text{tip}}$ there is a plateau, both in the experiment and in the simulations. The local maximum as was found in the simulations is also visible in the experiment. However in this example this local maximum is observed at a higher voltage than in the simulation. We neglected the effect of tip induced band bending (TIBB) in the simulations. An upward TIBB at $V > 0$ causes a reduced kinetic energy in the sample, which has the same effect as reducing the voltage in the simulation. Our data consisting of $\sim$ 50 sets of $\kappa$ versus $z_{\text{tip}}$ confirm the trend in the simulations, i.e. there is only a clear local maximum at relatively small positive voltages. This is a first indication that our approach is correct.

In the simulations the plateau is detached from the dash-dotted black line by $\sim 10\%$ (figure 9.3), which leads to an underestimation of $\kappa$. We
Figure 9.3: Simulated $\kappa$ versus $z_{tip}$ curves for 2 V, 1.6 V and −2 V for a tip work function of 3.9 eV. For the left column we used $\tilde{k}_t = 0.01 \text{ Å}^{-1}$ and for the right column $\tilde{k}_t = 0.5 \text{ Å}^{-1}$. We show both the curve as found when including the negative part of the potential (solid red line) and for the case that the negative part is neglected (long-dashed green).
therefore correct the plateau value by 10% to obtain an optimal estimate for $\kappa$ belonging to the original barrier. We realize that this is far from perfect, and we have to be careful about the absolute values for the tip work function and flat band voltage that we obtain. However as long as we compare measurements where the tip work function is measured at the same voltage, we can compare the relative positions of the flat band voltage without any problems. We find a flat band condition of 1.7 V ($\Phi_{\text{tip}} = 3.9\,\text{eV}$) for figure 9.1a-c and 0.4 V ($\Phi_{\text{tip}} = 5.5\,\text{eV}$) for figure 9.1d and e. The large difference in tip work functions might seem surprising, because the tip work function is usually assumed to be around 4.5 eV for tungsten in STM studies. However large variations are also reported in reference [111] for different crystal orientations. They find values ranging from 4.30 eV for the (116) plane to 5.99 eV for the (011) plane. They furthermore report that the work function depends on the annealing temperature, which is linked to the pureness of the crystal. They find a reduction of a few hundred meV for less pure crystals. Other studies show that the work function depends on the surface roughness [112]. They find a reduction of 0.6 eV when W is adsorbed on a (110) W single crystal for coverages below one monolayer. That means that we expect work functions ranging from 3.5 eV to 6 eV, which nicely corresponds to our measurements. This is the second indication that our method of extracting the tip work function is reliable.

Figure 9.4: Comparison of a $\kappa(z_t)$ measurement at positive (black) and negative (red) voltages. Both measurements are done with the same tip at the same area of the sample. The lines are added to guide the eye.
9.4 Analyses and interpretation

Returning to our observation of different $V_\phi$ for different tips, we come to the following conclusion. Tips with a high flat band condition, corresponding to a small tip work function, have a low $V_\phi$, whereas tips with low flat band condition, and thus a large tip work function, have a high $V_\phi$. This is indicated in figure 9.1.

In order to investigate this further, we measure $dI/dV$ maps. At every pixel we take an $I(V)$ spectrum, and afterwards we take the numerical derivative. We eliminate crosstalk with the topography by choosing a set-point where the contrast in the topography is vanishing. We measured $dI/dV$ maps at the same areas of the sample and with the same tips as the topography images shown in figure 9.1. We can thus directly compare the topography images with the spectroscopy data, and we furthermore know the relative flat band conditions. Figure 9.5a and b show the $dI/dV$ spectra. Figure 9.5a is measured with the same tip as the measurements in figure 9.1a-c. Figure 9.5b is measured with a different tip, but with the same tip as the measurements in figure 9.1d and e. In both graphs the solid black curve is a spectrum on top of a Zn-atom very close to the surface ($\sim$ layer 2), the dotted red line on top of a Zn-atom a bit deeper below the surface ($\sim$ layer 5) and the dashed blue line on top of a Zn-atom very deep below the surface ($\sim$ layer 8). The dash-dotted green curve is on the bare surface. The two graphs are very different; in figure 9.5a there are hardly any peaks visible in the bandgap, whereas in figure 9.5b very strong peaks followed by negative differential conductivity (NDC) are visible. The zoom shown in the inset of figure 9.5a shows some very weak peaks, but the NDC is absent.

Let us first explain the presence of the strong peaks in figure 9.5b, and afterwards explain their absence in figure 9.5a. Our explanation differs from the interpretation in reference [106]. This difference originates from the inclusion of image charges while extracting the flat band voltage, which shifts the flat band condition to lower voltages by $\sim 1$ V. Therefore our model is based on upward TIBB, whereas Loth et al. assume downward TIBB. We propose a mechanism as shown in figure 9.5c. The strong peaks indicate that we have a very efficient tunneling path and the NDC indicates that this tunneling path only exists in a small voltage window. Moreover, the NDC requires that this efficient channel vanishes at higher voltages. There are two requirements for an efficient tunneling process at $V > 0$ V (section 2.6). First the acceptor level should be neutral ($A^0$) and secondly the electron should be able to tunnel away from the acceptor into the bulk of the sample. The handle is the TIBB [38, 49, 60, 61, 69], which shifts
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Figure 9.5: (a and b) dI/dV spectra on top of Zinc atoms in various layers below the surface. $V_F$ is indicated. The inset in (b) shows the lateral contrast at the peak maxima. (c) Schematic of our model. The peaks in the dI/dV spectra occur around flat band, when the acceptor level close to the surface is aligned with the empty part of the impurity band in the bulk.

the acceptor level with respect to the bulk VB. The TIBB depends on the applied voltage relative to the flat band voltage $V_{FB}$. For $V > V_{FB}$ the bands bend upward and the acceptor is neutral ($A^0$). For $V < V_{FB}$ the bands bend downward and the acceptor is negatively charged ($A^-$). In order to meet the first requirement we need to apply a voltage above the flat band voltage. The second requirement is met when the acceptor level is aligned with the acceptor band in the bulk, which occurs around flat band. The samples are highly doped ($2 \cdot 10^{19} \text{cm}^{-3}$), and therefore there will be an acceptor band with a width of $\sim 30 \text{meV}$ [52]. This band will be partially filled, so there are empty states available in the bulk, slightly above the onset of the VB. This means that we have an energy window
9.4. Analyses and interpretation

around flat band where the tunneling is very efficient: at voltages below flat band the acceptor is filled preventing efficient tunneling, and at voltages above flat band the acceptor level is lifted above the empty acceptor band and therefore the electron cannot leave the Zn acceptor elastically. This immediately explains the negative differential conductivity: by increasing the voltage the efficient tunneling channel via the Zn impurity disappears.

We now return to the absence of the peaks in figure 9.5a. The difference in the two graphs is the tip work function and thus the flat band voltage. The flat band voltage is $\sim 1.7\, \text{V}$ and $\sim 0.4\, \text{V}$ for figure 9.5a and b respectively. We therefore expect the first peak in figure 9.5a at a $\sim 1.3\, \text{V}$ higher voltage than the first peak in figure 9.5b. This corresponds to an external voltage of $\sim 2\, \text{V}$, which is at the edge of the spectrum, where the signal is dominated by tunneling into the conduction band.

Finally we address the observation of more than one peak. Subtracting a reference spectrum measured on the bare surface from the spectra on top of the Zn atoms, reveals a fourth peak, as is shown in figure 9.6. A possible interpretation is that the acceptor level is split into (at least) four levels. A similar splitting is observed for Manganese in GaAs [78] (see chapter 5) and Manganese in InAs [31], where three peaks were observed in both cases. For Mn in InAs, the three peaks are interpreted as different spin states, where the splitting from the $F = 1$ ground state is due to spin orbit interaction [31], whereas the splitting is smaller for Mn in GaAs, and was therefore attributed to the three projections of the $F = 1$ ground state.
which are split due to strain near the surface [78]. Atomic Zinc has a 3d^{10}4s^{2} configuration, which carries no spin. However the hole has a spin of \( \frac{3}{2} \), which has four projections. These states can split for example due to strain present near the surface [77, 78] or the electric field due to the STM tip. It is surprising that all peaks have a similar lateral contrast (see inset in figure 9.5b). However, this is also the case for Mn-GaAs. Another possible interpretation is related to a TIQD. For voltages above the flat band voltage, a TIQD is created, in this case for holes. The interaction between the acceptor level and the TIQD could lead to additional states.

We return to the observation that the triangles appear at very different voltages in the topography images for different tips. Tips with a high flat band condition (figure 9.1a-c and figure 9.5a) have rarely any dI/dV peaks in the band gap, and in the topography images a very low voltage has to be applied in order to see the triangles \( (V_{\phi} = 1.55\,\text{V}) \). This also coincides with the onset of the conduction band; the onset of the conduction band in figure 9.5a is \( \sim 1.5\,\text{V} \). Tips with a low flat band condition (figure 9.1d and e and figure 9.5b) have strong dI/dV peaks in the band gap, and in the topography images the triangles already appear at a high voltage \( (V_{\phi} = 1.9\,\text{V}) \). This is slightly above the onset of the CB, but very close. This suggests that the triangles appear at a voltage where tunneling into the CB is mainly suppressed, as is indicated in figure 9.5a and b.

### 9.5 Summary

In summary, we have investigated the effect the tip work function on STM and STS. We have analyzed in detail the effect of image charges on the tunneling barrier in STM. Including the effect of image charges causes a shift of the flat band condition to lower voltages by \( \sim 1\,\text{V} \) compared to the method proposed in reference [30]. The range of tip work functions that we find corresponds to the expected range, indicating that our method of extracting the tip work function is reliable. This difference of \( \sim 1\,\text{V} \) in the flat band voltage leads to a different model to explain the negative differential conductivity. According to our model, the peaks in the dI/dV spectra occur when the acceptor level aligns with the empty part of the impurity band in the bulk, indicating that the wave function is imaged. The onset of the CB as found in the STS data coincides with the voltage where the triangles appear in the topography images. This confirms the idea that the triangles appear when tunneling into the CB is suppressed.
Chapter 10

Magnetic field vector microscopy using bulk diamond

10.1 Introduction

Visualizing magnetic field vectors has been an area of interest for many years. The familiar method of spreading iron filings around a bar magnet was a well practiced technique when Faraday first described “lines of magnetic forces” in 1831 [113]. In the last few decades, many techniques have been developed to locally probe much weaker magnetic fields on much smaller length scales. Superconducting quantum interference devices (SQUID) [114], Scanning Hall probe microscopy [115], magnetic force microscopy (MFM) [116], and magnetic resonance force microscopy (MRFM) [117, 118] are a few methods. Using the localized spin triplet state in nitrogen-vacancy (NV) centers in diamond as an atomic scale magnetic field probe has also been proposed [119, 120]. Theoretical lateral and magnetic resolution limits exceed those of previously mentioned techniques and inherent operation in ambient conditions and low external fields is also advantageous. Early experiments using NV centers as proximity magnetometers show promising results [121, 122]. In this chapter, we present a field imaging technique using ensembles of NV centers in much the same way that Faraday used iron filings to view magnetic field lines.

This chapter is published in *Appl. Phys. Lett.* 96, 092504 (2010)
10. Magnetic field vector microscopy using bulk diamond

Figure 10.1: (a) Crystal structure of diamond with an NV center. (b) Level structure of an NV center. (c) Example of an optically detected ESR spectrum, where three pairs of Zeeman-split peaks are visible.

10.2 NV centers in diamond

The research interest in NV centers in diamond has increased significantly over the last decade [123, 124], because of the potential application of single NV centers as qubits for a quantum computer [125]. The level structure of the NV center allows optical spin initialization, spin manipulation via electron spin resonance (ESR) and optical spin read-out, all performed on individual spins at room temperature and at ambient conditions.

An NV center in diamond consists of a substitutional nitrogen atom adjacent to a vacancy in the lattice. The symmetry axis is along any of the four tetragonal ⟨111⟩ crystallographic directions, see figure 10.1a. The level structure associated with the negatively charged NV center used in this experiment is depicted in figure 10.1b [126]. The NV center forms a spin triplet in the ground state (3A) and excited state (3E). The degenerate ms = ±1 states are split from the ms = 0 state by 2.87 GHz at zero
10.3 Experimental setup

For our measurements, we use a confocal microscope, schematically shown in figure 10.2a. A 532 nm laser is focused to a spot size of 0.3 µm² a few microns below the diamond surface. This initializes the spin state of the NV centers within the confocal volume to the $m_s = 0$ state. A fast steering mirror (FSM) is used to spatially scan across the sample, with a two-dimensional scanning range of $20 \times 20$ µm². Larger movements are done using translation stages. The PL intensity is measured with a fiber-coupled avalanche photodiode (APD), where the fiber acts as the pin-hole to obtain the confocal depth resolution. A signal generator is used in combination with on-chip waveguides to apply microwave fields for ESR measurements. We apply an external field with a permanent magnet on a rotation and translation stage. The range of motion leads to fields between 45 and 1000 G ($45 \cdot 10^{-4}$ to 0.1 T). The field is reversed by rotating the magnet.

We use (110) diamond substrates (Sumitomo type Ib grown with high-
10. Magnetic field vector microscopy using bulk diamond

Figure 10.2: (a) Schematic of the confocal microscope. (b) The geometry of the sample. The blue plane represents the surface of the (110) diamond substrate and the two blue arrows represent the symmetry axes of the NV centers. The red plane, perpendicular to the surface, contains the other two possible symmetry axes. The black square represents the patterned permalloy structure. Crystallographic directions are depicted, $x$ and $y$ are chosen. (c) Optical image of the sample showing $20 \times 20 \, \mu\text{m}^2$ square with 75 micron diameter microwave antenna.
10.4 NV centers as magnetic vector field probes

In order to extract the local magnetic field vector, we measure the Zeeman splitting for the visible NV centers along three directions. As shown in temperature high pressure methods) with sufficiently high concentrations of NV centers to have all four orientations within the confocal volume (\( \sim 1 \text{ \mu m}^3 \)) of our microscope. The four possible symmetry axes of the NV centers with respect to the sample surface are shown in figure 10.2b. The blue plane (110) represents the sample surface and the red plane (\( \bar{1}10 \)) is perpendicular to the sample surface. Two of the symmetry axes lie in the blue plane, and the other two in the red plane. Circular microwave antennas are patterned on the diamond, defining the magnetic sensing region. For this study, we used antennas that are 75 \( \text{\mu m} \) in diameter. Permalloy (\( \text{Ni}_{0.8}\text{Fe}_{0.2} \)) shapes are deposited in the center of the antennae, which are defined lithographically and aligned with respect to one in-plane NV center (\( x \)-axis, [\( \bar{1}1\bar{1} \)]), see figure 10.2c. Three different shapes were investigated in this work as follows: a 20 \( \times \) 20 \( \text{\mu m}^2 \) square, an equilateral triangle with 20 \( \mu m \) sides, and a 10 \( \times \) 40 \( \mu m \) rectangle.

Figure 10.3: Images of the magnetic field vectors around the permalloy (a) square and (b) triangle measured in a field of 45 G. Arrow’s size and direction represent the \((x, y)\) vector, while \(z\) is depicted with color. Each vector refers to one ESR spectrum, averaged for \( \sim 10 \) minutes. To get a sense of scale, the circled field vector is \([1.36 \pm 0.13, 2.48 \pm 0.22, 1.76 \pm 0.09]\) G.
...
10.4. NV centers as magnetic vector field probes

Figure 10.4: Hysteresis of the permalloy rectangle as measured by MOKE (a) and ESR (b). Increasing (decreasing) magnetic field sweep is in black (red). Vector field image of the field lines around a rectangle with the magnetization in the negative (c) and the positive (d) x-direction.

tings. This results in an ambiguity in the sign of the magnetic field. However, by using a subtractive method, we measure small changes with respect to the uniform external field. We choose an external field that is larger in magnitude than the measured local field, which insures that the sign of the total field will be the same as the sign of the external field. When we subtract the external field from the total field, we are left with the local field with the proper sign.

The magnetization of the permalloy is characterized in a magneto-optical Kerr effect (MOKE) microscope. The hysteresis of the magnetization along the length of the rectangle is shown in figure 10.4a. The MOKE measurement reveals a coercive field of $\sim 100\, \text{G}$ along the long axis.

Magnetization information was also investigated using ESR to probe the field produced by the permalloy rectangle. We focus on a spot next to the side of the rectangle and prepare the permalloy anti-parallel to the external field by first applying a large negative field ($\sim -1000\, \text{G}$) and then setting it to 45 G. While measuring ESR spectra, we step the magnetic field...
to 155 G and back to to 45 G. We also measure ESR spectra far away from the permalloy at each field step as a reference. By subtracting the reference magnetic field from the total magnetic field, we find the local magnetic field originating from the permalloy. The resulting data (figure 10.4b) reproduces the hysteretic behavior seen in the MOKE data. It is important to note that this is a measurement of the local magnetic field vector due to the magnetization of the permalloy, not the magnetization itself.

Images of the magnetic vectors before the forward sweep and after the backward sweep are shown in figures 10.4c and d respectively. Both images were taken in the same external field of 50 G. The reversal in direction of magnetic field vectors, and thus in the magnetization, is clearly seen.

The magnetic field and spatial resolutions of the measurements presented here are $\sim 0.2$ G and $\sim 0.3$ µm respectively, which can be improved by implementing a few techniques. Improvement of the magnetic field resolution up to 0.3 mG can be obtained by using pulsed techniques [120, 122]. The spatial resolution can be significantly improved by implementing a reversible saturable optically linear fluorescence transitions (RESOLFT) technique [128], such as stimulated emission depletion (STED) microscopy, which has been shown to improve imaging resolution of diamond NV centers to a few nm [129]. These improvements could bring the field sensitivity from a level similar to standard MFM methods, to the range achieved with MRFM techniques, as well as improving the spatial resolution to a level comparable with MFMs. This can all be done at room temperature with vector resolution in a single pass.

10.5 Summary

In summary we showed that NV centers in diamond can be used to measure local magnetic field vectors. The resolution in this work is $\sim 0.2$ G and $\sim 0.3$ µm. The important advantages of the technique presented here are simultaneous extraction of three orthogonal components of the magnetic field and operation in small external fields less than $\sim 50$ G and ambient pressure and room temperature.
Chapter 11

Outlook

11.1 Position in the field

The work presented in this thesis focuses on single dopants in semiconductors. There have been huge advances in the field of single dopants over the last years. The aim is for example to build single dopant transistors [8, 9, 10, 11, 130, 131] or single-spin devices, or to find an appropriate qubit for quantum computing [132, 133]. In this respect, detailed knowledge of single dopants is required, where it is essential to know the exact position on the atomic scale.

In this thesis, we presented our work mainly as fundamental science. Nevertheless, there are important implications for the development of future devices. The semiconductor industry lives by the existence of the transistor, consisting of a semiconducting channel, on top of which a metallic gate is placed, separated by a thin insulating oxide layer. This system closely resembles our STM, where a metallic tip is separated from the semiconducting sample by the vacuum barrier. For this semiconductor-vacuum-metal interface, we found that the binding energy is strongly enhanced if the dopant is located close to the interface, both for Si donors and for Mn acceptors. A next step would be to investigate whether this is a general result and also holds for the technically important semiconductor-oxide-metal interface. In the next section (section 11.2.2), I present a design for an experiment to investigate the binding energy close to a semiconductor-oxide-metal interface. Furthermore, theory is needed to understand the origin of the enhancement, to solve whether it is enhanced due to strain, dielectric effects, or even something else. Contemporary calculations are not able to explain the enhancement in case of Si donors. Effective mass theory predicts a reduction, and therefore more atomistic methods, such as
tight binding methods, are needed. However, state-of-the-art tight binding
calculations are limited to a super-cell of about \((4\,\text{nm})^3\), which is not suf-
ficiently large to describe Si in GaAs, which has a Bohr-radius of 10\,\text{nm}.
Therefore further development of theoretical models is required.

11.2 Suggested future experiments

In this section I present a few specific ideas for future experiments, which
are related to the general prospects presented in the previous section.

11.2.1 Explore the ionization rings further: combine STM
with a tunable laser

The first idea is related to the ionization rings and the enhanced binding
energy. It would be very valuable to prove the enhanced binding energy
with a independent method, and to measure the exact value without the
uncertainties related to the TIBB calculations. The binding energy is en-
hanced only in the first \(\sim 1\,\text{nm}\) of the crystal. This excludes standard
optical techniques such as PL due to its large penetration depth. However,
we can combine the excellent energy resolution of optical techniques with
the depth resolution of a STM in the following concept. If we illuminate
a Si:GaAs sample while performing STM, the ionization rings should dis-
appear, because the donors are photo-ionized and thus cannot be ionized
by the STM tip. The photo-ionization only occurs if the photon energy
is equal or greater than the ionization energy. Therefore, tuning the laser
from e.g. 1\,\text{meV} to 100\,\text{meV} should make the rings disappear one by one,
when their binding energy corresponds to the photon energy. This re-
quires a tunable laser in the regime from 1\,\text{meV} to 100\,\text{meV} (i.e. 1.2\,\text{mm} to
12\,\mu\text{m} wavelength). Quantum cascade lasers cover this regime. For exam-
ple Alpes Lasers SA [134] offers lasers ranging from 4.2\,\mu\text{m} (295\,\text{meV}) to
86\,\mu\text{m} (14\,\text{meV}). A drawback is that each laser has a small tuning range,
and multiple lasers are needed to cover the full range.

The following idea is perhaps more realistic — although less elegant in
my opinion. The difficult \mu\text{m}-wavelength regime can be avoided when ex-
citations just below the band gap energy can be employed. This can be
done in a Si:GaAs sample by focusing on the empty state wave function
(section 6.3, figure 6.9). The empty state wave function can only be seen
in STM when the donor is empty, thus positively ionized. The empty state
wave function typically appears at upward TIBB, thus the requirement is
typically fulfilled. If we optically pump the sample with a photon energy
just below the band gap energy, electrons will be excited from the VB
11.2. Suggested future experiments

Figure 11.1: (a) Photograph of a sample holder with a side gate. The various parts are indicated. (b) Schematic of the cross-sectional sample surface with a gate for an in-plane electric field. (c) $V_{\text{gate}}$ versus distance to the interface as expected for a constant binding energy (dashed line). The solid line indicates the reversed order of ionization, as observed in section 5.2.

into the donor level, creating a neutral donor. Therefore, the empty state wave function should disappear when optically pumping the system with a photon energy of $\geq (E_g - E_b)$. The empty state wave functions should again one by one disappear when tuning the laser from e.g. 1.4 eV to 1.5 eV (886 nm to 827 nm) when the photon energy equals $(E_g - E_b)$. This measurement therefore gives the binding energy, while employing a wave length regime that is easily accessible.

11.2.2 Investigate various interfaces

It would also be very interesting to investigate other crystallographic surfaces, and to investigate the influence of interfaces (e.g. the technologically important semiconductor-oxide-metal interface) on the binding energy. A possibility to investigate the influence of interfaces is to use a side gate. This concept was developed by Loth et al. [51] to tune the electric field in a p-i-n structure. We already designed and built a sample holder for this purpose, see figure 11.1a. One of the clamping bars is made of Teflon, which is an insulator. A piece of gold foil is put between the sample and the Teflon clamping bar, and a wire connects this gold foil with a contact tab. By putting a potential difference over the sample holder and the contact tab, we apply a potential difference over both sides of the sample, schematically shown in figure 11.1b.

An interesting experiment that could be done with such a sample holder
11. Outlook

is the following. We deposit a metal layer on a Si:GaAs sample, separated by an oxide. The metal layer acts as a gate, which we use to ionize the donors close to the gate. The STM tip is only used to probe whether the donor is ionized or not; the ionization is driven by the gate voltage. We measure the gate voltage that is needed to ionize the donors as a function of distance to the interface. If the binding energy is constant, a higher gate voltage is needed to ionize donors that are further away from the interface (dashed line in figure 11.1c). If a reversed dependence is observed (solid line in figure 11.1c), the binding energy is enhanced towards the interface.

11.2.3 Single spin manipulation

With the same sample holder, the effect of a tunable electric field can be investigated, if the structure of interest is positioned in the center of a p-i-n diode. A first experiment would be to investigate the influence of a static electric field, but a more advanced experiment involves AC electric fields. The authors in reference [135] propose that the Mn spin in GaAs can be manipulated by a small permanent magnetic field in combination with a tunable AC electric field. It is possible to add a small coil in our setup, in order to produce a small magnetic field. The ultimate experiment would be to manipulate the spin of a single Mn atom in GaAs, and to read the spin state with a spin polarized tip. In our group, we already established spin polarized STM (SP-STM) on metal surfaces. Therefore, all the building blocks for the experiment proposed in reference [135] are ready.

11.2.4 Further investigate the observed switching

The last idea that I discuss concerns further exploring the observed switching (chapter 7). In the current work, we only investigated Si:GaAs. This is a group IV donor, that replaces a Ga atom. An obvious next step is to investigate a group VI donor, which replaces a As atom, e.g. Te:GaAs. The buckling at the surface is an important ingredient in our interpretation. A surface Si donor replaces a Ga atom, and a surface Ga atom has an empty dangling bond and is buckled inward. However, a surface Te donor replaces an As atom, and a surface As atom has a filled dangling bond and is buckled outward. This probably significantly influences the switching dynamics, and it would be very interesting to see whether switching is observed at all.
Bibliography


List of abbreviations and symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>2DEG</td>
<td>two-dimensional electron gas</td>
</tr>
<tr>
<td>$\epsilon_r$</td>
<td>dielectric constant</td>
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<tr>
<td>$\kappa$</td>
<td>inverse decay length</td>
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<tr>
<td>$\chi$</td>
<td>electron affinity</td>
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<td>AL</td>
<td>atomic layer</td>
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<td>CB</td>
<td>conduction band</td>
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<tr>
<td>DFT</td>
<td>density functional theory</td>
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<tr>
<td>DMS</td>
<td>dilute magnetic semiconductor</td>
</tr>
<tr>
<td>$E_b$</td>
<td>binding energy</td>
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<td>$E_F$</td>
<td>Fermi level</td>
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<tr>
<td>$E_g$</td>
<td>band gap energy</td>
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<td>ESR</td>
<td>electron spin resonance</td>
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<td>LDOS</td>
<td>local density of states</td>
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<tr>
<td>LT-STM</td>
<td>low-temperature STM</td>
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<tr>
<td>$m^*$</td>
<td>effective mass (unit-less)</td>
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<tr>
<td>MBE</td>
<td>molecular beam epitaxy</td>
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<tr>
<td>NV center</td>
<td>nitrogen-vacancy center</td>
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<tr>
<td>PL</td>
<td>photoluminescence</td>
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<td>PLE</td>
<td>photoluminescence excitation</td>
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<td>QD</td>
<td>quantum dot</td>
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<td>QW</td>
<td>quantum well</td>
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<td>RF</td>
<td>radio frequency</td>
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List of abbreviations and symbols

<table>
<thead>
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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>STM</td>
<td>scanning tunneling microscopy/microscope</td>
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<tr>
<td>STS</td>
<td>scanning tunneling spectroscopy</td>
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<tr>
<td>TEM</td>
<td>transmission electron microscope</td>
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<tr>
<td>TIBB</td>
<td>tip-induced band bending</td>
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<td>TIQD</td>
<td>tip-induced quantum dot</td>
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<tr>
<td>UHV</td>
<td>ultra-high vacuum</td>
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<tr>
<td>VB</td>
<td>valence band</td>
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<tr>
<td>$V_{FB}$</td>
<td>flat band voltage</td>
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<tr>
<td>W</td>
<td>tip work function</td>
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<tr>
<td>X-STM</td>
<td>cross-sectional STM</td>
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<tr>
<td>$z_{tip}$</td>
<td>tip-sample distance</td>
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Summary

Manipulation and analysis of a single dopant atom in GaAs

This thesis focuses on the manipulation and analysis of single dopant atoms in GaAs by scanning tunneling microscopy (STM) and spectroscopy (STS) at low temperatures. The observation of ionization rings is one of the key results, showing that we can control the charge state of a single dopant atom by the STM tip. Using the ionization rings, we can study properties of a single dopant atom, such as its binding energy. The binding energy is an important property with respect to device applications. A low binding energy is needed for the impurities to act as donors or acceptors, and to induce free carriers in the conduction or valence band, respectively. Defects with a large binding energy act as traps and reduce the carrier density. We found that Si donors in GaAs close to the surface have a higher ionization threshold than donors buried deeper below the surface. This leads to the conclusion that the binding energy is enhanced towards the surface, which is corroborated by the reduced extension of the wave function towards the surface. Also for the Mn acceptor in GaAs, an enhanced binding energy towards the surface was found. This can have important consequences for future devices, where the surface to bulk ratio is larger than in current devices, due to the shrinking device dimensions.

The importance of the surface became furthermore apparent for Si atoms in the surface layer of GaAs. They were found to be bistable. A negatively charged acceptor-like configuration is favorable on the bare GaAs surface, which we can force into a hydrogenic donor configuration with the STM tip. From our analyses of the temperature dependence and the dependence on the current set-point of the switching rate belonging to the transition, we found that it probably involves a combination of inelastic excitations and quantum tunneling.

The effect of impurities in a functional device is explored as well. We
studied double barrier resonant tunneling p-i-n diodes, where the p-layer consists of Ga$_{1-x}$Mn$_x$As, with a Mn concentration of 5\%. During the growth of Ga$_{0.95}$Mn$_{0.05}$As, interstitial Mn ions (Mn$_i$) are formed, which act as double donors. The STM and STS measurements show the individual Mn$_i$ that have diffused towards the GaMnAs-GaAs interface during annealing, and reveal the potential landscape that arises due to clusters of Mn$_i$ ions.

The last chapter of the thesis concerns a very different system, viz. nitrogen-vacancy (NV) centers in diamond, studied with a confocal microscope. We use optically detected electron-spin resonance to measure the Zeeman-splitting of the spin-triplet ground state. The Zeeman-splitting depends on the inner product of the external magnetic field and the NV-axis. We can thus use the NV centers as a magnetic vector field probe. The spatial resolution and magnetic field sensitivity in this thesis are $\sim 0.3\ \mu$m and $\sim 0.2\ \text{G}$, which can be significantly improved, by implementing a few techniques, to the level of magnetic force microscopy and magnetic resonance force microscopy respectively. The important advantages of the technique are operation in ambient pressure, room temperature and low external magnetic fields and the simultaneous measurement of all three magnetic field components in a single pass.
Nederlandse samenvatting

Manipulation and analysis of a single dopant atom in GaAs

Dit proefschrift richt zich op het manipuleren en analyseren van individuele doteringsatomen in GaAs, door middel van scanning tunneling microscopy (STM) en spectroscopy (STS) bij lage temperaturen. Een van de kernbevindingen is de observatie van ionisatieringen, wat duidelijk maakt dat we de ladingstoestand van enkele doteringsatomen kunnen beïnvloeden met de STM naald. Vervolgens kunnen we deze ionisatieringen gebruiken om eigenschappen van de individuele doteringsatomen te bestuderen, zoals de bindingsenergie. De bindingsenergie is een belangrijke eigenschap als het gaat over toepassingen in devices. Een lage bindingsenergie is nodig, opdat de doteringsatomen zich als donoren of acceptoren gedragen, zodat ze vrije ladingsschagers in respectievelijk de conductie- en valantieband induceren. Onzuiverheden met een hoge bindingsenergie fungeren als traps, en verlagen de dichtheid van vrije ladingsschagers. Wij laten zien dat Si donoren in GaAs die zich dicht bij hetoppervlak bevinden een hogere ionisatie threshold hebben dan donoren dieper onder het oppervlak. Dit leidt tot de conclusie dat de bindingsenergie is verhoogd naarmate de donoren zich dichter bij het oppervlak bevinden. Deze conclusie wordt ondersteund door de gereduceerde uitgebreidheid van de golffunctie voor donoren dichtbij het oppervlak. Ook voor de Mn acceptor in GaAs vinden we een verhoogde bindingsenergie richting het oppervlak. Dit kan belangrijke consequenties hebben voor toepassingen in toekomstige devices, waar de oppervlakte-volumeverhouding groter is dan in hedendaagse devices, vanwege de afnemende device afmetingen.

Het belang van het oppervlak blijkt bovendien uit metingen aan Si atomen in de oppervlaktelaag van GaAs. Deze vertonen een bi-stabiel gedrag. De voorkeurstoestand op het vrije GaAs oppervlak is een negatief geladen, acceptor-achtige, toestand, die we met de STM naald in een water-
stofachtige donor toestand kunnen forceren. Onze analyses van de temperatuur- en stroomafhankelijkheid van de schakelfrequentie laten zien dat het zeer waarschijnlijk een combinatie betreft van inelastische excitaties en kwantumtunnelen.

Het effect van onzuiverheden in een werkend device is ook onderzocht. We hebben dubbelbarrière-resonanttunnel-p-i-n-diodes bestudeerd, waar de p-laag uit een $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ laag bestaat, met een Mn concentratie van 5%. Gedurende de groei van $\text{Ga}_{0.95}\text{Mn}_{0.05}\text{As}$ worden interstitiële Mn ionen ($\text{Mn}_i$) gevormd, die zich als dubbele donoren gedragen. Onze STM en STS metingen tonen de individuele $\text{Mn}_i$-ionen die tijdens het annealen naar het GaMnAs-GaAs interface zijn gediffundeerd. Verder wordt het potentiaillechamps, dat door clusters van $\text{Mn}_i$-ionen ontstaat, in beeld gebracht.

Het laatste hoofdstuk van dit proefschrift gaat over een behoorlijk ander onderwerp, namelijk nitrogen-vacancy (NV) centra in diamant, die we bestudeerd hebben met een confocale microscoop. We gebruiken optisch gedetecteerde electron-spin resonantie om de Zeemansplitsing te meten van de spintriplet grondtoestand. De Zeemansplitsing hangt af van het inproduct van het externe magneetveld en de NV-as. We kunnen dus NV centers gebruiken om een extern magneetveld te meten. De laterale resolutie en magneetveldgevoeligheid die behaald zijn in dit proefschrift zijn $\sim 0.3 \mu\text{m}$ en $\sim 0.2\text{G}$. Dit kan nog significant verbeterd worden door het implementeren van enkele technieken, tot het niveau van magnetic force microscopy respectievelijk magnetic resonance force microscopy. De belangrijke voordelen van de gepresenteerde techniek zijn de werking in atmosferische druk, kamertemperatuur, en lage externe magneetvelden, en het gelijktijdig meten van alle drie de magneetveldcomponenten in een enkele meetronde.
Acknowledgments

Finishing a PhD project is not the work of one single person. Without the help and support from many other people, and the discussions with even more people, I would never have been able to finish this project.

It all started several years ago, in August 2003, during a study tour to Brazil. Paul Koenraad was the scientific supervisor during this trip, and already then his enthusiasm – both for science as well as for culture and good food – was infectious. When I had to choose a supervisor for my master’s graduation project, the choice was easily made. I hadn’t forgotten Paul’s enthusiasm, and I was pleased and honored to work in his group. And it proved to be a good choice, which I never regretted. Paul, thank you for your supervision and support. I am especially grateful that you never gave up to convince me to stay in the group as a PhD student after my graduation.

When I entered the group in January 2007, my daily supervisor and roommate became Jens Garleff. We were a great team, and we have had many intense discussions. The one was very critical about ideas of the other, and we always discussed until we were both satisfied with the outcome. No compromises in science!

Special thanks goes to my other roommate Joris Keizer. I know that men hate it when a woman says: ”You are like a brother to me.” But that is definitely the way I feel about you, Joris.

When working with a complicated setup such as an STM in UHV, you have to work in a team. Thanks for everything, my fellow STM-ers Alexei, Aron, Cem, Erwin, Jens, Joris, Jose, Juanita, Murat, Ramon and Samuel, and my co-supervisor Andrei Silov. Of course I am very grateful for the work that was done by my two interns Marloes en Stijn. It was valuable and fun to have you both in the group. PSN would be a ship adrift without the motherly guidance of Margriet. The ship became so large that the secretariat was reinforced by Annebee.

The teamwork was not confined to the group PSN, but even extended abroad. We have had a very fruitful collaboration with Martin Wenderoth,
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Karen Teichmann and Sebastian Loth from the University of Göttingen. I really appreciated your thorough German way of doing science. For me, the pinnacle of our collaboration is the appointment of Martin as my co-promotor. Another successful collaboration was with the University of Nottingham. Laurence Eaves, Oleg Makarovsky, Bryan Gallagher and Richard Campion, thank you for the collaboration, for providing the samples and for the discussions. An experimental group is lost without the support of a theoretical group. Therefore many thanks to Mervyn Roy and Peter Maksym from the University of Leicester and to Michael Flatté from the University of Iowa.

Of course not everything is about science. I enjoyed the coffee breaks with Erwin, Frank, Guido, Harm, Jens, Joost, Joris, Jos, Juanita, Margriet, Martine, Murat, Niek, Nut, Peter, Ramon, Rene, Rian, Samuel, Tilman, and many others. Not infrequently, someone would ask a general question about some arbitrary subject, and an intense discussion would burst out. This resulted in the end in the installation of a “wikiputer” in the coffee room. Of course I also enjoyed the weekly drinks in the ‘Salon’ at SVTN “J.D. van der Waals” with the regular group, and the wine- and beer-tastings within our own group PSN. Rian, thank you for forming the beer-tasting-committee together with me. And to stay within this theme, I’d like to mention the table for the ‘Salon’ that Rian, Joris and me made. At the moment of writing the acknowledgements, the table is almost finished, and I am looking forward to the day that we can start using it.

Finally, I am very grateful to my friends and family. My parents have always been very supportive. They have always encouraged me to make my own decisions, which was sometimes difficult for me as a true Libra. Nevertheless, they always listened to all my considerations, asked the right questions, and when I really didn’t know what to do, they would give their opinion. My brother Frans had to deal with a sister and a girlfriend who both did a PhD, but he handled it well. Thank you for listening to my stories, and trying to convince me that traveling abroad is fun. Of course most of my thanks and gratitude goes to my boyfriend Thijs. You didn’t mind joining me in the lab during the weekends when I had to refill the setup with liquid nitrogen, you always had time for me to listen to problems that I had, and you never complained when I had to travel abroad, or even lived abroad for four months. Furthermore, your insights in group processes and leadership were extremely valuable for me, and it helped me to stay positive and cooperative when I was annoyed by something at work. Thank you for everything, I could never have done all this without you.

Ineke Wijnheijmer, July 2011
List of publications

A. P. Wijnheijmer, J. K. Garleff, K. Teichmann, M. Wenderoth, S. Loth, R. G. Ulbrich, and P. M. Koenraad, “A comprehensive study of single Si dopants in GaAs by scanning tunneling microscopy,” accepted for publication in Physical Review B.


J. K. Garleff, A. P. Wijnheijmer, A. Yu. Silov, J. van Bree, W. Van Roy,
List of publications


Curriculum vitae

Albertine Pauline (Ineke) Wijnheijmer
born 21st of October 1982 in Geldrop, the Netherlands

2008 - 2011 PhD student at the Eindhoven University of Technology
Photonics and Semiconductor Nanophysics group

fall 2009 Research visit at the University California, Santa Barbara
Center for Spintronics and Quantum Computation

2001 - 2007 Master in Applied Physics, Eindhoven University of
Technology Cum Laude

Master project at the Eindhoven University of Technology
Photonics and Semiconductor Nanophysics group
Low temperature scanning tunneling microscopy and
spectroscopy on single silicon donors in gallium arsenide

Internship at Toshiba Research Ltd. Cambridge (UK)
Quantum Information group
Quantum key distribution using an up-conversion detector

Side job at the Eindhoven University of Technology
Gas Dynamics group

Internship at the Eindhoven University of Technology
Low Temperature Physics group
Characterization counter-flow pulse-tube refrigerator

Internship at Shell, Rijswijk
Distributed Temperature Sensing

1995 - 2001 High school, Jan van Brabant College, Helmond