Study of imperfections near the cleaved GaAs(110) surface by low-temperature scanning tunneling microscopy

een wetenschappelijke proeve op het gebied van de Natuurwetenschappen

Proefschrift

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door

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Voor mijn ouders
Stellingen

behorende bij het proefschrift:

Study of imperfections near the cleaved GaAs(110) surface by low-temperature scanning tunneling microscopy

door: Maurice van der Wielen
I

Het bij lage temperatuur doen van raster tunnel mikroscoop (STM) metingen op schone halfgeleideroppervlakken, zoals beschreven in dit proefschrift, is een jonge onderzoekstak met heel veel mogelijkheden en waarin nog veel interessante resultaten zijn te verwachten.

II

Cryostaten gaan normaliter een leven lang mee.

III

Oppervlakken die worden verkregen door het bij lage temperatuur (4.2 K) breken van materialen, blijven bij dezelfde lage temperatuur een geruime tijd (> week) schoon. Dit proefschrift

IV

De naam atoomkelder geeft aan dat in deze ruimte wordt gekeken naar atomen.

V

Een metaal-halfgeleider STM junctie is dusdanig complex en bestaat uit zoveel onbekende parameters, dat een correcte kwantitatieve beschrijving van STM afbeeldingen aan de hand van theoretische modellen op dit moment niet mogelijk is.
VI

De invloed van Si doping atomen op de oppervlaktestructuur van GaAs(110) bij 4.2K, kan niet worden verklaard zonder het meenemen van electron-electron interacties. *Hoofdstuk 4 van dit proefschrift*

VII

Het leven is niet vanzelfsprekend, maar een kostbaar goed.

VIII

Omdat redelijkerwijs alle mensen zoeken naar een vergelijkbare vaste verhouding tussen arbeid en plezier, is bewezen dat van alle muzikanten de slagwerkers de meeste lol beleven aan het bespelen van hun instrumenten.

IX

Sluikreclame in een proefschrift is océ.

X

Dit proefschrift is een feit!
Voorwoord

Eindelijk dan mag ik beginnen aan het voorwoord van mijn proefschrift. Dat is een plezierig feit, want hoewel dit voorwoord helemaal vooraan staat in dit boekje, betekent dat niets anders dan dat alles wat hierna komt reeds op harde schijf is vastgelegd. Het proefschrift is hiermee dus bijna afgerond.

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Na de technici komen we aan bij de onderste trede van de afdelingsladder. We zijn aangekomen bij het voetvolk, het plebs of gepeupel van de

Naast de mensen op de afdeling zijn er natuurlijk ook veel mensen buiten deze afdeling geweest die een wezenlijke bijdrage hebben geleverd aan dit boekje. Ik denk hierbij in de eerste plaats aan de mensen van de werkplaats. Ik wil Ferry Derksen bedanken voor de goede begeleiding op de werkvloer van de zelfservice. Via Wim Schut wil ik iedereen van de service-instrumentmakerij bedanken voor het vervaardigen van vele onderdelen voor de opstelling.

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Maurice van der Wielen
13 augustus 1998
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Chapter 1

Introduction

With the development of new and better growth-techniques and lithographic processes, industry is able to produce ever smaller electronic devices. The number of imperfections inside decreases as the device dimensions shrink and therefore the device characteristics will be influenced by fewer and finally even single imperfections. Scanning tunneling microscopy (STM) allows individual imperfections to be studied and characterized on an atomic scale.

In this thesis we describe STM experiments performed at the GaAs(110) surface. GaAs is a III-V compound semiconductor and although this material can be grown, nowadays, in a very controllable way, the crystal always possesses some lattice imperfections. In addition to vacancies the most common type of point imperfections are substitutional impurity atoms. These impurities are also called doping atoms if they are purposely incorporated to increase the conductivity of these materials.

The GaAs(110) surface and in general every (110) III-V compound semiconductor surface is ideal for studying bulk imperfections with a surface sensitive tool as STM, since no surface states are present inside the bulk energy band gap. Therefore bulk effects are not screened at the surface. This has been recognized by a number of groups. In chapter 2 we give a survey of the STM experiments performed on the (110) surfaces of different III-V compound semiconductors. The survey is divided into sections dealing with (a) clean (110) surfaces, (b) doping atoms, vacancies and other defects below the (110) surface, (c) adsorbates on top of the (110) surface, (d) multilayer structures and (e) tunneling induced luminescence experiments.

In addition to technological motivations, studying imperfections is also interesting from a fundamental point of view. Questions like how single impurities influence neighbouring lattice atoms can now be tackled experimentally. In addition, since most of these imperfections have a valence charge different from the substituted atoms, a (model) system is found for
studying the influence of static point charges on the distribution of free charge carriers.

In chapters 4, 5 and 6 we describe the influence of different charged imperfections positioned near or at the GaAs(110) surface as observed by STM. We distinguish between dopant induced features (discussed in chapter 4 and 5) and vacancies, adatoms and steps (discussed in chapter 6). In chapter 4, the influence of substitutional Si donor atoms on the GaAs(110) surface electronic structure is studied. In the vicinity of the donor atoms charge density (Friedel) oscillations are visible. In chapter 5, Zn and Cd-induced features are studied. In addition to (weak) Friedel oscillations, triangular features are observed in the vicinity of the substitutional acceptor atoms. Chapter 6 deals with observed vacancies, adatoms and steps. These (point) defects are of interest from a fundamental viewpoint, but also because they have always played a critical role in discussions about surface kinetics of epitaxial growth, Fermi-level pinning and surface carrier recombination.

All our STM measurements are performed at 4.2 K. This gives advantages in comparison with STM measurements performed at room temperature. The first advantage is that by cooling the STM down to 4.2 K, measurements are not disturbed by temperature drift, causing displacements between tip and sample. Hence, spectroscopy measurements can be performed on single impurities for a time, long enough to obtain a good signal to noise ratio. A second advantage is the increase in energy resolution at low temperatures. At 4.2 K, $kT = 0.4 \text{ meV}$, while at 300 K, $kT = 25.9 \text{ meV}$. Since the Fermi level is positioned about 50 meV inside the valence or conduction bands of our GaAs samples, we expect (and also see, as described in chapter 4) more structure in topography and spectroscopy measurements performed at 4.2 K. Another advantage is the increase in time that GaAs(110) surfaces remain clean. As described in chapter 3 we are able to cleave our samples in situ at 4.2 K. At this temperature the vapour pressure of common gases like oxygen and nitrogen is below $10^{-17} \text{ Torr}$. This is many orders of magnitude better than it is under ultra high vacuum (UHV) conditions at room-temperature. At 4.2 K, we found that samples remain clean for more than one week.

In addition to these advantages, we foresee interesting abilities at low temperatures for optical spectroscopy measurements with STM on semiconductors structures. In chapter 2 we give a summary of tunneling induced luminescence experiments in which the STM tip is used as a localised source of low energy electrons. The advantage of low temperatures is that apart from an increase in spectral resolution, the photon yield should increase drastically. Performing tunneling induced luminescence experiments at low temperature will be an interesting step in the future.
Chapter 2

Survey: STM measurements on cleaved III-V compound semiconductors

In this chapter we give a summary of the STM experiments performed on the (110) cleavage plane of III-V semiconductor compounds. The experiments are divided in six different categories. In section 2.1 we start by discussing the experiments performed on the clean cleaved surfaces of respectively binary, ternary and quaternary III-V compounds. The experiments concern topography measurements as well as spectroscopy measurements. At the surfaces some irregularities are normally observed. These can be attributed to subsurface doping atoms, which will be discussed in section 2.2, or to vacancies and other kind of defects in the surface plane (section 2.3). In section 2.4 experiments on the influence of (metal) adsorbates on the (110) cleavage plane are summarised. This is an important topic concerning Schottky barrier formation. Finally, we briefly mention the experiments using cross-sectional STM on molecular-beam-epitaxy (MBE) grown thin layer structures (section 2.5) and the technique of tunneling induced luminescence (section 2.6).

2.1 Clean surfaces

GaAs(110):
The first III-V compound semiconductor studied by STM was GaAs. Feeen
Figure 2.1: Schematic representation of the GaAs(110) surface. The Ga and As atoms are respectively given by empty and filled circles. The small circles represent Ga and As atoms positioned in the first subsurface layer. In the side view the surface buckling is shown.

Feenstra et al. [1] presented the first STM images of the GaAs(110) surface\textsuperscript{1}. They deduced for the surface a 1 \times 1 periodicity. The dimensions for the surface unit cell are equal to 6.5 Å \times 5 Å. This is in fairly good agreement with the accepted values of 5.65 Å \times 4.00 Å for 1 \times 1 periodicity. Deviations were attributed to calibration errors in the piezo constants. Typical corrugation amplitudes in [001] direction were found to be 0.2 - 0.5 Å; in [\overline{1}10] direction it is smaller \sim 0.05 Å.

In 1987 Feenstra et al. [2] presented voltage dependent images of the GaAs(110) surface. In the filled state images the As lattice is visible; the

\textsuperscript{1}In general, the cleavage plane for III-V compound semiconductors is the (110) crystal plane since the concentration of constituents is the same, which makes the plane non-polar.
empty state images show the Ga lattice. This was predicted theoretically by Lubinsky et al. [3] and Tersoff et al. [4] and can be attributed to the relaxation of the GaAs(110) surface plane. The As anion is relaxed outwards while the Ga cation is moved inwards. This relaxation drives the surface states out of the energy gap and results in an occupied and empty dangling bond state located at the anion and cation, respectively. Since the interatomic distances (bond lengths) are nearly invariant, the relaxation can be described by a single parameter, the buckling angle \( \omega \). It is believed to be about \( 27^\circ \) [5]. This buckling angle cannot be determined directly by STM since the corrugation amplitude represents a combination of structural variation and variation in state density and is also strongly dependent on the atomic structure of the tip apex and tip sample distance. Feenstra et al. [2], however, showed the spatial separation of surface states varies with buckling angle. Combining experimental results together with theory they found a buckling angle between \( 29^\circ \) – \( 31^\circ \).

Ebert et al. [6] showed in their experiments and calculations that the dangling bond picture is too simple to explain the STM results completely. For the filled state image the dangling bond picture is a good approximation. For the empty state images, however, surface resonances have also to be considered.

These surface states can be studied in tunneling spectroscopy measurements. Feenstra et al. [7] published current-voltage curves measured on p-type and n-type doped GaAs. Near the band gap, the current is very small. A large dynamic range can be obtained by varying the tip sample distance. In the spectra three different contributions can be clearly distinguished: from the conduction band (CB), valence band (VB) and impurity band which is formed by the doping atoms. Feenstra et al. introduced a general formalism to calculate the size of the different current components. The first step in the computation follows exactly the calculations by Bono and Good [8], where their results for valence band tunneling are extended to include the conduction band and impurity bands. In the second step of the calculation the effect of band bending at the surface is included. By varying the sample voltage between tip and sample the electrostatic surface potential is changed. In their paper they show that the effect of tip induced band bending has to be incorporated in the computations to explain the experimentally obtained curves. One of the effects of tip induced band bending is that the band gap in the measurements is bigger than the bulk value (1.43 eV at \( T = 300 \text{K} \)).

Maboudian et al. [9] did experiments on samples with different doping concentrations. They showed the formalism proposed by Feenstra and Stros-
Figure 2.2: Tunneling spectroscopy measurement on the clean GaAs(110) surface of a p-type doped sample, after Feenstra et al. [7]. Contributions from respectively the conduction band (C), valence band (V) and doping induced band (D) can be distinguished.

cio can only explain the curves measured on the high doped samples (doping concentration higher than $10^{18}$ cm$^{-3}$). For lower doping concentration in reverse bias, however, the current voltage spectra strongly deviate from the calculations. This they attribute to the absence of an inversion layer. They believe no inversion layer is present because holes at the surface are not in equilibrium with the electrons in the bulk, since they are separated by the semiconductor band gap. They show that by excluding the presence of an inversion layer (in the so called depletion approach) that calculations describe the experimental derived data somewhat better. Discrepancies are attributed to the inadequacy of the planar 1-D model to describe the 3-D tip interactions.

Other direct band gap III-V binary compounds:
In the family of direct band gap III-V binary semiconductors, formed by the
2.1 Clean surfaces

materials GaAs, InP, GaSb, InAs, InSb and GaP, GaAs(110) has been the surface most extensively studied by STM. Relatively few publications deal with STM results obtained on the cleavage plane of the other materials.

Whitman et al. [10] studied the InSb(110) surface. By simultaneously imaging the occupied and unoccupied state densities, they determined the relative positions of the In and Sb dangling bonds within the unit cell. Their results are in good agreement with the calculations on the surface electronic structure and surface buckling. In spectroscopy measurements they could determine the band gap and recognize the contributions from the VB, CB, and impurity band, as in the case of GaAs.

Ebert et al. [11] studied the InP(110) surface with STM. In their spectroscopic results they could determine the onsets of the VB and CB and the presence of the occupied and unoccupied surface state.

Feenstra et al. [12] made a systematic spectroscopy study with STM on this family of materials. In their spectra they could reveal the CB and VB edges, the onset of the higher lying CB at the L-point in the Brillouin zone and various other features associated with surface states, for all the materials.

InAs(110) is a special kind of surface in the sense that it contains a surface 2-dimensional-electron-gas (2DEG), since the Fermi level is pinned in the CB\(^2\). Wildöer et al. [15] did STM spectroscopy measurements on this surface at low-temperature (4.2K) and applied a strong magnetic field perpendicular to the sample surface. They observed separate Landau levels and at zero field small resonances in the tunnel spectra are visible, which may be due to quantized states below the tip.

Ternary and quaternary III-V semiconductor alloys

Also ternary III-V's (AlGaAs [16, 17], InGaAs [18, 19]) and quaternary III-V alloys (InGaAsP [16]) have been studied by STM. In empty and filled state images different group III and group V sites can be distinguished because the elements appear with different corrugation in the images. The variation in corrugation results from differences in size and dangling bond energy. Pfister et al. [18] showed that in the empty state images of InGaAs the In atoms which are positioned in the first layer can be observed. In the filled state images the influence of In atoms in the second layer are visible. Smith et al. [17] did experiments on the AlGaAs(110) surface plane, where they distinguish between Al atoms in the first and second layer by symmetry considerations.

\(^2\)This has been shown by Tsui et al. [13, 14].
2.2 Doping atoms

The influence of single doping atoms on the surface electronic structure of the III-V compound (110) surface has been studied by a few groups. Salemink et al. [20–22] were the first, who showed the influence of Zn and Be dopants on the GaAs(110) surface. In the filled state images the Zn and Be doping atoms induce circular hillock-like features superimposed on the atomic lattice with a diameter of about 2 nm. Zheng et al. [23–25] studied both Si and Zn induced features on the GaAs(110) surface. They showed that the Si atom induces the same circular hillock-like features in both filled and empty state images. In the empty state images of the Zn doped GaAs sample the circular hillock-like features are replaced by triangular features. The origin of the triangular shape is not understood. Ebert et al. [26] showed the influence of Zn dopants on the InP(110) surface. The Zn induced features in the filled state images are similar to the Be and Zn induced features at the GaAs(110) surface. However, no empty state images were presented.

To prove that the observed features are indeed induced by doping atoms, samples with different doping density were systematically studied and it was found that the number of features was constant in time and indeed proportional to the doping concentration. Furthermore, by measuring the height of a large number of features and putting these in a histogram, doping atoms positioned in 5 to 6 different subsurface layers could be distinguished\(^3\). With this value, the doping concentration of the sample could be determined from a large scan image, in good agreement with the actual doping concentration.

Subsurface doping atoms induce these hillock-like features because they are charged. The Si donor atom is positive and therefore locally increases the density of states observed in the STM images. For Zn and Be acceptor atoms hillock features are observed in the filled state images. This can be understood since the negative charge locally increases the density of valence band states as shown in calculations by Johnson et al. [20].

Doping atoms in the top surface layer induce a different distinctive localized feature. This is calculated by Wang et al. [27] for Si\(_{\text{Ga}}\) in the GaAs(110) surface plane. Zheng et al. [23, 24] showed images of some observed features which fit quite well to these calculated images.

\(^3\)By symmetry considerations doping atoms positioned in alternating even and odd subsurface layers could be distinguished, see [20, 26]
2.3 Vacancies and defects

In addition to doping atoms missing atoms (vacancies) have also been studied together with other defects. Lengel et al. extensively studied Ga and As vacancies on the GaAs(110) surface [28, 29]. As-vacancies manifest themselves as missing atoms or local reductions in the density of states in filled state images of the GaAs(110) surface. The second nearest neighbour As atoms along the zig-zag chain are also slightly depressed. In the empty state image the nearest neighbour Ga atoms of the As-vacancy are raised out of the surface. No lateral displacements were observed. Lengel et al. only observed these As-vacancies on p-type doped samples. On n-type doped samples only Ga-vacancies are visible. The results for Ga-vacancies are complementary to the results for the As-vacancy. The observations are supported by tight binding molecular dynamics calculations. In addition to these local signatures a delocalized feature is also present around the vacancies. This is induced by the charge of the defects which causes the bands to bend. In this way it was shown that the As-vacancy on the p-type doped GaAs(110) surface is positive and the Ga-vacancy on the n-type doped GaAs(110) surface is negative. Chao et al. [30] found an experimental method to determine the charge of a vacancy. They derived for the As-vacancy a charge of +1e. This is in contradiction with the +2e charge found by Lengel et al. [29].

Lengel et al. also observed tip induced interchain vacancy migration [31]. The preferential movement of vacancies between different zig-zag chains instead of along the zig-zag chain is explained by bond breaking arguments. The observation that interchain vacancy migration only occurs in the [001] direction and not in the [001] direction is related to local phonon modes. In 1995 Lengel et al. showed that tip induced As-vacancy (Ga-vacancy) migration is only observed when the tip is negatively (positively) charged [32, 33]. They explained that the driving force for this vacancy migration is the capture of minority carriers (injected by the STM tip) in localized vacancy levels.

Ebert et al. studied P-vacancies on the InP(110) and GaP(110) surfaces [34]. They found that the P-vacancy is positively charged on p-type doped InP and GaP. It is negatively charged on n-type doped InP and neutral or negative on the GaP(110) surface. The manifestation of P-vacancies on p-type doped InP is identical to the As-vacancies on p-type GaAs. A local depression is visible and the second nearest neighbours along the zig-zag chain are slightly depressed. For n-type doped samples the vacancy again shows a local reduction in the density of states at the position of a P atom. However, the second nearest neighbour P atoms are lifted asymmetrically.
Figure 2.3: Schematic representation of the GaAs(110) surface with a missing As atom (As-vacancy). The first nearest neighbour Ga atoms and second nearest neighbour As atoms in the surface plane are indicated.

These charge dependent changes in morphology are explained by a simple model for bulk defects.

Feenstra et al. studied antisite As\textsubscript{Ga} defects in low-temperature grown GaAs(110) [35]. These defects induce a donor band. Images of this state reveal a central defect core with two satellites located about 15 Å from the core.

In addition to individual defects interactions have also been studied between vacancies [36] and between dopants and vacancies [26].

2.4 Adsorbates

Many STM spectroscopy experiments have been performed on metal (sub) monolayer and overlayer adsorbate systems at the GaAs(110) surface. The systems studied concern a variety of ordered and disordered systems, including Sb, Bi, Sn and Au as studied by Feenstra et al. and Fe and Cs studied by Stroscio et al.. These spectroscopy measurements are reviewed in a paper by Feenstra [37]. Measurements on the Sb-, Au- and Fe-GaAs(110) system show the same characteristic spectrum as band gap states. The spectra consist of an intense state in the upper part of the band gap and a tail of states
extending out from the valence band. The Fermi level is pinned between these two sets of states. The geometric structures which give rise to this spectrum vary from one system to another: the edge of ordered Sb terraces, small clusters of Au atoms, or the edge of large Fe clusters. Some questions relating to the physical origin of the gap states remain to be answered. In particular the relative contributions to the spectrum of evanescent semiconductor states, metal/semiconductor bonds and surface Ga dangling bonds, are not clear.

In addition to metal adsorbates, Stroscio et al. also studied oxygen adsorbates on the GaAs(110) surface [38]. In measurements on different doped samples they showed that the oxygen is negatively charged on the n-type doped sample but neutral on the p-type sample. The difference is attributed to the existence of acceptor states in the band gap.

Wildöer et al. observed band-switching effects near a conductive grain on top of the InAs(110) surface [39]. The observed features are explained by charge quantization effects on the grain.

### 2.5 Multilayers

For studying a variety of multilayer III-V semiconductor structures the method of cross-sectional STM is used. Salemink et al. initiated the cross-sectional STM work on multilayers and alloys (see for example reference [40]). In this method, a cross-section of the structure is prepared by cleaving. STM studies are performed on this cleavage plane. In these experiments one gains information about, for instance, interface roughness, band offsets, band structure, quantum well sub-bands, composition fluctuations and distribution of doping atoms. A review by Feenstra about cross-sectional experiments on III-V multilayers can be found in [41].

### 2.6 Tunneling induced luminescence

Another application of STM is to use the tip as a local source of electrons to induce light emission. Abraham et al. [42] showed that by the recombination of holes with electrons tunneling into cleaved (110) GaAs/AlGaAs heterostructures luminescence is induced and can be used to image the interface region with nanometer resolution. Alvarado et al. [43] showed that this method also can be used to determine the energy of bulk bands and to measure
transport parameters such as the thermalization length and diffusion length of minority carriers. Pfister et al. [44] performed STM measurements on GaAs/(AlAs)$_n$(GaAs)$_m$ quantum wires. With tunneling luminescence measurements the relative quantum efficiency of individual wires is quantified. The first local tunneling induced luminescence spectroscopy measurements at low temperature on III-V semiconductors were performed by Samuelson et al. [45, 46]. They reported sharp peaks in the luminescing spectra measured on InP and GaAs/AlGaAs quantum wire structures.

References


Chapter 3

Experimental details setup

In this chapter the experimental setup used in the experiments discussed in chapters 4, 5 and 6 is described. The STM is equipped with an automatic approach facility and a cleavage station. Also the design of a sample displacer is presented which is used to search for thin molecular-beam-epitaxy (MBE) grown multilayer structures at the edge of a sample. All measurements are performed at 4.2 K in a bath cryostat.

3.1 Low-temperature STM

The STM we use in the experiments was designed and built in our department. It is described in the literature [1] and in the theses of Wildöer [2] and Boon [3]. In this section we will briefly summarize the most important parts in the design.

Fig. 3.1 shows a cross section of our STM. The scan tube (A) is mounted inside a plunger (B) which is clamped into a plunger holder (C). The plunger can be moved stepwise upwards and downwards by inertial slip-stick movement. This motion is activated by applying an appropriate voltage pulse to the outer piezo tube (D) and forms the heart of the automatic tip to sample approach facility. The outer piezo tube is mounted on the STM housing (E). Below the tip (G) the sample holder (F) is placed. In order to obtain a high resonance frequency for the STM, the design is made as rigid, lightweight and compact as possible. All the parts of the STM are made from stainless-steel (except of course the piezo-electric tubes). The surface of the plunger is coated by a hard ceramic layer [4] to prevent it from wearing.

The automatic tip to sample approach works in the following way. By
slip-stick movement the tip approaches the sample in a stepwise way. During this approach the STM feedback system is active. After each step with the plunger a sawtooth voltage pulse is applied to the scantube. This voltage is generated by our commercial Omicron STM control unit [5] and elongates the tube. If a tunnel current is detected the approach is stopped and the feedback system of the STM control unit regulates the tip-sample distance. The waveform we use for the tip to sample approach consists of two parts. The first part contracts the outer piezo tube with constant acceleration and is parabolic in shape. In this part the inertial force on the plunger is smaller than the static friction force. In the second part the outer piezo tube is elongated rapidly so the inertial force overcomes the friction force and the plunger is moved downwards with respect to the holder. The waveform is generated by a Wavetek arbitrary waveform generator [6]. Typical voltage amplitudes used are between 150 V and 175 V at 4.2 K. This corresponds to a step size of about 1/3 of the total extension of the scan tube when applying the sawtooth voltage.

The STM is attached to an insert to be able to position the STM in a
bath cryostat. The mechanical connection between the STM and the insert (G) is chosen close to the sample holder. In this way the resonance frequency of the STM is less sensitive to the mass of the sample holder. This is important if one wants to cleave samples at low temperatures and a cleavage station is needed (see next section). The STM is enclosed by a vacuum can and together with the insert can be pumped down below $10^{-4}$ Torr. Before cooling down, the insert and STM are pumped down and flushed with clean helium gas a few times, in order to remove as much water vapour and other residual gases which can contaminate the STM and influence its operation (especially the approach facility). After flushing for the last time helium gas is introduced to atmospheric pressure as a heat exchange gas.

The insert fits in a stainless steel cryostat with a 10 T magnet\(^1\). To protect the STM from vibrations, the cryostat is damped by air dampers and the insert is connected by a double O-ring construction to the top of the cryostat [2, 7].

### 3.2 Cleaving

In order to obtain clean semiconductor surfaces, we cleave our samples at 4.2 K. At this low temperature the vapour pressure of common gasses is very low (vapour pressure of O\(_2\), CO\(_2\), N\(_2\), Ne, NO < 10\(^{-15}\) Torr). Only H\(_2\) (vapour pressure < 10\(^{-7}\) Torr) and of course He are present. The cleaved surface is therefore only exposed to these gases \(^2\).

A cleaving station was built on the sample holder to cleave the samples. This is shown in Fig. 3.2. The station consists of a house (A) together with a movable part (B) (a slider). Two windows (C) in the housing are necessary for correct alignment of the tip with respect to the sample. A copper wire (D) is connected to the slider. This wire leads to a small wheel just above the STM which can be turned from outside. By winding up the wire the slider is forced to move forward, cleaving the sample (E) which is glued in the sample holder. All the wafers we used were 0.3 mm thick and polished on one side. The surface plane of the substrates had the (001) crystal orientation. Ohmic contacts were made at the non-polished side. For n-type doped GaAs we used Au/Ge/Ni contacts annealed to 450°C, for

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\(^1\)The magnet is not used in the experiments described in this thesis.

\(^2\)We did not see any evidence in our STM experiments for the presence of these atoms at the surface. Keijser et al. [8] however showed in a break junction geometry that He has influence on the tunnel current, but only at small tunnel resistances (typically 100 MΩ).
p-type GaAs Au/Zn/Au contacts also annealed to 450°C were used. Conducting paint (silver paint) was used to glue our samples into the sample holder. The polished side pointed towards the slider and the (110) surface plane pointed towards the tip. The typical size of a sample was 3 mm × 4 mm (width × length). In order to improve the cleave, a scratch was made in the sample with a diamond point. The scratch was made at the polished side as close as possible to the edge of the sample holder. Sometimes the scratch was made over the whole width of the sample and sometimes just to the middle. No final conclusions can be drawn as to which of the two methods is the best. It probably depends on how parallel the scratch is made parallel to one of the crystal axes of the sample. We also found that some samples cleaved more easily than others and have no explanation for this. After cleaving many steps were always present at the cleavage plane as could easily be observed with an optical microscope. This was not disastrous for our experiments since with STM only a small surface area is studied. We attributed these steps to the fact that the direction of the scratch and/or cleaving station usually deviated from the real crystal axes.
3.3 Tip preparation

The STM tips are made from 0.5 mm PtIr wire (10 % Ir). A tip is formed by mechanically cutting (pulling) the wire under an angle with scissors. Beforehand, both the scissors and the wire are ultrasonically cleaned in isopropanol.

3.4 Sample displacer

The scan range of the STM tip at low temperatures is about $1 \mu m \times 1 \mu m$ (displacement of the piezo tube at 4.2 K is about 8 nm/V). This is a relatively small area. To study artificially fabricated nanostructures, one needs a facility to search for these structures. Therefore a small sample displacer which can operate at low temperature was designed and built. The displacer can move a small table (on which a sample can be prepared in a same way as described above) in a lateral direction with steps varying from a few nanometers to a few micrometers (dependent on applied voltage) by means of inertial slip-stick movement. The sample displacer is comparable to the displacer described by Wildöer et al. [1]. However, we replaced the shear piezo plates by a piezo tube. In this way we found that the sample displacer works more reliably at low temperature.

In Fig. 3.3 the sample displacer is schematically shown together with the cleaving station. With the displacer only movements in one direction can be made. The sample displacer consists of a piezo tube (A) with four quartered electrodes on the outside and one on the inside; a stainless steel support (B) which is connected to the tube by a screw; and a table (C) which is positioned on the support. Under the table two zirconium oxide rods are connected. The long rod fits into the grooves of the stainless steel support. The short rod has an elliptic shape and is positioned on the flat area of the support. In this way the table is supported by only three contact points. To prevent degrading by wear, the support is coated with a hard ceramic layer [4]. The contact surfaces were polished very carefully. At two sides of the table electrodes are connected (D). These electrodes are positioned opposite to the housing of the cleaving station and can be used to determine whether or not the table is in contact with the housing. The table is moved by applying an appropriate voltage pulse to the piezo tube. The waveform used is comparable to the waveform used for the tip approach, only the fre-
Figure 3.3: Sample displacer together with cleaving station. (A) Piezo tube, (B) stainless steel support, (C) table, (D) gold electrodes (E) cleaving station, (F) slider.

Frequency and amplitude are different. Typical voltages used are 30 V - 40 V, which cause a movement for the table of about 100 nm per step at 4.2 K. The table can be displaced over a maximum distance of about 1 mm. Just like in a scan tube, the voltage pulses to the electrodes are inverted with respect to each other to obtain the correct movement.

We used the sample displacer to search for MBE grown multilayer structures at the edge of a GaAs sample after cleaving at low temperature. Several attempts were made. None of them, however, was successful. We attribute this to the fact that due to the cleaving too many steps were present near the edge of the sample so that multilayers were no longer recognizable.

3.5 Electronics

For controlling the STM we used commercial Omicron [5] and Nanoscope [9] STM control units. These control units allow the STM to be operated in
different measurement and recording modes. All the images presented in
this thesis were measured in constant current mode. The tunneling spectra
were recorded with the Omicron control unit at constant tip sample distance.
The Omicron control unit also allows tunneling spectra and topography to
be recorded at the same time. At each scan pixel a spectrum is recorded. In
this mode, the feedback system remains on during scanning and is turned
off while measuring a tunneling spectrum.

The I-V converter necessary to convert the small tunneling current to a
measurable voltage is home built. A feedback resistor of 100 MΩ is used. A
small capacitor of about 6 pF parallel to this resistor prevents noise increase
due to gain peaking [3]. The I-V converter is connected from outside the
insert to the tip wire inside. The I-V converter therefore stays at room
temperature. The output of the I-V converter goes to a PAR amplifier [10]
(gain 20 ×) before it enters the STM control unit. The total gain therefore
is 2 × 10⁹. A 2 mV signal represents a tunneling current of 1 pA.

The bias voltage is applied to the sample. To reduce the noise on the
voltage coming from the STM control unit, it is divided by a 10× voltage
divider.

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Chapter 4

Silicon induced features at the GaAs(110) surface studied by STM

In this chapter the influence of individual Si donor atoms on the GaAs(110) surface planes is studied by STM. Samples with two different doping concentrations have been studied\(^1\): \(6 \times 10^{17} \text{ cm}^{-3}\) and \(2 \times 10^{18} \text{ cm}^{-3}\). The samples are cut from (001) wafers and cleaved in situ at 4.2 K. In section 4.1 empty and filled state images measured on the GaAs(110) surface are presented. The Si induced features are different in both images. This difference is attributed to the influence of tip induced band bending and is discussed in section 4.2. The filled state images show patterns of concentric rings. In section 4.3 these patterns are explained as direct observations of Friedel oscillations around Si atoms positioned below the surface. Two models are presented and discussed which give theoretically calculated line-profiles of the observed features. These line-profiles are compared with the experimental results. In section 4.4 the influence of sample voltage, tunnel current and depth of the Si atom below the surface on the observed features are studied. In section 4.5 the empty state images and differences to filled states will be discussed. In the final section (4.6) tunneling spectroscopy measurements obtained on top and next to the dopant induced features are presented. In these curves steps and peaks are visible, which are attributed to resonances in the transmission probability across the potential wells induced by the positively charged Si donors.

\(^1\)The doping concentration of both samples is verified by electrical conductivity measurements performed by P. M. Koenraad et al. from Eindhoven university of technology.
4.1 Empty versus filled state images

Fig. 4.1 shows four STM images and two line-profiles through two Si induced features. Fig. 4.1(a) shows an empty state image of the GaAs(110) surface. Clearly rows of gallium (Ga) atoms can be observed in the [1̅1̅0] direction\(^2\). Inside the rows resolution is not good enough to see the individual atoms in this image. In the middle of the picture a bright spot is present. This hillock feature in the electronic structure of the GaAs(110) surface is superimposed on the atomic lattice. The feature is induced by a subsurface positioned Si donor atom. This was proved by Zheng et al. [2]\(^3,4\). In Fig. 4.1(c) the same picture is plotted as in Fig. 4.1(a) but with the atomic lattice filtered out\(^5\). In this way only the Si induced feature is visible. In Fig. 4.1(e) a line-profile is plotted through the centre of the feature in Fig. 4.1(c). The feature strongly decays with distance from the centre. It is not perfectly circular symmetric, which is attributed to the influence of neighbouring doping atoms.

In Fig. 4.1(b) a filled state image is plotted of the same surface area as measured in Fig. 4.1(a). In this figure rows of arsenic (As) atoms are visible. In the middle of the picture a bright feature is again visible. The feature is surrounded by two concentric dark and bright rings, respectively. In Fig. 4.1(d) the same picture is plotted as in Fig. 4.1(b), but with the As lattice filtered out. In this way the outermost ring can be seen more clearly. These bright (b) and dark (d) regions in the image represent regions where the tip has to retract and approach the surface respectively, in order to keep the tunnel current constant and therefore can be related to regions with a

\(^2\)Feenstra et al. [1] showed that group III elements (Ga) are visible in the empty state images and group V elements (As) in the filled state images.
\(^3\)In their paper they showed by doing measurements on different samples with varying doping concentration that the number of bright spots is proportional to the Si doping concentration. By putting the apparent heights of the features in a histogram they recognized at least five discrete values for the height. These discrete values reflect the discrete spacing of the subsurface layers. They concluded that the influence of Si dopants positioned in the first five subsurface layers can be measured. They verified in large scan images that the density of bright features indeed was in agreement with the actual doping concentration.
\(^4\)Johnson et al. [3] were the first who recognized the influence of subsurface dopants on the GaAs(110) surface. Their GaAs samples were doped with Be atoms.
\(^5\)First the picture is transformed to fourier space by fast fourier transformation. Then a lowpass filter is put over the data. After that the filtered part is transformed back to real space.
Figure 4.1: (a) empty state image of the GaAs(110) surface: in the centre is a hillock feature induced by a subsurface Si donor atom. Sample voltage: +1.0 V, set-point current: 20 pA, scan size: 14.8 nm × 14.8 nm, Z-range: 0 - 0.22 nm. (b) filled state image of the same surface area. The dopant induced feature is changed into concentric rings, representing regions with varying electron state density. Sample voltage: -2.2 V, set-point current: 20 pA, Z-range: 0 - 0.13 nm. In (c) and (d) the same STM images are plotted as in (a) and (b) respectively but with the atomic lattice filtered out. (e) and (f) show line-profiles through the dopant induced features (shown by the dashed lines in (c) and (d)).
high and low electron filled state density. Summarizing, the surface shows concentric oscillations in the electron filled state density around a subsurface Si donor atom. In Fig. 4.1(f) a line-profile is plotted through the centre of the feature. One can see that the amplitude of the oscillation decays with distance from the centre. In sections 4.3 and 4.4 this line-profile will be analysed quantitatively together with other obtained line-profiles.

From these images it is clear that the Si induced feature in the empty state image is different from that in the filled state image. This can be understood from the effect of tip induced band bending and will be discussed in the next section.

### 4.2 Tip induced band bending

When two materials with different work functions are connected or in close proximity (distance < 1 nm) to each other, electrons will flow and tunnel, respectively, from the material with the lowest work function to the other material, until Fermi levels have lined up and equilibrium is reached (see for instance reference [4]). Since electrons have moved from one side to the other, the materials are not neutral anymore and an electric field exists between them. To screen out this electric field, an extended space charge region is built up near the surfaces. In metals, this space charge region is very narrow (≈ 0.05 nm), because of the high free electron density. For semiconductors, however, the free electron density is lower and therefore the space charge region is more extended. The width of the space charge region is dependent on the doping concentration and can be influenced by applying a bias voltage between the materials.

In our STM setup, the tunnel junction consists of a semiconductor sample, a vacuum barrier and a metal tip. The work function of the PtIr tip is higher than the work function of the Si doped GaAs. In bringing both materials in close proximity, negative charge moves from the semiconductor to the metal tip. The semiconductor surface becomes positive, the metal surface negative and an electric field exists between the two materials. Inside the semiconductor a space charge region is built up with barrier height \( \phi \) and width \( W \). This can be visualised in a schematic electron energy dia-

\[ W = \sqrt{\frac{2\varepsilon_s \phi}{\varepsilon_0 N} (\phi - V - kT/e)} \]

In reference [5], the following expression is derived for the width \( W \) of the space charge layer in case the electrons are depleted from the surface: \( W = \sqrt{\frac{2\varepsilon_s \phi}{\varepsilon_0 N} (\phi - V - kT/e)} \), with \( \varepsilon_s \) the semiconductor permittivity, \( N \) the impurity density, \( \phi \) the built-in potential, and \( V \) the applied bias-voltage. For a semiconductor with \( N = 10^{18} \text{ cm}^{-3} \), \( \varepsilon_s = 12.5 \varepsilon_0 \), \( \phi = 0.2 \text{ V} \), \( V = 0 \text{ V} \), we find \( W = 16.6 \text{ nm} \).
Figure 4.2: Left: schematic 1-dimensional electron energy diagram of a semiconductor-metal tunnel junction. Right: table with typical values for the constants defined in the diagram.

In this diagram the electron energy is plotted versus distance. The energy of electrons increases when moving up in the diagram. The semiconductor is plotted on the left side and can be recognized by the presence of a gap between the valence and conduction bands. On the right side the metal tip is plotted. In between the semiconductor and metal a tunnel barrier is present with width d. In this diagram several constants have been defined. $\phi_m$ is the metal work function, $\chi$ is the semiconductor electron affinity, $E_g$ the semiconductor band gap, $E_{F,s}$, $E_{F,m}$, $E_{CB}$ and $E_{VB}$ point out the Fermi energy inside the semiconductor, Fermi energy inside the metal, conduction band edge energy and valence band edge energy, respectively. In the adjacent table typical values are given for these constants. These values are also tabulated in appendix A and will be used in the calculations.

As discussed above due to the difference in work function between the semiconductor ($\phi_s = \chi - E_{F,s} + E_{CB}$) and metal ($\phi_m$), the metal surface becomes negative and a space charge region is built up near the semiconductor surface. In the electron energy diagram this is pointed out by an upward bending of the valence and conduction bands towards the surface. The negative charge is repulsive and therefore more energy is needed for electrons to overcome this barrier. The amount of band bending is given by the electrostatic surface potential ($\phi$). When applying a voltage between tip and sample the electrostatic surface potential is changed. Depending
on bias voltage the electrostatic surface potential becomes larger or smaller and can even change in sign. This effect induced by a biased tip in close proximity of a sample is called tip induced band bending. In appendix B six schematic energy diagrams are plotted showing the different possibilities for different applied sample voltages.

In the next section, we will present calculations on the electrostatic surface potential for a 1-dimensional metal-semiconductor tunnel junction. These calculations are comparable to the calculations done by Feenstra et al. [6], but this time performed for a temperature equal to 4.2K. After that we will shortly summarise the results which are obtained by modelling the tip as a three dimensional object. Both results (obtained in the 1- and in 3-dimensional models) will be compared with each other.

4.2.1 Tip induced band bending in 1-dimension

In this section the electrostatic surface potential at the semiconductor surface is calculated in 1-dimension as a function of the applied sample voltage. For these calculations the results for a degenerate semiconductor as obtained by Seiwatz et al. [7] are used. They found a relation between the electric field at the semiconductor surface ($E_s$) and the potential difference across the semiconductor space charge region ($\phi$). The relation is obtained by integrating Poisson's equation from the neutral bulk to the surface. We will briefly show the most important steps in the derivation.

In 1-dimension, Poisson's equation can be written as

$$\frac{d^2 \phi(x)}{dx^2} = -\frac{\rho(x)}{\epsilon_s \epsilon_0}, \quad (4.1)$$

with $\phi(x)$ the potential, $\rho(x)$ the charge distribution inside the semiconductor as a function of distance $x$ to the surface and $\epsilon_s$ and $\epsilon_0$ the dielectric constant of the semiconductor and the permittivity of free space, respectively. The charge density $\rho(x)$ is equal to

$$\rho(x) = e[N_D(x)^+ - N_A(x)^- - n_e(x) + p_v(x)], \quad (4.2)$$

with $N_D(x)^+$ the density of ionised dopants, $N_A(x)^-$ the density of ionised acceptors, $n_e$ the density of electrons and $p_v$ the density of holes. Using Fermi-Dirac statistics, expressions can be found for the different components in the charge density (see for example reference [5]). The densities are dependent on the position of the Fermi level with respect to the conduction ($E_C$) and
valence band edge \( (E_V) \). In the semiclassical approach these band edges shift linearly with the potential \( \phi(x) \). Therefore, by replacing \( E_C \) and \( E_V \) in the expressions for the charge densities by \( E_C - e\phi(x) \) and \( E_V - e\phi(x) \), respectively, \( \rho(x) \) is determined as a function of \( \phi(x) \). Substituting this into equation 4.1, a nonlinear differential equation is found for \( \phi(x) \). By integrating equation 4.1 from the neutral bulk \((b)\) to the surface \((s)\), we derive

\[
\left( \frac{d\phi}{dx} \right)_s = E_s = G(\phi), \tag{4.3}
\]

since \( (d\phi/dx)_b \) is zero. \( G(\phi) \) is an expression for the electric field at the semiconductor surface as a function of \( \phi \). This expression is derived in reference [7]. By using this expression, we can calculate the applied sample voltage \( V \) as a function of \( \phi \), as we will show now.

The total potential drop across the tunnel barrier \((V_b)\) and semiconductor \((\phi)\) is equal to the externally applied bias voltage \((V)\) plus the work function difference between metal and semiconductor \((\phi_m - \phi_s)\):

\[
V_b + \phi = V + (\phi_m - \phi_s), \tag{4.4}
\]

(see Fig. 4.2). At the semiconductor surface no surface states are present (see chapter 2). Therefore we are allowed to use the boundary condition: \( \epsilon_s E_{s,\perp} = E_{v,\perp} \) between semiconductor \((s)\) and the vacuum barrier \((v)\). The potential drop across the vacuum barrier is equal to \( V_b = E_v \cdot d \), where \( d \) is the tip sample distance. By combining the obtained results, we find

\[
V_b = \epsilon_s \cdot G(\phi) \cdot d + \phi - (\phi_m - \phi_s). \tag{4.5}
\]

Using equation 4.5, we can calculate the electrostatic surface potential \( \phi \) as a function of applied sample voltage \( V \).

In the expression \( G(\phi) \), Fermi-Dirac integrals \( F_j(\eta) \) have to be calculated. We used the following approximations. For \( \eta < -4 \):

\[
F_{1/2}(\eta) = \frac{2}{3} F_{3/2}(\eta) = \frac{1}{2} \pi^{1/2} \epsilon^{\eta}. \tag{4.6}
\]

For \( \eta > 20 \):

\[
F_j(\eta) = (j + 1)^{-1} \eta^{j+1}. \tag{4.7}
\]

In the range, \(-4 < \eta < 20\), tabulated values for the Fermi-Dirac integrals are used. Furthermore, the values tabulated in appendix A are put into
the calculations. The calculations are performed for a temperature equal to 4.2 K. The values for $\phi$, put in equation 4.5, are increased stepwise with 40 mV.

In Fig. 4.3(a) and 4.3(b) the results of our calculations are presented. In Fig. 4.3(a) two curves are plotted. These curves show the dependence between the applied voltage and the electrostatic surface potential for a semiconductor sample with doping concentration equal to $6 \times 10^{17}$ cm$^{-3}$ (curve 1) and $2 \times 10^{18}$ cm$^{-3}$ (curve 2), respectively, as used in our experiments. In Fig. 4.3(b) we show the electrostatic surface potential versus applied sample voltage for different tip sample distances: 0.5 nm (curve 1) and 0.9 nm (curve 2). The electrostatic surface potential is defined in the electron energy diagram in Fig. 4.2 and gives the potential difference between the semiconductor surface and bulk. It is positive when the bands bend upwards towards the surface, negative when the bands bend downwards and equal to zero when no band bending is present. Note that the shoulder in the curves around $\phi = 0$, is not real. This is due to a small error in the calculations induced by substitution of non-exact values for the Fermi-Dirac integral in the range, $-4 < \eta < 20$, since only tabulated values are used with $\eta$ being an integer.

In general, three different regions can be identified in all calculated curves. First, the region where the electrostatic surface potential is negative. In this region bands at the surface are bending downwards and electrons are accumulated at the surface. Secondly, the region where the electrostatic potential is positive but smaller in size than the band gap energy of the semiconductor. In this region electrons are pushed away from the surface, thus a depletion layer is created. Finally, the region where the electrostatic potential is positive and larger than the semiconductor band gap. In this region valence bands at the surface cross the Fermi level and holes are accumulated at the surface. An inversion layer is built up. The electrostatic surface potential is equal to zero at the point the sample voltage is equal but opposite to the potential difference built up due to the difference in work function between the two materials (point A in Fig. 4.3(a) and (b)). The slope of the curves is steepest in case when the surface is depleted from free carriers. This can be understood since in this region no free charge carriers are present at the surface to screen out the electric field. Only positive static charges are present from the ionised Si donor atoms.

Fig. 4.3(a) shows the influence of sample doping concentration on the amount of tip induced band bending. In the accumulation region the absolute value of the electrostatic surface potential for the lower doped sample (curve 1) is somewhat larger than for the higher doped sample. This is be-
Figure 4.3: Electrostatic surface potential ($\phi$) at the semiconductor surface versus sample voltage calculated in 1-dimension. (a) Two curves 1 and 2 showing the results for two different sample doping concentrations: $6 \times 10^{17}$ cm$^{-3}$ and $2 \times 10^{18}$ cm$^{-3}$, respectively. Tip sample distance is 0.9 nm. (b) Curve 1 and 2 show the results for tip sample distance equal to 0.5 nm and 0.9 nm, respectively. Doping concentration is equal to $2 \times 10^{18}$ cm$^{-3}$. Indicated are the experimental voltages, -2.2 V (F.S.) and +1.0 V (E.S.), respectively, of Fig. 4.1.
cause for the lower doped sample, the Fermi energy inside the conduction band is positioned closer to the band edge than for the higher doped sample and therefore less free charge carriers are present to screen out the electric field. In the inversion region the situation is reversed, the absolute value of the electrostatic potential at the surface is a little bit smaller for the lower doped sample. This is because more holes are present to screen out the electric field. In the depletion region the curve for the lower doped sample is steeper than for the higher doped sample. This can directly be related to the difference in doping density. For the lower doped sample fewer positive charges (ionized doping atoms) are present to screen out the electric field. Therefore changing the sample voltage results in a steeper increase of the electrostatic potential than for the higher doped sample.

Fig. 4.3(b) shows the effect of tip sample distance on the electrostatic surface potential. For the tip sample distance of 0.5 nm, the absolute value of the electrostatic potential is larger in all three regions: accumulation, depletion and inversion. This can be understood easily because by decreasing tip sample separation the tunnel resistance is reduced and therefore also the potential drop across the tunnel barrier. The potential drop across the semiconductor increases and so does the electrostatic surface potential. The crossing point of the two curves is exactly at the point where the electrostatic surface potential is equal to zero. At this point the applied sample voltage is equal but opposite to the work function difference of the two materials. This is independent of tip sample distance.

4.2.2 Tip induced band bending in 3-dimensions

Several authors have made attempts for modelling a 3-dimensional metal-semiconductor tunnel junction and did calculations on the size of the surface electrostatic potential and width of the space charge region [8–11]. Generally, one found the amount of tip induced band bending is smaller in 3-dimensions than in 1-dimension. Feenstra et al. [8] calculated that the tip induced band bending in 3-dimensions is about 40% smaller than in 1-dimension, because of the larger divergence of the potential. In their model they considered a sharp probe tip, consisting of a 1 nm radius hemisphere on a 50 nm radius of curvature paraboloid and a tip sample separation of 1 nm. They only did calculations for tunneling on a depletion layer, not for an accumulation layer. But it is reasonable to expect the same reduction in band bending for the situation of accumulation.
4.2.3 Conclusion

By applying a voltage between tip and sample a surface electrostatic potential is built up at the semiconductor surface. Depending on bias polarity energy bands are pushed upwards or downwards. For an n-type doped semiconductor as studied in this section the surface area is depleted from free carriers when the bands are pushed upwards and accumulated with free carriers for downward bending of the bands. In the measurement shown in Fig. 4.1(a), a sample voltage of $\pm 1.0 \text{V}$ is applied. Following our calculations in Fig. 4.3(a), curve 1, we expect the electrostatic surface potential to be positive for this sample voltage. In the measurement shown in Fig. 4.1(b) a sample voltage of $-2.2 \text{V}$ is applied. For this situation the electrostatic potential is expected to be negative. The difference, therefore, between Fig. 4.1(a) and 4.1(b) is the absence and presence respectively of free charge carriers (electrons) at the surface. In the next section we will discuss the situation of accumulation where screening effects have to be considered around Si donor atoms.

4.3 Screening

4.3.1 General introduction

When a particle with positive (negative) charge is placed in an environment where free electrons are present, the electrons will be attracted (repelled) by this charge. The movement of electrons will reduce the local electric field induced by the positive (negative) charge. The positive (negative) charge is screened by the electrons. The electrons, however, will not only interact with the point charge but also with other electrons. In order to calculate the correct resulting potential around such a positive (negative) point charge one must therefore also take into account the effect of electron-electron interaction. This can be done in a relative simple way in the situation the point charge is positioned in an environment where no other potentials are present. In Appendix C we show the derivation of the screened potential around a point charge assuming this potential is slowly varying. This is the Thomas-Fermi approach. The resulting potential decays exponentially with distance $r$ like $\exp(-r/R)$, with $R$ the screening distance, and is known as the screened Coulomb potential or Yukawa potential. An expression for the screening distance $R$ is derived by Dingle [12] for screening of charged

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$^7$ a free electron gas is considered.
impurities in semiconductors. The expression is also given in Appendix C (equation (C.14)). If the electron Fermi wavelength $\lambda_F$ is comparable to the screening distance $R$, the Thomas-Fermi approach is not valid. In that case a more sophisticated theory is needed.

The screening distance $R$ can be calculated using expression (C.14) in Appendix C as derived by Dingle [12]. Putting in the values as tabulated in appendix A, we find for a GaAs sample with Si doping concentration $6 \times 10^{23} \text{m}^{-3}$ a value of $R$ is 5.43 nm.\(^8\) Using the free electron dispersion relation $E_F = \hbar^2 k_F^2 / 2m_e$ (with $k_F = 2\pi / \lambda_F$ the electron Fermi wave vector, $\lambda_F$ the electron Fermi wavelength, $m_e = 0.067m_0$ the effective electron mass), and putting in the bulk value for the Fermi energy $E_F = 0.0385$ eV, we find $\lambda_F = 24.1$ nm. We see $\lambda_F$ is larger than $R$ and therefore Thomas-Fermi approach is not valid. Both values for $\lambda_F$ and $R$ are calculated here using bulk parameters. At the surface $\lambda_F$ and $R$ will be somewhat different. The Fermi energy is larger due to tip induced band bending. At the surface, the Fermi energy is increased by the electrostatic surface potential $\phi$. From Fig. 4.3(a) we determine a value of about -0.4 V for $\phi$ at a sample voltage of -2.2 V. Using again the dispersion relation for free electrons and using $E_F = 0.4$ eV, we find $\lambda_F = 7.5$ nm. The screening distance $R$ at the surface we expect to be a little bit smaller than in the bulk due to the accumulation of charge carriers. In total, this does not change the situation. Screening distance $R$ and electron Fermi wavelength $\lambda_F$ are still comparable in size and Thomas-Fermi approach is not valid.

In Appendix D the screened potential of a point charge in a free electron gas is calculated with no extra conditions on the lateral extension of the potential. This is the random phase approximation (RPA) also known as the Lindhard method. In equation (D.6), we can see the screened electrostatic potential is not a smoothly decaying function with distance from the centre of the particle but shows oscillations. At a long distance the period of the oscillations is equal to $\lambda_F / 2$, with $\lambda_F$ the electron Fermi wavelength. The amplitude decays as $1/r^3$ at $T = 0$. These oscillations are known as Friedel oscillations and were first derived by Friedel [13] in 1958.

In section 4.1 we described the observation of concentric rings in the filled state image on the GaAs(110) surface. We will show now that the feature can be ascribed to oscillations in the charge density (Friedel oscillations) around a subsurface postioned positively charged Si donor. In section 4.1 we already discussed that Johnson et al. [3] and Zheng et al. [14, 15] proved the hillock features in the surface electronic structure are induced by

\(^8\)The Fermi-Dirac integrals have been calculated with Maple.
doping atoms positioned below the surface. They showed the concentration of hillock features in a given volume is equal to the doping concentration. We will now first explain why the Si atom is positively charged with respect to its environment.

For Si it is known that it has four valence electrons and can be a substitute for the Ga (valence 3) atom as well as the As (valence 5) atom in the GaAs III-V compound. The substitutional $\text{Si}_{\text{Ga}}$ has a charge equal to $+4e$ and contributes 4 valence electrons, one extra electron with respect to the gallium atom. The substitutional $\text{Si}_{\text{Ga}}$ therefore is a donor atom and positive when it is ionised. The substitutional $\text{Si}_{\text{As}}$ also has charge $+4e$ and contributes 4 valence electrons, one electron less than the arsenic atom. The substitutional $\text{Si}_{\text{As}}$ therefore is an acceptor atom and negative when ionised. Our GaAs substrate is an n-type material. From literature [16], it is known that (depending on growth conditions) more than 80% of the substituted Si atoms will act as donor atoms and only a few percent as acceptor atoms. Since a majority of the observed features are comparable to the feature shown in Fig. 4.1(b), we attribute this feature to the influence of a substitutional $\text{Si}_{\text{Ga}}$ donor atom.

We will now explain why it is reasonable to believe all the donor atoms are ionised. Therefore we will first calculate the binding energy of the electron to the donor. One can calculate this binding energy in a relative simple way by using the result for the binding energy of the electron in a hydrogen atom following Bohr\(^9\). Using the correct electron effective mass ($m_n = 0.067m_0$) and relative permittivity ($\varepsilon_s = 12.5$) we find for the binding energy a value of 6 meV. The Bohr radius ($r_B$) is equal to 9.9 nm. The binding energy has also been calculated from data obtained in photoconductivity experiments [18]. For the binding energy of an electron in a Si donor, incorporated in GaAs, a value of 5.839 meV is found. By looking at these values one may conclude that at 4.2 K ($kT = 0.4$ meV) most of the donor atoms will not be ionised but neutral, since $kT \ll E_0$. This, however, is not true because of the following argument. From the doping concentration one can calculate the average volume which possesses exactly one doping atom. If we simply approximate these volumes by spheres with radius $r_s$, we can write for the average volume per doping atom: $\frac{4}{3}\pi r_s^3 = 1/(6 \times 10^{17} \text{cm}^{-3})$, with $6 \times 10^{17} \text{cm}^{-3}$ the doping concentration of the sample. By solving this expression, we find $r_s$ is equal to 7.4 nm. For the Bohr radius, we derived $r_B$.

\(^9\)The following expressions can be derived for the binding energy $E_0$ and first Bohr radius $r_B$ of an electron in a hydrogen atom: $E_0 = -(m/2\hbar^2) (e^2/4\pi\varepsilon_0)^2$ and $r_B = (4\pi\varepsilon_0\hbar^2/me^2)$ (see reference [17]).
is 9.9 nm. Since \( r_B > r_s \), wave functions of donor electrons do overlap and the localised impurity levels are broadened to impurity bands\(^\text{10}\). The extra electrons of the Si donor atoms are therefore not localised to the individual atoms but free to move inside the impurity band at any temperature, even at low temperatures. The substitutional Si\(_{Ga}\) atoms are therefore not neutral but ionised and so have a positive charge.

In order to observe Friedel oscillations around the positive Si donor atoms, free carriers (electrons) must be present to screen the point charge. These free carriers are only present when the Fermi level at the surface is positioned inside the conduction band. Due to tip induced band bending this is only true, as shown in Fig. 4.3, when the applied sample voltage is negative and larger than the work function difference between the metal and semiconductor. This is indeed true for the measurement shown in Fig. 4.1, where a bias voltage of -2.2 V is applied to the sample and therefore Friedel oscillations are to be expected around the positively charged Si donor atom.

In the empty state image no Friedel oscillations can be observed. The empty state image is measured at a sample voltage of +1.0 V. At this voltage, as can be seen in Fig. 4.3, the semiconductor surface is depleted from free charge carriers. The positive Si atom, therefore, is not screened. The hillock feature in the surface electronic structure is the result of the bare Coulomb potential\(^\text{11}\).

We now like to compare the experimental determined line-profile in Fig. 4.1(f) with a model calculation. Since the charge density oscillations are close to the point charge we cannot use the expression determined in Appendix D which is only valid in approximation for \( r \rightarrow \infty \). Therefore, we have to use the more exact solution for the distribution of charge around a point charge. We will present two models. In the first model we use the results from Langer \textit{et al.} [20] who numerically calculated the charge density around a point charge in a high density electron gas applying the Hubbard model\(^\text{12}\). From the charge density we can derive the local density of states (LDOS) around the point charge at the surface. This is converted to a corrugation picture which shows the local deflection of the tip when

\(^\text{10}\)Proof for the existence of impurity bands which do overlap the conduction band follow directly from electrical conductivity measurements as done by O. V. Emel'yanyenko \textit{et al.} [19]. They found that n-type GaAs samples with doping concentration higher than \( 4 \times 10^{17} \text{ cm}^{-3} \) are in a metallized state. That means the carrier concentration is independent of temperature and the electron gas is degenerate.

\(^\text{11}\)In section 4.5 these features will be discussed more thoroughly.

\(^\text{12}\)The Hubbard model introduces a correction factor to the RPA and is regarded as an improvement.
moving across the screened point charge. In the second model, published by Kobayashi [21], the corrugation is calculated by deriving the wave functions of electrons scattered by a screened Coulomb potential (Thomas-Fermi) located near a surface. Both models are discussed individually and compared with each other.

4.3.2 Model 1

In this model the deflection of a STM tip is calculated when scanning across a screened fixed point charge positioned at a certain depth $d$ below the surface. We make use of the results obtained by Langer et al. [20]. The model concerns a quantum mechanical electron gas in its ground state with a uniform positively charged background, so that the whole system is neutral. The system is infinitely large and therefore no boundary conditions are included. Into this system a fixed charge is inserted. Langer et al. presented the numerical derived results for four different electron densities. The electron densities are $7.5 \times 10^{21} \text{cm}^{-3}$, $1.8 \times 10^{22} \text{cm}^{-3}$, $6.0 \times 10^{22} \text{cm}^{-3}$ and $4.8 \times 10^{23} \text{cm}^{-3}$. The model, however, is also valid for different electron densities. The result of the calculations is an oscillatory displacement of charge density ($\Delta \rho$) with distance ($r$) from the charge. (The displaced charge density ($\Delta \rho$) is defined as the number of electrons (holes) displaced per unit volume due to the presence of a fixed point charge.) For $r \to \infty$ the displaced charge density decays like $1/r^3$ and the period becomes equal to $\lambda_F/2$, in agreement with the RPA results derived in Appendix D. At small distances from the charge no single period can be indicated. The first minimum in the displaced charge density ($\Delta \rho$) is around $r = 3/k_F$. With increasing electron density this minimum is shifted to larger distances. The amplitude of the displaced charge density is decreasing with increasing electron densities.

The electron densities used in the calculations are high in comparison with the doping concentration of the studied semiconductor material. Due to tip induced band bending, however, the electron density increases at the semiconductor surface. Using Gauss law we can calculate the surface electron density given the electric field at the surface. We already calculated the electric field in section 4.3. For a sample voltage of $-2.2 \text{V}$ we find an electric field at the semiconductor surface of $1.1 \times 10^8 \text{Vm}^{-1}$. This corresponds to a surface electron density of $7.5 \times 10^{10} \text{cm}^{-2}$ or in 3-dimensions an electron density of $2.1 \times 10^{19} \text{cm}^{-3}$. This electron density is higher than the doping concentration in the bulk of the sample ($6 \times 10^{17} \text{cm}^{-3}$), but still
smaller than the electron densities used in the calculations. To compare the theoretical calculations with our experimental data we will use the results derived for the lowest electron density \((7.5 \times 10^{21} \text{ cm}^{-3})\). This still is a factor of 100 higher than the estimated electron density at the semiconductor surface. In the calculations, the position of the first minimum will therefore be overestimated and the amplitude underestimated.

The numerically determined values for the displaced charge density \((\Delta \rho)\) as a function of distance \((r)\) from the point charge for an electron density of \(7.5 \times 10^{21} \text{ cm}^{-3}\) are given in column 1 and 5 of the table in Appendix E. These values are directly taken from the paper of Langer et al. and given in units of \(k_F\). In our experiment, however, the point charge is not positioned in a homogeneous, infinitely large system. The point charge is positioned at a depth \(d\) below a surface. In this model we like to compare the experimental results with calculations assuming the surface has no influence at all on the distribution of charge around the point charge. This is probably not true, but a good starting point. The displaced charge density at the surface as a function of \(r_\parallel\), with \(r_\parallel = \sqrt{r^2 - d^2}\), is then simply calculated by making a cut through the spheres of constant displaced charge density at a distance \(d\) from the centre. This is schematically shown in Fig. (E.1) in Appendix E. The results for different depth \(d\) are given in column 2, 3 and 4 together with column 5, in Appendix E.

Based on the model of Tersoff and Hamann\,[22], Lang\,[23] proposed the following simplified expression to calculate the tunnel current in a STM junction:

\[ I_t \propto \int_0^e dE \text{LDOS}_t(E - V)LDOS(E)e^{-2\kappa}, \quad (4.8) \]

with \(\text{LDOS}_t\) and \(\text{LDOS}\), respectively, the local density of states at the surface of the tip and sample, \(z\) the distance between tip and sample, \(V\) the applied bias voltage and \(\kappa = [(2m/\hbar^2)W]^{1/2}\) the inverse decay length for electrons in vacuum with \(W\) the height of the tunnel barrier. In this model, the two electrodes (tip and sample) are assumed to be planar and are described as independent systems. This formalism is known as the independent electrode approximation. Wave functions (which quantum-mechanically describe the electrons) are calculated, therefore, separately for each electrode. The tunneling probability for these wave functions is calculated following the expression derived by Bardeen\,[24] and is assumed to be dependent on the energy and not on the direction of the wave vectors. The tunnel barrier is assumed to be a square (with height \(\phi\)).

Equation 4.8 can be simplified further by assuming that the local density
of states at the tip (LDOS$_t$) is constant and that only the electrons with energy $E$ participate in the tunnel process. In that case, we derive for $I_t$ as a function of distance $r$:

$$I_t(r) \propto LDOS(r, E) \exp(-2\kappa z),$$  \hspace{2cm} (4.9)

In order to find an expression for the deflection ($\Delta z$) of a STM tip when scanning across a screened subsurface point charge, we first have to find an expression for the $\Delta LDOS$ at the surface. This we can calculate from the in Appendix D derived displaced charge density, using the following arguments. For $r \to \infty$ the expression for the displaced charge density is

$$\Delta \rho(r) \propto \frac{\cos(2k_F r)}{r^3},$$  \hspace{2cm} (4.10)

(see equation (D.6)\textsuperscript{13}). We know the LDOS and the charge density $\rho$ at $T = 0$ are related by

$$\rho(r, k_F) = \int_0^{k_F} LDOS(r, k) dk.$$  \hspace{2cm} (4.11)

Combining expressions 4.10 and 4.11 gives

$$\Delta LDOS(r, k_F) \propto \frac{\cos(2k_F r)}{r^2} = r \cdot \Delta \rho(r).$$  \hspace{2cm} (4.12)

This expression gives that $\Delta LDOS$ can be calculated in assumption from the displaced charge density $\Delta \rho$ by multiplying $\Delta \rho$ by the distance $r$. We use this expression in our model. The results are printed in column 6 of the table in Appendix E, where the values in column 1 and 5 are multiplied with each other. The $\Delta LDOS$ is given in arbitrary units.

From $\Delta LDOS$ we can calculate the deflection $\Delta z$ of the tip by using expression 4.9. Rewriting this expression gives

$$z(r) \propto \frac{1}{2\kappa} \ln \left( \frac{LDOS(r)}{I_t} \right)$$  \hspace{2cm} (4.13)

$$z(\infty) \propto \frac{1}{2\kappa} \ln \left( \frac{LDOS(\infty)}{I_t} \right).$$  \hspace{2cm} (4.14)

\textsuperscript{13}In principle the electrostatic potential $\Delta \phi$ is given in equation (D.6) in Appendix D and not $\Delta \rho$. But it easy to show that both constants are linearly related to each other. For metals it is known that $\rho = k_F^2/(3\pi^2)$. Differentiating by the Fermi energy $E_F$ gives $\Delta \rho \propto (k_F/\pi^2)\Delta E_F$ and so $\Delta \rho \propto (k_F/\pi^2)\Delta \phi$. 

Since the STM pictures are measured with constant current $I_t$, we derive

$$\Delta z(r) \propto \frac{1}{2\kappa} \ln \left( \frac{LDOS(r)}{LDOS(\infty)} \right), \quad (4.15)$$

where $LDOS(r) = LDOS(\infty) + \Delta LDOS(r)$, with $LDOS(\infty)$ the $LDOS$ from the background and $\Delta LDOS(r)$ the change in $LDOS$ due to the point charge. Since, $\Delta LDOS(r) \ll LDOS(\infty)$, we derive

$$\ln \left( \frac{LDOS(r)}{LDOS(\infty)} \right) \propto \Delta LDOS(r), \quad (4.16)$$

and we get:

$$\Delta z(r) \propto \Delta LDOS(r). \quad (4.17)$$

The deflection of the tip $\Delta z$, therefore, is in assumption proportional to $\Delta LDOS$.

We now have all the ingredients to convert the numerically determined displaced charge density ($\Delta \rho$) by Langer et al. to a picture which gives the deflection of a tip ($\Delta z$) when scanning across a point charge positioned at depth $d$. In Fig. 4.4(a) the displaced charge density $\Delta \rho$ is plotted as a function of distance $r$ together with the calculated deflection $\Delta z$ of the tip for $d = 0$, with $d$ the depth of the point charge. These data are tabulated in columns 1, 5 and 6 in Appendix E. At zero distance ($r = 0$) the displaced charge density shows a maximum. The first minimum is around $r = 3/k_F$. One can see the amplitude of the oscillations decays less rapidly for $\Delta z$ as it does for $\Delta \rho$. This immediately follows from the calculations where the $\Delta LDOS$ is determined by multiplying the charge density $\Delta \rho$ with $r$.

In Fig. 4.4(b) we plot the deflection of the tip $\Delta z$ versus distance $r_{||}$ (see Fig. (E.1) in Appendix E) as calculated for point charges at a depth $d$, equal to $0.1/k_F$, $1.9/k_F$, and $3.1/k_F$, as straight lines. From these curves it is clear that in the centre of the feature dependent on depth $d$ a maximum or minimum can be present. If $d > 3/k_F$ the centre shows a minimum. With increasing depth, starting at zero, the distance $r$ of the minimum ($r_{min}$) is decreasing. In the same figure we have plotted the experimental derived line-profile as shown in Fig. 4.1(f) as a full drawn line (—). The x-scale at the top and the y-scale on the left of the graph belong to the curve. One can see the curve fits best to the calculation belonging to the impurity at depth $1.9/k_F$. Both x-scales at the bottom and top coincide when $k_F$ is equal to $1 \times 10^9 \text{m}^{-1}$. For this $k_F$ the depth is equal to 1.9 nm and the Fermi energy at the surface is $0.57 \text{eV}$ (using the dispersion relation for free electrons).
Figure 4.4: (a) $\Delta \rho$ (following Langer et al. [20]) and $\Delta z$ versus $r$. The numbers are tabulated in Appendix E, columns 1, 5 and 6. (b) Calculated $\Delta z$ versus $r_{\parallel}$ for point charges positioned at depth $d$ is 0.1/$k_F$, 1.9/$k_F$ and 3.1/$k_F$, respectively. The experimental derived line-profile is given as a drawn line (---).
These are reasonable numbers as discussed in section 4.2.1. The results of this model will be discussed in detail in section 4.3.4.

### 4.3.3 Model 2 (Kobayashi)

In this model Kobayashi [21] calculated the wave functions for a subsurface screened Coulomb (Yukawa) potential. The screened Coulomb potential is given by

\[ V(r) = f_0 \frac{e^{-k_0 r}}{r}, \quad (4.18) \]

with \( f_0 \) the strength of the scattering potential and \( k_0 \) the inverse of the screening length \( R \). The centre of the potential is positioned at a distance \( d \) below the surface of a semiconductor material. No other atomic potentials are assumed in the model. At the surface, an interface exists between semiconductor and vacuum. Here, the potential makes a step. The step height is equal to the work function of the semiconductor material. A schematic of the model is plotted in Fig. 4.5.

To find the wave functions, the Kobayashi model decouples the z-direction from the plane parallel to the surface. The wave functions (\( \Psi \)) are solved exactly by the recursion-transfer-matrix (RTM) method. Analytical expressions for wave functions are found by using perturbation theory. The results are used for calculating the LDOS as

\[ LDOS(r, E) = \frac{2k}{(2\pi)^3} \int_{k_z > 0} |\Psi|^2 d\Omega, \quad (4.19) \]
where $\Omega$ is the solid angle. The tunneling current is approximated by the LDOS, comparable to equation 4.9. Since the LDOS is proportional to $\exp(-2\kappa z)$, with $\kappa = [(2m/\hbar^2)\phi]^\frac{1}{2}$ and $z$ is tip sample distance, the deflection of the tip can be calculated as

$$\Delta z(r) \propto \frac{1}{2\kappa} \ln \left( \frac{\text{LDOS}(r)}{\text{LDOS}(\infty)} \right),$$

(4.20)

equal to expression 4.15 in the previous section.

In discussing the results two regimes are considered for $k_0 \gg k_F$ and $k_0 \ll k_F$, with $k_0$ the inverse of the screening length $R$. When $k_0 \gg k_F$ Friedel oscillations are obtained. For $r \to \infty$ the oscillation period is equal to $\pi/k_F$, in agreement with the results derived in Appendix D. The corrugation amplitude measured by STM in the centre of the ring structure is calculated as a function of impurity depth. An oscillating behaviour is found for this corrugation amplitude. For a shallow impurity, the amplitude is found to increase with depth below the surface. A maximum is reached at $d \approx 1/k_F$. Beyond this value the amplitude is decreasing and can even become negative, with respect to the background level. For $k_0 \ll k_F$ no Friedel oscillations are
obtained. This is in agreement with the result obtained by using Thomas-Fermi approximation in Appendix C, where the scale of the potential is much larger than the electron Fermi wavelength.

In Fig. 4.6 the deflection of the tip is plotted as calculated numerically by Kobayashi [21] together with the measured line-profile from Fig. 4.1(f). In the calculation the following values are used: \( k_F = 4.5 \times 10^8 \text{ m}^{-1} \) (this corresponds to a Fermi energy of 0.12 eV using the dispersion relation for free electrons), \( R = 1/k_0 = 1.3 \text{ nm} \), \( d = 2.2 \text{ nm} \) and a work function \( W = 4 \text{ eV} \). Again the numbers used are reasonable and the calculated curve describes the experimental derived line-profile quite well.

### 4.3.4 Discussion

Before discussing the results of model 1 and 2, it is important to understand differences and resemblances between the two models. The model by Kobayashi gives more exact results, since in calculating the deflection of the tip the exact numerically determined wave functions are used for the model described in Fig. 4.5. In model 1 the numerical values for the wave functions as determined by Langer et al. are not known, only the values for the displaced charge density. Therefore assumptions are made to derive the LDOS and deflection of the tip.

Apart from this, there is an essential difference in how the problem is described. In model 1 the problem is described in terms of screening. The positive charge is surrounded by electrons which screen out the electric field. Since the electrostatic potential from the positive charge is comparable to the electron Fermi wavelength the charge density near the point charge shows oscillations, so does the LDOS which in approximation is measured by STM. In model 2 the problem is described in terms of scattering theory. A screened Coulomb potential (Thomas-Fermi) is present in the vicinity of a surface and electron wave functions are scattered by this local potential and the surface plane. The LDOS are determined by integrating the square of the wave function at each position over all possible incident angles. These are two different approaches of the same problem. In both models the heart of the problem is solving Schrödinger’s equation in the presence of a local point charge, in order to find the correct wave functions. The real difference in both models, however, is found in the way how electron-electron interactions are incorporated. In model 1 Schrödinger’s equation is solved for the total electrostatic potential, arising from both the external charge and the charge density it induces in the electron gas. The problem therefore is solved self-consistently, which includes electron-electron interactions. In
model 2 Schrödinger's equation is solved, by using the screened Coulomb potential, following the Thomas-Fermi model. Electron-electron interactions are included by incorporating the wave functions which are reflected by the surface. Only by including the reflected waves can oscillations in the LDOS be found [21]. This is the most important and essential difference between the two models.

Another difference, apart from the mathematical techniques used, is that in model 1 the Schrödinger equation is solved for a homogeneous infinitely large environment, while in model 2 the wave functions are first decoupled in components parallel ($r_\parallel$) and perpendicular ($z$) to the surface, subsequently, and Schrödinger's equation is solved including the presence of a surface. In this way also the depth of the impurity is incorporated by replacing $z$ by $z + d$.

Also resemblances exist between the two models. In calculating the deflection of the tip in both models the tunnel current is taken proportional to the LDOS following Tersoff and Hamann [25]. Another resemblance and important simplification in both models is that no space charge (band bending) region is included. Both models discuss the situation where the electrostatic potential inside the semiconductor is flat apart from the present Coulomb potential. This of course is not true as discussed in section 4.2, because of the effect of tip induced band bending. Great influences may be expected from this accumulation layer on the charge density, since the width of this layer is comparable to the range of the Coulomb potential. We will now continue in discussing the results of the two models individually.

In Fig. 4.4(b) both the theoretical result following model 1 together with the experimentally derived line-profile in 4.1(f) are plotted. In spite of the crude assumptions made, the model describes the measurement reasonably well. As mentioned before, the amplitude of the calculated curve is given in arbitrary units. Therefore, the calculated peak amplitude at $r = 0$ is normalised to the experimental value. The model gives the positions of the different maxima and minima and describes the decay of the oscillations. From the figure one can see the decay of the oscillation is in good agreement with the measurement. The position of the second maximum, however, is too close to the centre in comparison with the measurement. Quantitatively, a value of $1 \times 10^9 \text{m}^{-1}$ is found for $k_F$, which corresponds to a Fermi energy of 0.57 eV at the surface and an impurity depth of 1.9 nm. The value for the Fermi energy is reasonable only when an electrostatic surface potential ($\phi_s$) induced by tip induced band bending is included (although in the model no space charge region is assumed). Concerning the depth, it is expected, an impurity atom still can be seen at the surface when it is positioned at
a depth equal to about $\lambda_F/2$, with $\lambda_F$ the electron Fermi wavelength. For $k_F = 1 \times 10^9 \text{ m}^{-1}$, we derive $\lambda_F/2 = 3.1 \text{ nm}$. This value is beyond the value of $1.9 \text{ nm}$\textsuperscript{14}. Johnson et al. [3] and Zheng et al. [14, 15] recognized in their STM measurements performed at room-temperature the influence of doping atoms positioned in the first to sixth layer below the surface. This corresponds to a maximum depth of $1.2 \text{ nm}$. This value is smaller than the value found by us ($\sim 3.1 \text{ nm}$). This will be commented in section 4.7.

In Fig. 4.6 the experimental line-profile from 4.1(f) is plotted together with a calculated line-profile following model 2. The numbers put in are: $k_F = 4.5 \times 10^8 \text{ m}^{-1}$ which corresponds to a Fermi energy of $0.12 \text{ eV}$, screening distance $R = 1.3 \text{ nm}$, $d = 2.2 \text{ nm}$ (depth of the donor atom) and $W = 4.0 \text{ eV}$ (work function). These are reasonable values for our sample and comparable to the values found in model 1. The screening distance is perhaps a little bit small (compare with the bulk value of $5.43 \text{ nm}$), but not unreasonable because of the accumulation of charge at the surface.

### 4.4 Filled state images

In this section we study the influence of bias voltage and set-point current on the oscillation period and amplitude of the dopant induced features as observed in the filled state images. By counting the number of induced features in a certain surface area, we make an estimation for the maximum depth an impurity atom can be positioned and still be observed at the surface by STM. Remember that all the measurements are performed at $4.2 \text{ K}$.

#### 4.4.1 Bias voltage

In Fig. 4.7 eight pictures are shown of a same surface area measured at different sample voltages and set-point currents. The doping concentration of the sample is $6 \times 10^{17} \text{ cm}^{-3}$. The sample is cleaved \textit{in situ} at $4.2 \text{ K}$. For the moment we will concentrate on the pictures (a) to (d) which are measured at the same set-point current but with different sample voltage. The set-point current is $100 \text{ pA}$. The sample voltages for picture (a) to (d) are respectively $-3.0 \text{ V}$, $-2.5 \text{ V}$, $-2.25 \text{ V}$ and $-2.0 \text{ V}$. In the pictures four dopant in-

\textsuperscript{14}In section 4.4.3 we discuss another way for determining the maximum depth an impurity atom can be positioned and still be observed at the surface.
Figure 4.7: Eight STM images of the same surface area (34.7 × 34.7 nm²) measured on the 6 × 10¹⁷ cm⁻³ Si doped GaAs(110) surface. Different set-point voltages and currents are used as noted in the insets. Indicated are tunnel current and bias sample voltages.
duced features are visible, which are numbered 1, 2, 3, and 4, respectively. The features visible in each image (a) to (d) have different amplitudes and sizes. This is attributed to Si atoms positioned in different subsurface layers and will be explained in section 4.4.3. The size is quantified by the distance between the centre and the first minimum of the feature \( r_{\text{min}} \). The amplitude \( A \) is defined as the deflection of the tip in the centre of the feature \( \Delta z(r = 0) \) with respect to the background level. The background level is determined by the deflection of the tip at a distance \( \gg r_{\text{min}} \) from the feature \( \Delta z(r \to \infty) \). It will be shown that the amplitude and feature size increase with lowering voltage. In order to make quantitative analysis of the amplitude \( A \) and size \( r_{\text{min}} \) for the different features at different bias voltage, the average line-profile through each feature is calculated. This is done by first filtering out the atomic lattice (described in section 4.1) and next averaging each feature over 360 degrees.

In Fig. 4.8 four of these rotationally averaged line-profiles through feature 1 are plotted. They are measured respectively at -3.0 V, -2.5 V, -2.25 V and -2.0 V. From this figure it is clear that both the amplitude \( A = \Delta z(0) \) and the size \( r_{\text{min}} \) increase with decreasing voltage. Values determined for \( V_{\text{sample}} \), amplitude \( A = \Delta z(0) \) and \( r_{\text{min}} \) are given in table 4.4.1. The accuracy of the amplitude \( A \) is limited by the accuracy at which the background level can be determined and is approximately \( \pm 0.01 \text{ nm} \) for the line-profiles recorded at -3.0 V, -2.5 V and -2.25 V. At a sample voltage of -2.0 V features show overlap with each other (see Fig. 4.7(d)) and the background level is determined less accurately, approximately \( \pm 0.02 \text{ nm} \). The accuracy of \( r_{\text{min}} \) is approximately \( \pm 0.2 \text{ nm} \). The functional dependence of \( r_{\text{min}} \) and amplitude \( A \) is plotted as a function of sample voltage in respectively Fig. 4.9 and 4.10.

In Fig. 4.9(a), \( r_{\text{min}} \) is plotted for the features 1 to 4 as a function of sample voltage. The values are taken from table 4.4.1. Between the different discrete values a straight dashed line is plotted to guide the eye. In this figure one can see that \( r_{\text{min}} \) increases with decreasing bias voltage for all features. The reason for this can be understood from the argument of tip induced band bending. When decreasing the bias voltage between tip and sample, bands are not pushed as far down and the surface electrostatic potential is decreased. This corresponds to a decrease in \( k_F \) and therefore an increase in the distance \( r_{\text{min}} \) as derived in model 1 and 2, discussed in

\(^{15}\)The feature above the dopant induced feature numbered 2 we ascribe to the influence of an adsorbed oxygen atom and will be further discussed in chapter 6. At the top of the empty state image in Fig. 4.7(h) the surface is destroyed, probably by making mechanical contact between the tip and sample.
Figure 4.8: Rotationally averaged line-profiles through feature 1 (see Fig. 4.7) measured respectively at a sample voltage of -3.0 V, -2.5 V, -2.25 V and -2.0 V.

<table>
<thead>
<tr>
<th>$V_{sample}$ (V)</th>
<th>$A = \Delta z(0)$ (nm)</th>
<th>$r_{min}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3</td>
<td>0.08 ± 0.01</td>
<td>1.9 ± 0.2</td>
</tr>
<tr>
<td>-2.5</td>
<td>0.09 ± 0.01</td>
<td>2.4 ± 0.2</td>
</tr>
<tr>
<td>-2.25</td>
<td>0.13 ± 0.01</td>
<td>3.3 ± 0.2</td>
</tr>
<tr>
<td>-2.0</td>
<td>0.17 ± 0.02</td>
<td>5.1 ± 0.2</td>
</tr>
</tbody>
</table>

Table 4.1: Tabulated values for $V_{sample}$, amplitude $A = \Delta z(0)$ and $r_{min}$ for the rotationally averaged line-profiles in Fig. 4.8.
section 4.3\textsuperscript{16}.

Further, one can see that the increase in $r_{\text{min}}$ grows stronger than linear with decreasing bias voltage. This is best demonstrated by features 1 and 2. With model 1 and 2, in the previous section, we can derive a functional behaviour between $r_{\text{min}}$ and sample voltage, by making use of the following arguments. The distance $r_{\text{min}}$, as found in the previous section, is proportional to $1/k_F$. So,

$$k_F \propto \frac{1}{r_{\text{min}}} \quad (4.21)$$

By changing the bias voltage the electrostatic surface potential ($\phi$) is changed due to tip induced band bending. In section 4.2, we showed the electrostatic surface potential varies more or less linearly with sample voltage in the region of accumulation, thus $V_{\text{sample}} \propto \phi$. The electrostatic surface potential ($\phi$) shifts the conduction band edge energy $E_C$ at the surface to $E_C + \phi$. The Fermi energy which is determined with respect to the conduction band edge energy $E_C$, therefore increases at the surface by the same value $\phi$. Since the Fermi energy in the bulk is much smaller than the electrostatic surface potential $\phi$, the Fermi energy at the surface can be approximated by $\phi$, thus $E_F = \phi$. Using the dispersion relation for free electrons ($E_F = \hbar^2 k_F^2/2m_n$), we find:

$$V_{\text{sample}} \propto k_F^2. \quad (4.22)$$

Using the dependence of equation 4.21 gives,

$$V_{\text{sample}} \propto \frac{1}{r_{\text{min}}^2}. \quad (4.23)$$

In Fig. 4.9(b) we have checked this relation between $V_{\text{sample}}$ and $r_{\text{min}}$, by plotting $1/r_{\text{min}}^2$ as calculated from Fig. 4.9(a) versus $V_{\text{sample}}$ for all four features. Through the discrete data points a least square fit is plotted. One can see that the data points are indeed positioned approximately on a straight line.

We also studied the dependence between the amplitude $A = \Delta z(0)$ as a function of $V_{\text{sample}}$. The data are extracted from the rotational averaged line-profiles and plotted in Fig. 4.10(a). Straight dashed lines are plotted between the discrete points to show the tendency. From this figure it is

\textsuperscript{16}This observation strengthens the argument that tip induced band bending indeed plays a role in the experiment and can therefore be used in explaining the difference between the empty and filled state images.
Figure 4.9: (a) $r_{\text{min}}$ versus sample voltage for features 1 - 4. (b) $1/r_{\text{min}}^2$ versus sample voltage. Straight lines are fitted through the different data points.
seen that the amplitude $A$ decreases with increasing bias voltage. This we can understand by the following arguments. The tunnel current as already discussed in the previous section can be approximated by the LDOS at the Fermi level (see expression 4.9). From the bottom of free electron bands, the LDOS as a function of energy $E$ is described by the relation

$$LDOS(E) = \frac{m}{\hbar^2 n^2} \sqrt{\frac{2mE}{\hbar^2}}.$$  \hspace{1cm} (4.24)

The Fermi energy $E_F$ can be approximated by the electrostatic surface potential $\phi$ ($E_F = \phi$), which is proportional (in the region of accumulation) to the applied sample voltage ($V_{sample} \propto \phi$). Therefore, using expression 4.24, we find $LDOS \propto V_{sample}^{1/2}$. The amplitude $A$ is given by the expression

$$A = \Delta z(0) = \frac{1}{2\kappa} \ln \left( \frac{LDOS(0)}{LDOS(\infty)} \right),$$  \hspace{1cm} (4.25)

with $LDOS(0) = \Delta LDOS(0) + LDOS(\infty)$ (see expression 4.15 in model 1 or expression 4.20 in model 2), or in approximation when $\Delta LDOS(0) \ll LDOS(\infty)$,

$$A = \Delta z(0) \propto \frac{\Delta LDOS(0)}{LDOS(\infty)},$$  \hspace{1cm} (4.26)

where $\Delta LDOS(0)$ is the variation in LDOS at zero distance due to the presence of a point charge and $LDOS(\infty)$ is the LDOS of the background given by expression 4.24. If we assume $\Delta LDOS(0)$ to be constant in energy$^{17}$, we see, using expressions 4.26 and 4.24, that the amplitude $A$ varies with $1/\sqrt{E}$. Since, $E_F \propto V_{sample}$, we derive $V_{sample} \propto A^{-1/2}$. Thus, we indeed expect a decrease in the amplitude with increasing sample voltage.

In Fig. 4.10(b) we plotted $1/\sqrt{A}$ versus $V_{sample}$ together with the least square fits. Indeed, an approximately linear behaviour is found between $1/\sqrt{A}$ and $V_{sample}$. In addition to $1/\sqrt{A}$, we have also plotted $1/A$ and $1/A^2$ versus $V_{sample}$ (not shown here). The experimental graphs, however, are not accurate enough to see which functional behaviour is more correct.

$^{17}$This is probably not true. Most probably $\Delta LDOS(0)$ decreases with increasing energy, since high energy electrons will be less influenced by the point charge. Therefore we expect the amplitude $A$ to decay even more rapidly than $1/\sqrt{E}$.
Figure 4.10: (a) Amplitude $A(= \Delta z(0))$ versus sample voltage for features 1 - 4. (b) $1/A^{0.5}$ versus sample voltage. Through the different data points straight lines are fitted.
4.4.2 Tunnel current

In addition to the bias dependence we have also studied the effect of set-point current on the dopant induced features at the surface. In Fig. 4.7(e), (f) and (g) images are plotted which are measured at a same set-point current of 500 pA. The surface area is the same as in the pictures 4.7(a) to (d). The top part of the pictures, however, is removed because the STM was instable at that position, probably because of the presence of some adatoms. Therefore only features 1, 2, and 4 are visible. The sample voltages in Fig. 4.7(e) to (g) are respectively, -3.0 V, -2.5 V and -2.25 V (filled electron states are imaged), the same as in Fig. 4.7(a) to (c). At -2.0 V sample voltage, no stable measurement could be done with a set-point current of 500 pA in this area of the sample. This is ascribed to the reduced tip sample distance, which allows some protrusions at the tip to hit the sample surface during scanning and make the tunneling junction instable. The averaged line-profiles for features 1, 2, and 4 are determined in the same way as described before. These line-profiles are similar in shape than the line-profiles presented in Fig. 4.8. From these line-profiles the amplitude \( A = \Delta z(0) \) and the position of the minimum \( r_{\text{min}} \) is determined. The results are tabulated in table 4.2 and compared with the values derived for the measurements performed at 100 pA, tabulated in table 4.4.1. At -2.25 V sample voltage and 500 pA set-point current, \( r_{\text{min}} \) could not be determined for features 1, 2 and 4, because the features overlap each other.

From the values in this table it is seen that both the amplitude \( A = \Delta z(0) \) and the distance \( r_{\text{min}} \) increase with increasing set-point current. The increase of distance \( r_{\text{min}} \) with set-point current, is in contradiction with what one would expect from the argument of tip induced band bending. Following this argument one would expect a decrease in amplitude \( A = \Delta z(0) \) and the distance \( r_{\text{min}} \) with increasing set-point current. This is shown in the following example. By increasing the set-point current, the tip sample distance decreases. Changing the set-point current from 100 pA to 500 pA, results in a decrease in tip sample distance of approximately 0.07 nm, using expression 4.9 with work function \( W = 4.5 \text{ eV} \). This leads to an increase in the electrostatic surface potential \( \phi \), since the tunnel resistance is reduced and therefore less voltage drops across the tunnel barrier (see also Fig. 4.3(b)).

Assuming a tip sample distance of 0.9 nm at the set-point values -2.5 V and 100 pA and a sample doping concentration of \( 6 \times 10^{17} \text{ cm}^{-3} \), we calculate, using the model presented in section 4.2.1, an electrostatic surface potential of \( \phi = -0.48 \text{ V} \). Reducing the tip sample distance to 0.83 nm, results in an electrostatic surface potential of \( \phi = -0.52 \text{ V} \). The electrostatic surface
4.4 Filled state images

<table>
<thead>
<tr>
<th>Feature</th>
<th>$V_{\text{sample}}$ (V)</th>
<th>$r_{\text{min}}$ (nm)</th>
<th>$r_{\text{min}}$ (nm)</th>
<th>$A = \Delta z(0)$ (nm)</th>
<th>$A = \Delta z(0)$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>current</td>
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<td>100 pA</td>
<td>500 pA</td>
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</tr>
<tr>
<td>1</td>
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<td>0.08 ± 0.01</td>
<td>0.09 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>-2.5</td>
<td>2.4 ± 0.2</td>
<td>2.9 ± 0.2</td>
<td>0.09 ± 0.01</td>
<td>0.09 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>-2.25</td>
<td>3.3 ± 0.2</td>
<td>-</td>
<td>0.13 ± 0.01</td>
<td>0.21 ± 0.02</td>
</tr>
<tr>
<td>2</td>
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<td>2.6 ± 0.2</td>
<td>0.05 ± 0.01</td>
<td>0.05 ± 0.01</td>
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<tr>
<td></td>
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<td>0.06 ± 0.01</td>
<td>0.07 ± 0.01</td>
</tr>
<tr>
<td></td>
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<td>3.8 ± 0.2</td>
<td>-</td>
<td>0.08 ± 0.01</td>
<td>0.31 ± 0.02</td>
</tr>
<tr>
<td>4</td>
<td>-3.0</td>
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<td>4.0 ± 0.2</td>
<td>0.01 ± 0.01</td>
<td>0.02 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>-2.5</td>
<td>4.4 ± 0.5</td>
<td>4.0 ± 0.5</td>
<td>0.02 ± 0.01</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>-2.25</td>
<td>4.9 ± 0.5</td>
<td>-</td>
<td>0.03 ± 0.01</td>
<td>0.21 ± 0.02</td>
</tr>
</tbody>
</table>

Table 4.2: Tabulated results for feature 1, 2 and 4 in Fig. 4.7.

potential therefore increases with 0.04 V. An increase in the electrostatic surface potential $\phi$ of 0.04 V results in an increase of the Fermi energy $E_F$ at the surface of approximately the same value and therefore an increase of the Fermi wave vector $k_F$ (in approximation $E_F = \hbar^2 k_F^2 / 2m_n$). Since, $r_{\text{min}} \propto 1/k_F$ (see expression 4.21), the distance $r_{\text{min}}$ is expected to decrease.

A possible explanation for the observed behaviour can be given by considering the limiting transport velocity of charge carriers inside the semiconductor. In current transport models across Schottky barriers in metal semiconductor contacts, as discussed for example in [4], it is shown that transport is limited by the transmission probability of charge across the barrier and by the transport from the interior of the semiconductor to the interface. In our tunnel junction at negative sample voltage, however, no Schottky barrier is present, since the surface is in accumulation. Since the metal electrode is a sharp tip, a large spreading resistance $R_S$ exist at the semiconductor surface. The magnitude of this resistance can be approximated by the expression [5] $R_S = 1/(2\pi r_0 \sigma)$, with $r_0$ the tip radius, $\sigma$ the conductivity of the sample. For $\sigma = 2 \times 10^2 \Omega^{-1} \text{cm}^{-1}$, and $r_0 = 1 \text{ nm}$, we find $R_S = 8 \times 10^5 \Omega$ (the conductivity $\sigma$ is calculated by the expression $\sigma = n e \mu$, with $\mu = 2.03 \times 10^3 \text{ cm}^2/\text{Vs}$ the electron mobility at 4.2 K of the $6 \times 10^{17} \text{ cm}^{-3}$ GaAs sample, measured by Koenraad et al. from Eindhoven university of technology). The result of a large resistance below the tip is that the Fermi level inside the semiconductor is not linear with respect to distance from the surface but must be described by a quasi-Fermi level, as
Figure 4.11: Schematic electron energy diagram of a metal-semiconductor tunnel junction. At the semiconductor surface the quasi-Fermi level is plotted.

described in the diffusion theory of Wagner, Spenke and Schottky [4]. The quasi-Fermi level drops down towards the surface as schematically plotted in Fig. 4.11. By raising the set-point current, the current flow increases and therefore more collisions occur between electrons at the surface. In this way, the spreading resistance increases and the Fermi level drops further down at the surface which causes a decrease in the wave vector of electrons at the surface. Following this model, therefore, the distance $r_{\text{min}}$ increases with increasing set-point current, which is in agreement with the experimental observations.

4.4.3 Depth

In the previous sections we have discussed four different dopant features in the same surface area at different bias voltage and set-point current. The differences between the features in one scan image we attribute to the fact that the impurity atoms are positioned in different subsurface layers. Johnson et al. [3] and Zheng et al. [14, 15] proved in their measurements that doping atoms positioned at different depth are observed by looking at the amplitude $A = \Delta z(0)$ and the symmetry of the induced features. By putting the amplitudes of the observed features in a histogram, the influence of doping atoms positioned in at least 5 different subsurface layers could be recognised. By looking at the symmetry of the features, they determined whether the doping atoms were positioned in an odd or even subsurface layer.
Figure 4.12: (a) Filled state image measured on the $2 \times 10^{18} \text{cm}^{-3}$ Si doped GaAs(110) surface. Surface area: $100 \times 100 \text{nm}^2$, sample voltage: $-2.0 \text{V}$, set-point current: $50 \text{pA}$. (b) Empty state image of the same surface area as in figure (a) measured at $+1.6 \text{V}$. The six arrows in figure (a) correspond to the arrows in figure (b) and point at the same imperfections. (c) Filled state image of the $6 \times 10^{17} \text{cm}^{-3}$ Si doped GaAs(110) surface. Surface area: $100 \times 100 \text{nm}^2$, sample voltage: $-2.1 \text{V}$, set-point current: $20 \text{pA}$. 
Similar experiments have been performed by us. The amplitudes $A = \Delta z(0)$ of different features were plotted in a histogram. However, no discrete values were found, representing the discrete number of subsurface layers in which the doping atoms are positioned. This we attribute to the fact, that in our measurements the accuracy of the background, which determines the accuracy of the amplitudes, is comparable to the amplitude difference induced by doping atoms positioned in subsequent subsurface layers. Although no discrete values were found, it is clear from the values tabulated in table 4.2, that the amplitudes of the dopant features measured at a single bias voltage are different. Using the results obtained by Johnson et al. and Zheng et al., we may conclude that indeed impurity atoms positioned in different subsurface layers can be observed.

An estimation can be made of the maximum depth at which an impurity atom is positioned and still can be observed at the surface. Therefore we study large scan images in which many features are present. The number of features is a measure of the concentration of doping atoms in a volume equal to: scan area $\times$ depth. If the scan area is large enough the concentration can be approximated by the doping concentration of the sample. In this way the maximum depth can be determined.

This is done for two samples with different doping concentration. In Fig. 4.12 three images are shown. The scan size of all three images is the same; 100 nm $\times$ 100 nm. Fig. 4.12(a) and (b) show images measured on the sample with doping concentration equal to $2 \times 10^{18} \text{cm}^{-3}$. Fig. 4.12(c) is measured on the lower doped GaAs sample at $6 \times 10^{17} \text{cm}^{-3}$. Fig. 4.12(a) shows a filled state image measured at -2.0 V. Fig. 4.12(b) shows an empty state image of the same surface area as in Fig. 4.12(a) measured at +1.6 V. Fig. 4.12(c) is measured at -2.1 V. Some of the features in Fig. 4.12(a) are changed into local depressions in Fig. 4.12(b) (six of these features are pointed out by arrows in the figure). These features are induced by negatively charged impurities on top of the surface and will be discussed in chapter 6. Excluding these features, the number of Si induced features was counted in the images in Fig. 4.12(a) and (c).

<table>
<thead>
<tr>
<th></th>
<th>Fig. 4.12(a)</th>
<th>Fig. 4.12(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>doping concentration</td>
<td>$2 \times 10^{18} \text{cm}^{-3}$</td>
<td>$6 \times 10^{17} \text{cm}^{-3}$</td>
</tr>
<tr>
<td>number of features</td>
<td>60</td>
<td>32</td>
</tr>
</tbody>
</table>

Putting in the scan area and the doping concentration we derive a maximum depth of 3 nm (15 subsurface layers) and 5.3 nm (26 subsurface layers) for Fig. 4.12(a) and Fig. 4.12(c), respectively. The maximum depth is higher for the low doped sample than it is for the high doped sample. This can be
understood, since screening in the lower doped sample is less effective. Using expression (C.14) in appendix C, we derive for the Thomas-Fermi screening length $R$ the values 4.6 nm and 5.4 nm respectively for the samples with doping concentration $2 \times 10^{18}$ cm$^{-3}$ and $6 \times 10^{17}$ cm$^{-3}$. The maximum depth derived for the $6 \times 10^{17}$ cm$^{-3}$ doped sample (5.3 nm) is in good agreement with the Thomas-Fermi screening length ($R = 5.4$ nm). For the $2 \times 10^{18}$ cm$^{-3}$ doped sample a maximum depth of 3 nm was derived which is smaller than the Thomas-Fermi screening length ($R = 4.6$ nm). One should, however, remark that the number of features in Fig. 4.12(a) may have been underestimated (about 10%). This is because features overlap with each other due to the high concentration and therefore may no longer be recognisable as individual features (especially the less intense features). This is not the case for Fig. 4.12(c). In this figure the doping concentration is more than three times smaller and the features hardly overlap. From this picture, the depth can be determined more precisely. A reasonable estimate is that the depth should be comparable to the radius of the feature observed at the surface. This is indeed true for the $6 \times 10^{17}$ cm$^{-3}$ doped sample where the radius of the features is found to be typically 6 nm (compare with 5.3 nm).

By looking in table 4.2, we can see that when the feature in a scan image becomes weaker ($A$ decreases), the distance $r_{min}$ increases. The question arises which features belong to Si atoms positioned close to the surface and which to Si atoms further separated from the surface? To answer this question we will have a look again at the models presented in the previous section, section 4.3. Both models predict a decrease of $r_{min}$ with increasing depth of the Si atom. For certain depth the distance $r_{min}$ even goes to zero. Both models, however, do not agree concerning the dependence between the amplitude $A$ and the depth of the Si atom. Following model 1 the amplitude should decrease with increasing depth. However, the second model by Kobayashi predicts that the amplitude should first increase with depth, reaching its maximum at depth $1/k_F$, and then decrease to become finally negative. Our experimental observations (increasing amplitude $A$ with decreasing distance $r_{min}$), can only be explained with Kobayashi’s model. Following this model the experimentally observed features are induced by Si atoms at a depth smaller than $1/k_F$ and the amplitude of the features increases with increasing depth of the Si atoms. In section 4.5.3 we will debate this proposition.
4.5 Empty state images

In this section we discuss the Si induced features observed in the empty state images of the GaAs(110) surface. As has been shown in section 4.1 the feature in the empty state image is different from the feature in the filled state image. This is also explained by the effect of tip induced band bending. As calculated in section 4.2 the surface is depleted from free charge carriers when applying a positive sample voltage. Therefore no screening effects are to be expected in the scan images around the positively charged Si atoms. Only the effect of the bare Coulomb potential is visible. The result is a hillock feature in the surface electronic structure which decays gradually with distance from the centre. In subsection 4.5.1 we calculate the influence of the Coulomb potential on the local density of states by using the results of Kobayashi (section 4.3.3) and compare this with our experimental results. In subsections 4.5.2 and 4.5.3 we look at the bias dependence and influence of depth, respectively, on the feature and compare this with the model.

4.5.1 Coulomb potential

If a point charge is present in a surface region it will influence the surface electronic structure. The influence of a positively charged Si donor atom on the density of empty states can be observed in the scan image in Fig. 4.1(a) and the images in Fig. 4.13(a) to (c). Bright hillock features superimposed on the atomic lattice are visible in these empty state images. This behaviour can be understood easily because the present Coulomb potential will locally bend the energy bands downwards (see Fig. B.1 in Appendix B). In this way the local surface density of empty states is increased which results in a retraction of the STM tip.

Just as in section 4.3 for a screened Coulomb potential one can also model the effect of a bare Coulomb potential on the local density of surface states. Therefore we repeat the calculations done by Kobayashi but this time taking the inverse screening distance \( k_0 \) equal to zero. For \( k_0 = 0 \) the screened Coulomb potential changes into the unscreened Coulomb potential (see expression (C.13) in Appendix C). Kobayashi showed that for \( k_0 = 0 \) the local density of surface states can be calculated by using standard scattering theory [21]. The wave function can therefore be written as,

\[
\Psi(r) = e^{ik \cdot r} + f(\theta) \frac{e^{ikr}}{r},
\]

with \( f(\theta) \) the scattering amplitude. For a pure Coulomb potential acting between two charges \( q_A \) and \( q_B \) the scattering amplitude \( f(\theta) \) is given in
Figure 4.13: Three empty state images of the same surface area (18.9 x 18.9 nm²) measured at different sample voltages. Set point current: 90 pA.

The first Born approximation as

\[ f(\theta) = \frac{q_A q_B}{4\pi \varepsilon_0} \frac{1}{4E \sin^2(\theta/2)} \]  \hspace{1cm} (4.28)

where \( E \) is the energy (see reference [17]). The absolute square of the scattering amplitude corresponds to the differential line-profile \( d\sigma/d\Omega \). From expression 4.28 one can see that the differential line-profile is infinite for \( \theta \) equal to zero. The total scattering line-profile for a Coulomb potential is therefore not defined. This is a well known problem [17]. However, one can argue that in real physical systems at some distance from the centre of a point charge screening charges are present and therefore the Coulomb potential will be modified. The scattering amplitude for a screened Coulomb potential is given by

\[ f(\theta) = \frac{q_A q_B}{4\pi \varepsilon_0} \frac{1}{\alpha^2 + 4E \sin^2(\theta/2)} \]  \hspace{1cm} (4.29)

with \( \alpha^2 = k_0^2 \hbar^2/2m \) using the first Born approximation [17]. For this expression the differential line-profile is finite at \( \theta \) is zero and therefore the total line-profile is defined.

Kobayashi used this expression for calculating the LDOS. The LDOS is obtained by taking the absolute square of the wave function and integrating over the equienergy surface in k-space at radius \( k \):

\[ \text{LDOS}(r, E) = \frac{2k}{(2\pi)^3} \int |\Psi|^2 d\Omega, \]  \hspace{1cm} (4.30)

where \( (2\pi)^3 \) is the volume per allowed k-value in k-space. From the LDOS the corrugation is calculated in the same way as pointed out in section 4.3.3
by expression 4.20. In his paper Kobayashi showed results for a screened Coulomb potential with $1/k_0$ equal to 3 nm at three different depths $d$. In Fig. 4.14 we plotted the numerically derived result by Kobayashi for $k_Fd = 1$ using expressions 4.27, 4.29, 4.30 and 4.20, together with the experimental derived line-profile through the hillock feature in Fig. 4.1(a). The values put into the calculation are: work function $W$ is 1.7 eV, Fermi wave vector $k_F$ is $5 \times 10^8$ m$^{-1}$ (depth of the doping atom $d$ therefore is 2 nm). We can see that the calculation fits quite well to the measurement. A similar calculation was performed by Feenstra et al. [26] to explain their STM results on the oxygen adsorbed GaAs(110) surface. Johnson et al. [3] repeated these calculations to understand the influence of subsurface positioned Zn atoms on the filled state images at the GaAs(110) surface.

Based on the result shown in Fig. 4.14 we conclude that the experimentally obtained line-profile in Fig. 4.1(a) can be ascribed to the influence of an unscreened Coulomb potential.

Figure 4.14: Model calculation by Kobayashi together with the experimental derived line-profile in Fig. 4.1(a).
4.5.2 Bias voltage

In Fig. 4.13 three STM images are plotted of the same hillock feature measured at three different bias voltages; -1.5 V, -2.0 V and -2.5 V. The set-point current in all three images is equal to 90 pA. In Fig. 4.15 the rotationally averaged line-profiles through the different features are plotted. One can see that the amplitude of the features is decreasing with increasing bias voltage. This behaviour is the same as measured before in the filled state images. Again this is explained by the fact that at increasing bias voltage the number of states which participate in the tunnel process increases. The effect of the local potential is reduced causing the amplitude of the feature to decrease. Moreover, expression 4.28 tells that the differential line-profile for a pure Coulomb potential is proportional to $1/E^2$. Since the scattering angle $\theta$ and the energy $E$ are decoupled, the total line-profile is also proportional to $1/E^2$ and therefore decreases with increasing energy.

The angular distribution is also independent of energy. The differential cross section, therefore, is scaled at all angles by the same factor. The same holds for the total line-profile. As a function of bias; we therefore do not expect differences in the shape of the line-profiles through the features. This is verified by looking at the normalised line-profiles calculated from the pictures shown in Fig. 4.15(a) and shown in Fig. 4.15(b). The amplitudes of the average line-profiles are normalised to one. One can see that these line-profiles are comparable in shape.

4.5.3 Depth

In Fig. 4.7(h) an empty state image is plotted of the features 1, 2, and 4 as discussed before in section 4.4 and the height of the features is measured. We find

<table>
<thead>
<tr>
<th>feature (Fig. 4.7(h))</th>
<th>amplitude $A = \Delta z(0)$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05 ± 0.01</td>
</tr>
<tr>
<td>2</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td>4</td>
<td>0.01 ± 0.01</td>
</tr>
</tbody>
</table>

Just like for the filled state images, feature 1 has the largest amplitude and then, respectively, feature 2 and 4.

The model of Kobayashi predicts a gradually decrease of the amplitude with depth in case $k_0 \ll k_F$, which is true for an unscreened Coulomb potential. Following this model therefore we may believe that feature 1 is
Figure 4.15: (a) Rotationally averaged line-profiles through the dopant induced features in Fig. 4.13(a) - (c). (b) The line-profiles are normalised to 1.
induced by a Si donor atom positioned more close to the surface then the other donor atoms inducing feature 2 and 4. In section 4.4.3 the contrary was concluded. Using Kobayashi’s model for $k_0 \gg k_F$, which is true for a screened Coulomb potential, we found respectively that feature 1, 2 and 4 are induced by doping atoms positioned at regressive depth. The contradictory results are attributed to the neglection of a space charge region in Kobayashi’s model. The influence of band bending leads to $k_F$ decreasing with progressive depth below the surface, hence an increase of $r_{min}$. Therefore, including the presence of a band bending region, it is derived, that the filled state features 1, 2 and 4 in Fig. 4.7(a) to (d) belong to Si doping atoms positioned at progressive depth. This is in agreement with the results obtained for the features 1, 2 and 4 in the empty state image in Fig. 4.7(h).

In conclusion, considering Kobayashi’s model and a band bending region at the surface it is derived that features 1, 2 and 4 in Fig. 4.7 belong to Si doping atoms positioned at progressive depth.

4.6 Tunneling spectroscopy

In this section we present scanning tunneling spectroscopy (STS) measurements performed on top of the Si induced features. On top of these dopant induced features an increase in tunnel current is observed, inside and outside the band gap region. In the derivative of the current-voltage spectra (I-V curves) peaks are present and even negative differential resistances (NDR) are observed. The steps and peaks in tunnel current and conductance are explained qualitatively with help of a schematic model of the tunnel junction. The spectra obtained on different features are not identical. Differences exist in the number and the position of peaks. In addition to doing tunneling spectroscopy measurements on a single position, also measurements have been performed as a function of position. In this way the lateral extension of peaks in the conduction is studied for two different dopant induced features.

The STM control unit used in these experiments was built by Omicron Vacuumphysik. Spectra are measured at constant tip sample distance. The derivative of the I-V curves is calculated numerically.

Fig. 4.16 shows spectroscopy measurements on top of and next to two dopant induced features. In the insets, filled state images of the two features are shown. The features are similar to those discussed in section 4.4. The measurements were performed on two different samples (doping concentra-
Figure 4.16: Tunneling spectroscopy measurements on two different Si induced features of a $2 \times 10^{18} \text{cm}^{-3}$ Si doped GaAs sample. Figure (a) and (c) show two I-V curves. The curves marked 1 are measured with the tip in the center of the features shown in the insets. Scan area of the images in the insets is $10 \text{nm} \times 10 \text{nm}$. The curves marked 2 are measured next to the features at a distance of 5 nm. Set points figure (a): -2.0 V, 250 pA, $\Delta V = 40 \text{mV}$. Curves are averaged over 150 measured curves. Set-points figure (c): -3.0 V, 500 pA, $\Delta V = 30 \text{mV}$. Average of 10 measured curves. Figure (b) and (d) show the numerically determined derivative of curve 1 in figure (a) and (c) respectively. The approximated valence band (VB) and conduction band (CB) onsets are drawn.

tion $2 \times 10^{18} \text{cm}^{-3}$) with two different tips. In Fig. 4.16(a) and 4.16(c) the I-V curves are shown. The curves marked 1 are recorded with the tip positioned in the center of the dopant induced feature as pointed out by the arrow in the inset. The curves marked 2 are measured at a distance of 5 nm from the feature. Set-point current and bias are equal for both curves. The approximated onsets for the valence band (VB) and conduction band (CB) are plotted with CB at 0 V and VB at -1.52 eV. Due to tip induced band bending these onsets can be shifted (see references [8, 9, 11]). In Fig. 4.16(b) and Fig. 4.16(d) the derivatives of curves 1 in Fig. 4.16(a) and Fig. 4.16(c), respectively, are plotted.

The two I-V curves marked 2 show the normal characteristic known for
STS measurements on the GaAs(110) surface [6, 8]. Inside the band gap region (-1.52 V < \( V_{\text{sample}} < 0 \) V) there is almost no current flow. A small current component may be present from the electrons coming from the donor band, as pointed out by Feenstra et al. [6]. Below -1.52 V the tip Fermi level coincides with valence band onset and a tunnel current is observed. The current increases with sample voltage. Above 0 V, electrons tunnel to conduction band states. From these spectra the band gap cannot be determined exactly because of the effect of tip induced band bending [6, 9, 11].

The I-V curves measured in the center of the dopant induced features, marked 1, deviate from these characteristic STS measurements. Inside and outside the band gap region the transmittance from charge carriers across the tunnel junction is larger on top than next to the dopant induced feature. This we already knew from topography measurements, since at both positive and negative sample voltage, features are represented as hills in the surface electronic structure. In Fig. 4.16(a), however, curve 1 and 2 cross each other at positive bias. This is because the tip sample distance is larger for curve 1 than for curve 2 since the STM is operating in constant current mode. For the same tip sample distance the tunnel current in curve 1 would be larger\(^{18}\). Inside the band gap, curves 1 show a finite tunnel current.

In addition to an increase in the total transmittance from charge carriers also steps and even peaks appear in the I-V curves measured on top of the dopant induced features. These variations can be seen more clearly in Fig. 4.16(b) and Fig. 4.16(d) where dI/dV curves are shown. The positions of the different peaks are tabulated:

<table>
<thead>
<tr>
<th>Fig. 4.16(b)</th>
<th>peak positions (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.60</td>
<td>-1.36</td>
</tr>
<tr>
<td>-0.96</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fig. 4.16(d)</th>
<th>peak positions (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.76</td>
<td>-2.28</td>
</tr>
<tr>
<td>-1.89</td>
<td>-0.96</td>
</tr>
</tbody>
</table>

The peaks have different amplitudes. Furthermore, in Fig. 4.16(d) NDR is observed in the regions (-2.55 V < \( V_{\text{sample}} < -2.43 \) V) and (-1.32 V < \( V_{\text{sample}} < -1.08 \) V). At positive sample voltage, these two curves do not show peaks in the conductance. Only a little shoulder is present in Fig. 4.16(b) around +0.4 V.

The increase in tunnel current on top of a doping atom is due to an increment in the local state density. Kobayashi [21] did calculations for tunneling on top of a positively charged doping atom (like Si) as discussed in section 4.3.3. He calculated the local state density around the positive.

\(^{18}\)We can state this because the empty state image of the same feature shows a hillock in the surface topography.
Figure 4.17: Schematic energy diagram of the total tunnel junction with the tip positioned on top of a subsurface positioned Si donor atom.

charge using scattering solutions for a screened Coulomb potential. Depending on screening length, depth and scattering strength a local increase in the state density was indeed found.

In order to explain the variations in the tunnel current observed in Fig. 4.16, an energy diagram is sketched in Fig. 4.17, which is a simplified model of the tunnel junction at negative sample voltage. On the left, the free electron like valence and conduction bands (VB and CB) are plotted in $k$-space. At the bottom of the CB a grey enhanced peak in the density of states represents the donor band (DB), formed by Si donors. The DB overlaps the CB. In the middle of the picture $k$-space is replaced by real space. In addition to the VB, CB and DB the potential of a single Si$^+$ donor is sketched. On the right side the tunnel barrier and tip are shown. We assume the density of states at the tip to be constant in energy\textsuperscript{19}. Part of the applied bias between tip and sample will drop over the semiconductor (see section 4.2). It will push the Si induced potential well downwards in energy as shown in Fig. 4.17. With $E_{F,\text{metal}}$ inside the gap region only

\textsuperscript{19} Although the tips are prepared ex situ and therefore all kinds of impurities can adsorb at the tip apex, no evidence is found for the formation of sharp tip states as discussed theoretically by Lang [23].
electrons from the DB crossing the Si induced potential well can contribute to the tunnel current. By moving $E_{F,metal}$ further down, VB states can also participate.

In fact, Fig. 4.17, describes the situation of a potential well in series with a potential barrier. For 1-dimension it is known that at certain energies the transmission probability for electron wave functions across a potential well shows resonances [17]. These resonances occur when wave functions perfectly fit into the well. The peaks and steps observed in the tunnel current are attributed to the same kind of variations in the transmission probability across the tunnel junction. When sweeping the sample voltage ($\Delta V$) the tunnel junction changes since the potential well is pushed downwards in energy due to tip induced band bending (see the dashed lines in Fig. 4.17). For certain voltages the electron wave functions coming from the DB fit better to the junction than for other set-points. This results in a discontinuous increase of the transmission probability with sample voltage. This is in correspondence with the observations presented in Fig. 4.16, where steps and peaks in the I-V curves measured on top of the dopant induced features are visible.

The peaks observed in the dI/dV curves are broad in comparison with $kT$ (0.4 meV). This is attributed to the participation of all DB states in the tunnel process. An estimate can be made for the width of the DB, using the density of state function derived in [28], which has a Gaussian shape. The width at which the state density has dropped to 1/e of its maximum value is equal to $\sqrt{2} \Delta E$, with:

$$\Delta E = \frac{1}{4\pi\epsilon_0} \frac{1}{0.171} \left( \frac{m_n}{m_+} \right) \left( \frac{e^2}{2} \right) \left( \frac{a}{r_s^2} \right),$$  

(4.31)

and $r_s = [1/(4\pi\epsilon N)]^{1/3}$, N is the doping concentration, $\epsilon_0$ the dielectric constant in vacuum, $m_n$ the effective electron mass in the CB, $m_+$ the effective mass

---

Recently, Rosentreter et al. reported low temperature STM spectroscopy curves measured on a clean area of the GaAs(110) surface [27]. They also observed steps in the tunnel current when sweeping the sample voltage. They attributed these steps to the presence of quantized subbands in the low dimensional tip induced band bending region. In our model these subbands are not incorporated. We argue the importance of these states in understanding the observed effects. We believe the contribution from these states in the tunnel process is small. First, because the tunnel barrier for charge carriers coming from these states is larger than for the electrons coming from the DB in the bulk. Second, because wave functions inside the tip induced accumulation region are not only quantized in the direction perpendicular but also parallel to the surface plane due to the limited tip radius. Therefore wave functions possess a finite $k_\parallel$ value, which reduces the transmission probability.
Figure 4.18: (a) Two dI/dV curves measured in the middle of feature 1 and 2 shown in Fig. 4.18(b). (b) Topographic image of two Si induced features measured in constant current mode. Set-point current is 50 pA, sample voltage is -1.8 V. Figures 4.18(c)-4.18(e) show the local dI/dV at different sample voltages measured simultaneously with the topographic image in figure 4.18(b) by interrupting the feedback loop. Sample voltages are -1.1 V, -0.8 V and +0.2 V for respectively figure 4.18(c)-4.18(e).

electron mass in the DB, $e$ the elementary electron charge. Filling in the values tabulated in Appendix A, we find $\sqrt{2} \Delta E = 0.20$ eV. This indeed is much larger than $kT$ and is comparable to the width of the observed peaks.

In Fig. 4.16 only two spectra are shown. We have studied many spectra on different samples with different tips. In studying all these curves we found no curves are identical. Differences exist in the position, the number and the amplitude of the different peaks. This can be understood from the argument that resonances depend critically on the shape of the potential well and potential barrier.

A way to look at lateral variations in the tunneling spectra is by doing spectroscopy measurements in combination with topography. In plotting the local dI/dV measured at a certain voltage we can study the lateral extension
of the observed peaks. In Fig. 4.18 two dI/dV curves are plotted together with four images. The image in Fig. 4.18(b) shows two dopant induced features. The measurement is performed in constant current mode. At each scan point in the topography a current vs. voltage curve is recorded and derivative is determined numerically. Fig. 4.18(a) shows the spectra taken in the centre of features 1 and 2. In the pictures in Fig. 4.18(c), 4.18(d) and 4.18(e), the local dI/dV is plotted in grey scale at three different sample voltages. The voltages correspond to three peak positions in the dI/dV, respectively -1.1 V, -0.8 V and +0.2 V, pointed out by the three arrows.

From these images it is clear that peaks in the dI/dV only appear near the doping atom. The peaks decay, moving away from the centre. The lateral extension of the peaks is different for the two induced features at different sample voltage. At +0.2 V the peak at feature 2 is more extended than at feature 1. The reverse is true at -0.8 V. The difference is probably due to the fact that dopant 1 and 2 are positioned in different subsurface layers.

In contrast to the features measured at +0.2 V and -0.8 V, a minimum is measured in the dI/dV at the centre of the feature above dopant 2 at -1.1 V (and perhaps in a less convincing way above dopant 1). We believe this is a real effect not induced by an increase in tip sample distance, since the positions of the minima and maxima in the line-profile through feature 2 in Fig. 4.18(b) and Fig. 4.18(c) are totally different. We believe this is another observation of Friedel oscillations around Si doping atoms, measured by looking at the local dI/dV which is closely related to the LDOS (see Lang [23]). The oscillations are observed at -1.1 V sample voltage, with the Fermi energy of the metal tip positioned inside the semiconductor band gap. Kobayashi showed in his calculations that it is indeed possible that in the middle of the oscillation pattern of a positive charge a maximum as well as a minimum can be present [21].

From these measurements we can see that the observed peaks in the dI/dV curves decay over a distance of about 5 nm. This is typically the screening distance for electrons in bulk GaAs\textsuperscript{21}, and is a measure for the lateral extension of the Si\textsuperscript{+} induced potential. These measurements therefore support the idea that the discontinuities in the spectra are indeed induced by the Si\textsuperscript{+} charged impurity.

In this section we reported scanning tunneling spectroscopy measurements on top and next to Si induced features on the GaAs(110) surface. We

\textsuperscript{21}Using Dingle [12], we derive a screening distance of 5.43 nm for a $6 \times 10^{17}$ cm$^{-3}$ doped bulk GaAs sample at 4.2 K.
showed that the total transmittance of charge carriers is larger on top of dopant induced features than next to the features. This we already knew from topography measurements and is theoretically verified by Kobayashi [21]. Peaks in current and conductivity are attributed to resonances across the potential well induced by the subsurface positioned positively charged Si doping atom. Combining topography and spectroscopy measurements allows the lateral extension of the observed peaks in the conductivity near a doping atom to be studied. The decay length is about 5 nm and is comparable to the calculated Thomas-Fermi screening length for this material. This strengthens the argument that the peaks are indeed induced by the well of the Si point charge. By using this method we observed Friedel oscillations around a doping atom with the tip Fermi level positioned in the band gap.

4.7 Summary and discussion

In this chapter we studied the Si induced features in the empty and filled state images of the GaAs(110) surface. In the filled state images Friedel oscillations are visible around the positively charged Si donor. Two models were presented to calculate the deflection of the tip in constant current mode when scanning across the point charge. The first model describes the problem in terms of screening, the second model by scattering theory. Both models describe the experimentally derived line-profiles reasonably, although an important simplification is made by neglecting the presence of a band bending region. In addition to individual line-profiles through the dopants, the dependence of amplitude and period (position of the first minimum) of different line-profiles was studied as a function of applied bias voltage, set-point current and depth of the impurity atom.

As well as filled state images we discussed Si induced features in the empty state images. No screening effects are visible since free charge carriers are depleted from the surface and this is understood by tip induced band bending. The results are modeled by using bulk scattering theory.

Using Kobayashi's model we cannot derive which features in the empty and filled state images are induced by Si donors close to or farther from the surface, since the calculations are in contradiction to the experimental results. The model fails on this topic which may be due to the neglect of the space charge region. Taking into account the space charge region one can argue, somewhat speculatively, that the weakest features are induced by Si donors in a deep subsurface layer, while the more pronounced features
are induced by Si donors in one of the shallow subsurface layers.

The results discussed in this chapter are different from the results derived by other authors who performed their measurements at room temperature. First of all, no Friedel oscillations are reported in the room temperature measurements. Secondly, the induced features are smaller in size and can only be observed in 5 to 6 different subsurface layers at 300 K. We believe these observations are related and can be explained by the slightly diffuse Fermi surface at room temperature. Adawi [29] has calculated the influence of such a diffuse Fermi surface on the amplitude of charge density oscillations around a point charge in a metal. The results are summarized in Appendix D. For large distances from the point charge \((X \rightarrow \infty)\) his calculations predict an exponential decay of the amplitude. From appendix D we see, the amplitude reaches \(1/e\) of its original value at a distance \(X_{1/e} = \hbar^2 k_F/(2\pi k T m_n)\). Putting in the values: \(k_F = 1 \times 10^9\) m\(^{-1}\) and \(m_n = 0.067 m_0\), we find respectively for \(T = 300\) K and 4.2 K the distances: \(X_{1/e} = 7 \times 10^{-9}\) m and \(X_{1/e} = 5 \times 10^{-7}\) m. For \(T = 300\) K, therefore, a much faster decay is expected than for \(T = 4.2\) K. This explains the observation of smaller dopant induced features at room temperature. This also can explain the fact that no Friedel oscillations are observed at room temperature. Before the oscillations reach their first minimum, the amplitudes already decayed to a minimum value. This is in agreement with our measurements where the first minimum at 4.2 K is observed around 2.5 nm which is typically the size of the induced features measured at 300 K.

The observation of Friedel oscillations around subsurface positioned doping atoms incorporated in a semiconductor was first reported by us, in reference [30]. It is certainly not the first observation of charge density oscillations by STM. Earlier experiments on metal surfaces showed charge density oscillations in the vicinity of steps [31, 32], adsorbates and defects [33–36] and artificially made structures [37, 38]. These charge density oscillations are induced by electrons occupying nearly-free electron-like 2D surface states. The situation we described is different in the sense that the Friedel oscillations are induced by electrons which are not limited to a 2D surface plane.

Finally we presented tunneling spectroscopy measurements on top of the dopant induced features. In comparison with characteristic spectroscopy measurements adjacent to a dopant feature, a current increase is found. As calculated by Kobayashi, the presence of the point charge increases the density of states. Apart from an increase in the total current, steps and peaks are present in the spectra. These are explained by resonances across the potential well induced by the subsurface positioned positively charged Si donor.
References


Chapter 5

Zn and Cd induced features at the GaAs(110) surface studied by STM

In this chapter we present the results obtained by STM at the p-type doped GaAs(110) surface plane. All the measurements were performed at 4.2 K in this chapter. After a short introduction, empty and filled state images will be presented of the dopant induced features in GaAs. The doping atoms Zn and Cd are studied forming p-type impurities. The filled state images show centro-symmetrical elevations while the empty state images show local depressions. In a few empty state images the depressions are surrounded by a a maximum, which are direct observations of Friedel oscillations (comparable to the results on n-type doped GaAs in chapter 4). If the tip Fermi level is near the bottom of the conduction band (applied sample voltage \( V_s \approx 1.6 \text{ V} \)), the dopant induced features turn into triangular shaped elevations. The orientation of these features is determined with respect to the GaAs lattice. For one particular example the position of the doping atom with respect to the triangle feature is derived. Although the measurements strongly suggest that the triangular feature is a direct image of the acceptor state, no satisfying explanation has yet been found for the origin of the triangular shape. Finally, we present local tunneling spectroscopy measurements, recorded on top of and next to a dopant induced feature.
5.1 Introduction

In the previous chapter we discussed extensively the results obtained on the Si-doped GaAs(110) surface. Screening effects (Friedel oscillations) were observed around individual positively charged Si atoms. Stimulated by these exciting results, the STM measurements on the GaAs(110) surface were continued. In this chapter we discuss the results obtained on p-type doped GaAs. The scattering centres are formed by ionized acceptor atoms which possess a negative charge. The charge carriers are empty states in the valence band (holes) and have a positive charge equal to +e. In principle similar features are expected on these materials as for the n-type doped GaAs discussed in chapter 4. At negative bias voltage the surface is depleted from charge carriers and the influence of the positive bare Coulomb potential can be studied (see the sketches in Appendix B). At positive bias voltage, beyond the flat band condition where the applied sample voltage is equal but opposite to the work function difference between tip and sample, the surface is accumulated with charge carriers and Friedel oscillations are to be expected following the arguments given in section 4.3. In the previous chapter we found the oscillation period for \( r \to \infty \), with \( r \) the distance from the point charge, is approximately equal to the electron Fermi wavelength \( \lambda_F/2 \), where \( \lambda_F = (\hbar/2\pi)(2m_eE_F)^{-1/2} \). The same expression we adopt for doing calculations on holes. For holes, however, the effective mass \( (m_h = 0.37m_0) \) is quite larger in GaAs than for electrons \( (m_n = 0.067m_0) \). The Fermi energy \( (E_F) \) including tip induced band bending will be smaller, about a factor of 2 following the 1-dimensional model described in section 4.2.1, for a tip work function of 4.5 eV, an electron affinity of 4.07 eV and a band gap \( (E_g) \) of 1.52 eV for GaAs at 4.2 K. Therefore, adopting the expression for the electron Fermi wavelength \( \lambda_F \) for the wavelength of holes, we find that on p-type doped GaAs Friedel oscillations are to be expected with a period about 1.5 times smaller than observed on Si-doped GaAs.

5.2 Experiment

For these measurements two different p-type doped GaAs samples were studied. One sample was doped with Zn with a bulk concentration \( > 8 \times 10^{18} \text{ cm}^{-3} \), the other sample with Cd at a concentration of \( 7.4 \times 10^{17} \text{ cm}^{-3} \). The doping concentrations were not experimentally verified but copied from the specification lists enclosed with the commercially buyed wafers. Ohmic con-
tacts were made at the back of the samples as described in section 3.2. The STM used for these experiments is the same as for the experiments performed on Si doped GaAs and is described in detail by Wildöer et al. [1]. To obtain clean surfaces the samples were cleaved in situ at 4.2K along the (110) plane by a cleaving station as described in section 3.2. The STM tips were made from PtIr wire and mechanically cut with scissors. For operating the STM a commercial control unit (Omicron [2]) was used.

5.3 Empty versus filled state images

In Fig. 5.1 three STM images are presented together with four plots showing line-profiles in the (110) and (001) direction, respectively. The measurements were performed on the Zn-doped GaAs sample. Fig. 5.1(a) is a filled state image measured at -1.8 V sample voltage. Fig. 5.1(b) and (c) are empty state images measured at respectively +1.8 V and +1.55 V. The observed features are induced by the same Zn doping atom. The scan area is 5.4 × 5.4 nm². As expected the filled state image shows a hillock feature superimposed on the As sublattice. This feature is induced by a negatively charged Zn doping atom which locally increases the density of valence band states, see for example [3]. In the empty state image, in Fig. 5.1(b), a local depression is visible. To understand the origin of this feature, consider the schematic energy diagram plotted in Fig. 5.2. In this diagram the semiconductor sample is plotted on the left and the metal tip on the right. In this example the sample is positively biased. Tip induced band bending is present which causes the bands to bend upwards towards the surface. The negatively charged Zn atom locally increases the density of valence band states as indicated by the dashed line. As a consequence the density of conduction band states is decreased in the vicinity of the Zn impurity. Two tunneling contributions can be distinguished as pointed out by the two arrows: (arrow 1) electrons tunneling from the tip to the empty conduction band states and (arrow 2) holes coming from the impurity induced band tunneling to the tip. These contributions are not equal in size. The electrons have to tunnel across a potential barrier which is about 1.5 eV lower (value for $E_g$) than the tunnel barrier for holes. The transmission probability for the electrons, which is approximately proportional to $\exp(-2\kappa z)$ with $\kappa = [(2m/\hbar^2)\phi]^{1/2}$ and $\phi$ the average barrier height, is therefore much higher than it is for holes. For this reason the contribution from electrons coming from the conduction band is dominant in the tunnel current and in
Figure 5.1: Three scan images of the same scan area (5.4 × 5.4 nm²) measured at different sample voltages: (a) -1.8 V, (b) +1.8 V, (c) +1.55 V. Set-point current: 100 pA. Doping concentration: > 8 × 10¹⁸ cm⁻³ (Zn). The meaning of the (dashed) lines in figure (c) is explained in the text. (d)-(g): Line-profiles through pictures (a) and (c) in respectively the (110) and (001) direction. The numbers 1 - 5 and letters a - f indicate the positions of the different line-profiles in respectively figure (a) and (c).
Figure 5.2: Schematic energy diagram of the STM tunnel junction. The sample is positively biased with respect to the metal tip. Two current contributions can be distinguished as pointed out by arrow 1 and 2.

particular conduction band states are imaged by the STM at +1.8 V sample voltage. Since in the vicinity of the Zn impurity the density of conduction band states is reduced, a depression in the surface topography is visible as observed in Fig. 5.1(b).

In Fig. 5.3 two rotationally averaged line-profiles through the features in Fig. 5.3(a) and (b) are plotted after filtering the atomic lattice out. Corrugation amplitudes in the centre are +0.025 nm and -0.025 nm for the features measured at -1.8 V and +1.8 V, respectively. No Friedel oscillations caused by the scattering of holes with the Zn doping atom are visible in this figure around the local depression. In Fig. 5.4 another STM picture is plotted measured on the Zn-doped GaAs(110) surface. In this image three local depressions are visible induced by three Zn doping atoms. This time, the depressions are surrounded by a maximum, although it is very weak. The fact that the charge density oscillations observed by STM around the negatively charged Zn doping atoms are so weak, can be understood because of the following arguments.

In the previous chapter we found that the corrugation amplitude as
Figure 5.3: Rotationally averaged line-profiles through the Zn induced features shown in Fig. 5.1(a) and (b). The atomic lattice is filtered out.

measured by STM and caused by oscillations in the charge density at distance \( r \) from a point charge can be described in approximation by the ratio \( \Delta LDOS(r)/LDOS(\infty) \), with \( \Delta LDOS(r) = LDOS(r) - LDOS(\infty) \), assuming only electrons at the metal Fermi energy participate in the tunnel process. This is of course not true, but a good approximation since the transmission probability \( (T) \) for electrons decays exponentially with energy. From the above mentioned expression we see the corrugation amplitude will be small either when \( \Delta LDOS(r) \) is small or \( LDOS(\infty) \) is large. In Fig. 5.3 and Fig. 5.4, we see the corrugation amplitudes are -0.025 nm and -0.005 nm, respectively, at the centres of the features. These amplitudes are indeed small comparing with the results obtained on Si-doped GaAs. Typical values found for the corrugation amplitude in the centre of the Si induced features, of course dependent on bias voltage, are around 0.1 nm (see figure 4.8). For the minimum at half oscillation period an amplitude is found below 0.05 nm, dependent on the depth of the dopant atom. With a corrugation amplitude of 0.025 nm at the centre an amplitude below 0.01 nm is expected at half oscillation period. This is below the corrugation of the atomic lattice in the [001] direction, which is equal to 0.02 nm. We believe the atomic corrugation disturbs the observation of Friedel oscillations in Fig. 5.3. In Fig. 5.4 the corrugation of the atomic lattice in the [001] direction is equal to 0.005 nm and very weak Friedel oscillations can be observed.
5.3 Empty versus filled state images

Figure 5.4: Left: empty state image of the Zn-doped GaAs(110) surface. Sample voltage: +2.5 V. Set-point current: 50 pA. Scan area: 11 × 11 nm². Three Zn induced features are visible. The circular depressions are surrounded by a maximum. Right: line-profile through one of the Zn induced features indicated by the dashed line. The atomic lattice is filtered out.

We believe the corrugation amplitude for these Zn induced features is small because the tip Fermi level is positioned deep in the conduction band of the semiconductor sample at a bias-voltage of +1.8 V. This means that \( LDOS(\infty) \) is large which indeed results in a small corrugation amplitude as mentioned above. On the other hand \( \Delta LDOS(r) \) will be small in comparison with the n-type doped GaAs, since the effect of tip induced band bending in p-type is not as strong as in n-type. We find, respectively, a surface electrostatic potential \( (\phi) \) equal to 0.07 V \( (V_s = +1.8 \text{ V}) \) and -0.32 V \( (V_s = -1.8 \text{ V}) \) for a p-type and n-type doped GaAs sample by using the tabulated values in Appendix A, a tip-sample distance of 0.9 nm and the 1-dimensional model presented in section 4.2.1. The effect of tip induced band bending in p-type, therefore, is a factor of 4 smaller than in n-type for the mentioned set-point values. This limits the density of free holes at the surface which is directly related to \( \Delta LDOS(r) \). Furthermore the density of free holes will be limited since the samples we studied are not fully degenerate. Following the paper by Emel’yanenko [4] p-type GaAs samples become degenerate when the doping concentration is above the \( 10^{19} \text{ cm}^{-3} \) and strong degeneracy \( (E_F/kT > 2) \) occurs at doping concentrations above the \( 3 \times 10^{19} \text{ cm}^{-3} \). The sample we studied here has a doping concentration larger than \( 8 \times 10^{18} \text{ cm}^{-3} \). For n-type samples degeneracy occurs already at lower doping concentrations. Degeneracy occurs at a doping concentration larger than \( 5 \times 10^{17} \text{ cm}^{-3} \) and strong degeneracy \( (E_F/kT > 2) \) at doping
concentrations larger than $1.5 \times 10^{18}$ cm$^{-3}$ [4]. This is due to the small effective mass of electrons.

### 5.4 Triangular features

The contribution from holes coming from the impurity band and tunneling to the metal tip can be increased relatively by decreasing the applied voltage between tip and sample thereby moving towards the band gap energy of the GaAs sample. The result is plotted in Fig. 5.1(c), which shows a scan image of the same surface area as shown in Fig. 5.1(a) and (b) but measured at a sample voltage of $+1.55$ V. The depression is replaced by an elevation in the surface topography. The elevation, however, is not circular, but has a triangular shape. One side of the triangle (the base), shown by the solid line in Fig. 5.1(c), is positioned along the $(\overline{1}10)$ direction. The mirror plane of the feature (parallel to the $(001)$ direction) has the $(\overline{1}10)$ direction as its normal. A line-profile through this plane is also plotted in Fig. 5.1(c) and given by the dashed line along the $(001)$ direction. By making large scan images we can see whether all the triangular features are oriented in the same direction.
5.4 Triangular features

Figure 5.6: Schematic representation of the GaAs(110) surface. The first and second layer Ga (open circles) and As (closed circles) are plotted. The two possible orientations of the triangular feature with respect to the lattice are shown.

In Fig. 5.5(a) and (b) two large scan images are plotted measured on a Zn doped and Cd doped GaAs sample, respectively. Many triangular features are visible. All features have the same orientation as mentioned above. This is in agreement with the observations in Fig. 5.1(c). The chemical nature of the acceptor atoms probably does not influence the induced feature at the GaAs(110) surface plane, since both images on the Zn-doped and Cd-doped sample show comparable results.

By looking at the crystal structure of the GaAs(110) surface plane one can see that the triangular features can have two different orientations. This is because the GaAs(110) surface has no mirror symmetry in the (001) direction. Both orientations are schematically drawn in Fig. 5.6. The orientation in our measurements can be determined by studying the line-profiles plotted in Fig. 5.1(d) - (g). The result is drawn in Fig. 5.7. This orientation corresponds to orientation 1 in Fig. 5.6. By examining the line-profiles 2 and 5 in Fig. 5.1 the position of the doping atom with respect to the As lattice is determined\(^1\). Line-profile 2 shows only one maximum. This means using

\(^1\)This method is described before by Johnson et al. [5].
symmetry arguments that the doping atom is positioned in one of the odd subsurface layers (1st, 3rd, 5th, ...). From line-profile 5 one can see the As atoms around the maximum are lifted asymmetrically. The lower As atom seems to be lifted more strongly than the upper one. With this observation the orientation of the triangle is determined completely and given in Fig. 5.7.

Together with the other line-profiles, the location of the triangular feature with respect to the impurity atom can be determined as shown in Fig. 5.7. One can see the impurity atom is not positioned in the centre of the triangle, but more towards the top corner (the corner opposite to the base). This is the case for all the observed features.

After characterizing the triangular features, the question of their origin still remains open. Although we do not have a satisfactory answer for this, several remarks are made. First, the feature is of electronic nature, since it varies with changing sample voltage. If it would be a real geometric distortion the feature should be visible at all sample voltages. Which element is substituted as acceptor atom does not seem to matter. Both Zn-doped and Cd-doped GaAs samples show the same kind of features (see Fig. 5.5). Secondly, the triangular features are only visible when we are looking at empty states and the Fermi level of the tip is positioned near the bottom of the conduction band or even inside the band gap region. In this regime, the contribution from impurity band holes dominates the tunnel current. These observations suggest that the triangular features are real images of the acceptor state near the GaAs(110) surface. The results are comparable to the results from Feenstra et al. [6] on antisite defects.

Feenstra et al. published results where they observed non centro-symmetric features with two satellite structures at the (110) surface of a low-temperature-grown GaAs sample. They proved the features are induced by isolated subsurface positioned arsenic antisites (As on a Ga site). These features are only visible by STM when tunneling inside the band of defect states. The

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2Another way of determining the correct orientation is by recording both filled and empty state images in the same time in the forward and backward scan direction. By looking at the positions of the filled state maxima (As atoms) with respect to the empty state maxima (Ga atoms) the orientation can be determined. We, however, observed contradictory results using this method. We attribute this to the fact that a huge capacitive peak is induced in the current when switching the bias voltage \( I = CdV/dt \) between tip and sample at the end of each scan line. The feedback system corrects for this current by applying a voltage pulse to the piezo tube. The recovering time is limited due to the presence of piezo creep and gives rise to lateral displacements, since z-direction is not totally separated from x- and y-direction in a piezo tube. To optimize this method the feedback should be interrupted when switching the bias polarity.
features extend over a few atomic distances and the shape is determined by the electron wave functions of the antisite defect. Our results are comparable to these results. The observed triangular features also extend over a few atomic distances and are only visible when tunneling into the impurity induced energy band. The triangle shape therefore should be an image of the wave functions belonging to the acceptor atom.

We do not believe the features we observe are induced by the tip, since in this case the features should critically depend on the shape and chemical nature of the tip apex. This is probably not the case, since we used more than five different tips in the experiments on p-type doped GaAs and each time the same kind of triangular features with the same orientation are observed. Therefore we believe it is a property of the sample. Besides,
Figure 5.8: Spectroscopy curves on top of and next to a Zn induced feature shown in the inset. The measurements are performed at constant tip sample distance. Set-point current is 100 pA, sample voltage is +1.6 V. Both curves are the average of 5 different measurements recorded on the same position. The abbreviations VB, CB and IB respectively point out the contributions from the valence, conduction and impurity band states.

Independently from our experiments the same kind of triangular features on Zn-doped GaAs were observed by Zheng et al. [3] at room temperature (see chapter 2).

5.5 Spectroscopy measurements

Similar to the results on the n-type doped GaAs samples, reported in section 4.6, spectroscopy measurements were performed on the p-type doped GaAs samples. In Fig. 5.8 two I-V curves are shown measured on top of and next to a dopant induced feature at the GaAs sample with doping concentration larger than $8 \times 10^{18} \text{ cm}^{-3}$. For the current axis a logarithmic scale is used. The curves are measured at constant tip sample distance. Set-point current is 100 pA and sample voltage +1.6 V. The curves shown are the average of
5.6 Summary

In this chapter we have presented and discussed the dopant induced features observed at the p-type Zn and Cd doped GaAs(110) surface. The filled state images show centro-symmetric elevations while the empty state images show circular depressions. These observations can be explained as charge induced band bending effects. No or only weak charge density oscillations (Friedel oscillations) are observed in the empty state images. This we explained by the large density of states at the background and the lack of free charge carriers at the surface. Moving the tip Fermi level near the conduction band edge or in the band gap region of the GaAs sample, the circular depressions are replaced by triangular shaped elevations. The orientation of these triangles is the same for every doping atom in each subsurface layer and is geometrically determined with respect to the GaAs lattice. Since the feature is only visible when tunneling to the impurity band states, we believe the feature is a direct image of the acceptor state. Both Cd and Zn acceptor atoms give the same results. The origin of the triangular shape is not clear at this moment.

References


Chapter 6

Oxygen adsorbates, vacancies and steps near/at the GaAs(110) surface observed by STM

In addition to substitutional doping atoms other kinds of imperfections in the crystal lattice can be present near the cleaved GaAs(110) surface. One can mention for instance vacancies, antisite defects, interstitial or misplaced atoms. Adsorbates and cleavage induced steps can also be present on the surface plane. A survey of the reported STM measurements on this topic is given in chapter 2. Historically, these kinds of imperfections played an important role in the correct physical interpretation of the GaAs(110) surface plane [1]. Around 1970 it was thought that the GaAs(110) surface exhibits intrinsic surface states in the band gap region since the Fermi level was generally found to be pinned close to the middle of the bulk band gap. These findings were in agreement with theoretical studies of that time which assumed unrelaxed GaAs(110) surfaces. When cleavage techniques improved, more evidence was found for an extrinsic nature of the surface band bending. Cleavage induced steps and defects should be responsible for the Fermi level pinning. Inspired by these experiments a model came up assuming a relaxed GaAs(110) surface, which indeed predicts a shift of the intrinsic surface states outside the band gap region. With STM we are now able to study these (cleavage induced) surface defects on the atomic scale.

In this chapter we will present STM measurements on some of these imperfections. It is due to their charge that we can observe them in our
STM images. In spectroscopy measurements we will show that the observed imperfections indeed induce a shift of the Fermi level towards the middle of the energy band gap. In addition to point defects we will also show the results obtained near mono-atomic steps. The steps seem to possess a certain charge, too, and therefore band bending effects are visible in the vicinity of the step. Besides charge induced effects, localized states are visible at the step edge. A simple rebonding model is suggested to explain the results. The results obtained on n-type doped and p-type doped GaAs, respectively, will be discussed separately.

6.1 Oxygen atoms adsorbed to the n-type doped GaAs(110) surface

In chapter 4 we studied the features at the GaAs(110) surface plane induced by substitutional Si$_{Ga}$ donor atoms. We saw that the Si atoms induce hillock like features in the empty state images, because of their positive charge. This is shown, for example, in the inset of Fig. 3.11(a). Next to the hillock features also local depressions can be observed clearly in this image. These features cannot be induced by Si donor atoms but must be caused by another kind of defect. In Fig. 6.1(a) we show a magnification of such a feature. Next to an empty state image also a filled state image is shown, in Fig. 6.1(b). The measurements are performed at the same surface area. Scan size is $5.5 \times 5.3 \text{ nm}^2$ and set-point current is 100 pA. The empty state image is measured at a sample voltage of $+2.0 \text{ V}$, the filled state image at a sample voltage of $-2.0 \text{ V}$. In both images we observe a localized and delocalized feature. In order to study both effects separately we respectively put a high and low pass filter over the original images. The results are plotted in Fig. 6.1(c) - (f).

A clear centro-symmetric depression is visible in Fig. 6.1(c). A rotationally averaged line-profile through this feature is plotted in Fig. 6.2, and we see the depression extends over a range a little bit smaller but at the same order of magnitude (3-4 nanometers), than the Si induced hillock feature in Fig. 3.1(a) (plotted in the same figure). In contrast with the Si donor atom, this defect must be negatively charged. The repulsive Coulomb potential locally reduces the density of empty conduction band states, and therefore a delocalized depression in the surface topography is visible. As we know, the radius of the repulsive Coulomb potential decreases with increasing energy. This may explain why the depression is less extended than the Si induced
Figure 6.1: (a)-(b) Respectively, empty (+2.0 V) and filled (-2.0 V) state STM image of a typical defect observed on the GaAs(110) surface. Sample doping concentration: $6 \times 10^{17}$ cm$^{-3}$ (Si). Set-point current: 100 pA. Scan area: $5.5 \times 5.3$ nm$^2$. (c)-(d) Result for pictures (a) and (b), respectively, after low pass filtering of the data. (e)-(f) Result for pictures (a) and (b), respectively, after putting a high pass filter over the data.
Figure 6.2: Two rotationally averaged line-profiles 1 and 2 through respectively the feature imaged in Fig. 6.1(c) and the Si induced feature in Fig. 4.1(a).

feature.

The filled state image in Fig. 6.1(d) shows a maximum in the centre surrounded by a depression. In principle no maximum is expected to be present in the centre of a negatively charged defect. One however has to realise that two tunnel components are in competition, when looking at the filled states at the GaAs(110) surface. One can distinguish between the contribution from respectively electrons coming from the donor induced band and electrons coming from the valence band. In the centre of the feature the second component is most probably dominant causing a maximum in the corrugation\(^1\). In Fig. 3.11(b), we see another maximum is present surrounding the depressions. These again are observations of Friedel oscillations, but this time around a negatively charged point charge.

Besides delocalized features caused by the charge of the defect, also localized features are visible. In Fig. 6.1(e) and (f) empty and filled states are shown, respectively, where the low frequency part is removed. In the empty state image the Ga lattice is visible with its $1 \times 1$ periodicity. This

\(^1\)A similar explanation is given by Stroscio et al. [2] for the features induced by adsorbed oxygen atoms on the GaAs(110) surface.
periodicity is disturbed at the position of the defect in an area of a size comparable to two Ga atoms. Two Ga dangling bonds seem to be displaced from their original position. In the filled state image the As lattice is imaged. It looks different from the normally obtained surface lattice. An extra state seems to be present in between the rows of As bonds. This is only the case in the vicinity of the defect, on a scale comparable to the charge induced effects. Outside this region the extra state disappears. We ascribe this to a tip artifact and is induced by the reduction (about 0.5 Å) of tip sample distance when scanning across the defect. In the centre of the feature in an area comparable to about four As atoms no individual dangling bonds can be recognized anymore. A distinct surface state is formed by the defect. This in contrast with the Si induced features where no localized features have been observed.

The question now arises what kind of defect is causing the observed feature? From the depression visible in the empty state image we conclude that it must have a negative charge. The range of this feature is comparable to the hillock feature induced by a Si donor atom. For an ionized Si donor atom we know the charge is equal to one elementary electron charge $+1e$. This suggests the charge of the defect is equal to $-1e$. Further we saw the defect induces a distinct localized feature. The range of this feature is about two atomic distances. Because of this short range we conclude the defect must be positioned on top of the surface, in the surface plane or in the first subsurface layer. A clue for the origin of the observed features is given by the observation that the density of features increases after switching the bias polarity between tip and sample. By doing this, either material in the surface plane is moved from its original position, creating surface defects (atomic manipulation), or simply material coming from the tip apex is transferred to the surface plane. The first possibility is not plausible, for two reasons. From papers about atomic manipulation with STM we know the bias polarity determines whether atoms can be picked up or not [3]. In our situation the sign of the bias voltage seems not to be important at all in creating the defects. Only switching the bias polarity seems to be important. Further, we recognized that these defects are not necessarily created directly below the tunnel point of the tip but in an area much larger than this. This makes atomic manipulation even more unlikely since this would preferably take place at the position below the tip where the electric fields and therefore the forces are largest. Most likely therefore is the possibility that material is moved from the tip apex to the sample surface. The most plausible candidate for this is oxygen.

Stroscio et al. published two papers about oxygen atoms adsorbed on
the GaAs(110) surface [2, 4]. The results they reported in these papers are identical to the results we described above. In the empty state images the electronegative oxygen induces a local depression in the surface topography of the n-type doped GaAs(110) surface. In the filled state images a maximum is present in the centre of the feature surrounded by a depression. In their explanation of the centre maximum they refer to a paper by Lang [5]. In this paper, calculations show that electronegative adsorbates (like oxygen) increase the state density below the Fermi level and correspondingly deplete the state density above the Fermi level. This is clearly visible when doing local spectroscopy measurements on top of the induced features, as reported by Stroscio et al. [4]. We repeated these measurements on the features we observed. In Fig. 6.3 two spectroscopy curves are plotted, one measured in the middle of the defect induced feature, the other one next to the feature. Clearly the curve on top of the feature is shifted towards positive sample voltage, which corresponds to an increase in filled states and a decrease in empty states.

The above arguments strongly suggest that our observed features are
indeed induced by the adsorption of oxygen atoms. In principle no oxygen is expected to be present at 4.2 K (vapour pressure of \( O_2 \) is \( \ll 10^{-17} \) Torr). The oxygen is adsorbed to the walls of the STM chamber, but of course also to the tip which is prepared \textit{ex situ}. During scanning or switching the bias polarity (which moves the tip over a small distance) the oxygen can be transferred from the tip apex or even shaft to the surface.

All the features observed in our measurements on n-type doped GaAs can now either be related to Si\(_{Ga}\) induced features or features induced by oxygen atoms adsorbed to the surface plane. This leaves open the question why no other defects like Si\(_{As}\) defects or Ga- or As-vacancies as described by Lengel \textit{et al.} [6, 7] are identified? We believe two reasons can be given for this. First, it is expected that the density of these kind of defects is very low. From literature it is known that Si\(_{As}\) defects, dependent on the growth technique, only appear in high doped samples (Si concentration \( > 10^{18} \) cm\(^{-3}\)) [8]. For these samples the ratio of Si\(_{As}\) to Si\(_{Ga}\) substitutionals is about 0.2. Also for cleavage induced surfaces vacancies, as reported by Ebert \textit{et al.} [9], the density is expected to be low and dependent on the temperature of the substrate. To form more vacancies samples are annealed between 395 and 480 K for more than 24 hours. Our samples are cleaved at 4.2 K and therefore even fewer vacancies are expected to be present than at room temperature. Furthermore, it is not unlikely that features induced by some other kind of defects are hidden by the Si\(_{Ga}\) induced feature, since in our STM images the number of Si\(_{Ga}\) induced features is large and they are so well pronounced.

### 6.2 Oxygen atoms and vacancies near/at the p-type doped GaAs(110) surface

In Fig. 6.4 two large scan images of the same surface area but recorded with opposite bias voltage are shown. The images are measured on the p-type doped GaAs(110) surface doped with Zn to a doping concentration larger than \( 8 \times 10^{18} \) cm\(^{-3}\). As discussed in chapter 5, depressions are visible in the empty state image and elevations are observed in the filled state image. These features are induced by subsurface positioned Zn\(_{Ga}\) doping atoms. Other features are also visible.

First of all tiny white spots are present in the empty state image. The same spots are visible in the filled state image. We believe these features are induced by oxygen atoms adsorbed on the surface. In the same way
Figure 6.4: Six STM images of the p-GaAs(110) surface. Doping concentration: $> 8 \times 10^{18} \text{ cm}^{-3}$ (Zn). (a)-(b) Filled (-1.5 V) and empty (+1.8 V) state image, respectively, of a 72 x 72 nm$^2$ surface area. Set-point current: 100 pA. (c)-(d) Filled (-1.8 V) and empty (+2.0 V) state image of one of the features numbered 1 in Fig. (a). (e)-(f) Filled (-1.8 V) and empty (+1.8 V) state image of feature 2 in Fig. (a).
as described in the previous section, oxygen can be deposited on the clean surface by the tip. In contrast with n-type doped samples no depressions are visible surrounding the oxygen. As shown by Stroscio et al. [2] oxygen is neutral on the p-type surface. For this reason no band bending effects are to be expected around the tiny spots.

In addition to the hillock features in the filled state image also depressions are visible. Two different kind of depressions are recognized and numbered respectively 1 and 2, in Fig. 6.4(a). In Fig. 6.4(c) - (f), we zoomed in on both features. Empty and filled state images of the features are shown. We see the defect numbered by 1 causes an elevation in the empty state image. This behaviour is opposite to the behaviour of the negatively charged Zn doping atoms. The defect which causes this feature must be charged positively. In Fig. 6.5 the two rotationally averaged line-profiles are plotted through the empty and filled state features, together with the line-profiles through the dopant induced feature in Fig. 4.1(a) and (b). We see the empty and filled state feature have a comparable extention. The amplitude decays to a negligible value over a distance of about 3 - 3.5 nm. The dopant induced feature has a comparable extension. Therefore we believe the defect has a positive charge equal to +1e. The exact line-profile of course strongly depends on the subsurface layer in which the defect is positioned. Further it is sensitive for the applied sample voltage and set-point current. This may explain the small differences which exist between the line-profiles.

The feature numbered 2 is magnified in Fig. 6.4(e) and (f). Fig. 6.4(e) and (f) show a smaller surface area than Fig. 6.4(c) and (d). The filled state image shows strong reductions in the density of states in an area equal to four As atoms. We believe this is an image of four missing As atoms in the surface plane. Lengel et al. [7] studied single As vacancies on the p-type doped GaAs(110) surface. As discussed in chapter 2, they found the As vacancy is positively charged and therefore band bending effects are present around the missing atom. In the empty state image they found the two nearest neighbour Ga atoms of the defect are raised out of the surface. Similar effects are visible in the empty state image in Fig. 6.4(f). We see that six Ga atoms are lifted out of the surface plane. These Ga atoms are nearest neighbour atoms of the absent As atoms. The two Ga atoms in the middle (with two missing nearest neighbour As atoms in the surface plane) are lifted less strongly.

The difference between feature 1 and 2 is that feature 1 does not distort the Ga and As sublattices visible in the empty and filled state images, respectively. Therefore, the defect must be positioned in one of the subsurface layers. Following theoretical calculations by Zhang et al. [10] As-vacancies
Figure 6.5: Rotationally averaged line-profiles through the features shown in Fig. 6.4(c) and (d), together with the line-profiles through the Zn$_{Ga}$ induced features shown in Fig. A.

inside the bulk of p-type doped GaAs are charged positively by either $+3e$ or $+1e$. The observed feature can therefore be attributed to a subsurface positioned As-vacancy.

### 6.3 Steps at the n- and p-type doped GaAs(110) surface

In addition to point defects, steps are also observed at the GaAs(110) surface on both n- and p-type doped samples$^2$. In Fig. 6.6(a) and (b), we show two large scan images measured on top of a n-type doped sample with doping concentration equal to $6 \times 10^{17}$ cm$^{-3}$. Fig. 6.6(a) and 6.6(b) are measured with a sample voltage of $-2.5$ V and $+2.5$ V, respectively. Four steps are visible, numbered 1 to 4. Since atomic resolution is obtained in the surface plane, the orientation of the steps can easily be determined. Step 1 to 3 ex-

$^2$Möller et al. [11] studied cleavage induced steps on the GaAs(110) surface. They found steps along the $(112)$, $(114)$ and $(001)$ direction.
Figure 6.6: Four scan images and two line-profiles measured on a stepped GaAs(110) surface of a $6 \times 10^{17}$ cm$^{-3}$ Si doped GaAs substrate. Four mono-atomic steps are visible and numbered 1 to 4. (a) and (b) are respectively measured with a sample voltage of -2.5 V and +2.5 V. Set-point current is 50 pA. Scan area: $33.3 \times 33.3$ nm$^2$. (c) and (d) are recorded with a sample voltage of -2.5 V and +2.0 V. Scan area and set-point current for (e) and (f) are respectively $22.2 \times 22.2$ nm$^2$ and $11.1 \times 11.1$ nm$^2$ and 50 pA and 90 pA. The line-profiles in (c) and (d) are taken along the white lines plotted in (a) and (b).
tend along the (112) direction (normal to (11\bar{1}) direction), step 4 is oriented in the (111) direction (normal to (11\bar{2}) direction). The step edges are not perfectly straight, some kinks are present.

In Fig. 6.6(c) and (d) two line-profiles are plotted taken through the steps. The height of the steps is equal to about 0.2 nm. The steps therefore must be mono-atomic steps. From the line-profiles one can see that the terraces in between the steps are not perfectly flat. In the filled state image the terraces on both sides of the step are bent upwards. In the empty state image the reverse effect is visible, the terraces are bent downwards. This effect has been observed before by Heinrich et al. [12] on the n-type doped GaAs(110) surface, and is attributed to a charge induced effect. The presence of charge gives rise to band bending effects near the step. In these measurements the step seems to be negatively charged, in agreement with the observations by Heinrich. The negative charge causes an increase in valence band states and a decrease in conduction band states, which means that the Fermi level is moved towards the middle of the semiconductor energy gap. This can be verified easily by doing spectroscopy measurements near the step edge. The result is plotted in Fig. 6.7. This curve is measured at a set-point current of 200 pA, where the sample voltage is swept from +2.0 V to -2.0 V. The presented curve is the average of three recorded spectra measured at the same position. Clearly the Fermi level is moved away from the conduction band edge, where it is positioned on a step free surface. On a stepped surface, the Fermi level seems to be located near the middle of the energy band gap.

Fermi level pinning inside the band gap region by cleavage induced steps has been suggested before by Pashley et al. [13] for the GaAs(001) surface. Furthermore, it is in agreement with previous observations of band bending effects at the (110) surface of badly cleaved GaAs samples [1]. The step probably creates an acceptor state inside the energy band gap region, which by definition is negative when occupied and neutral when unoccupied. This state cannot be observed in our spectroscopy measurements, probably because it is a localized state which therefore is unlikely to participate in the tunnel process.

By zooming further in on the step edge, we observe some localized features, see Fig. 6.6(e) and (f). First of all at the edge an extra state seems to be present. This state is imaged three times, which we attribute to a tip artifact. This idea is strengthened by the imaged adsorbate at the bottom left of Fig. 6.6(e), which is also imaged three times in the same line as the

---

3 This step can also be seen as a step along the (112) direction but with many kinks in the step edge.
states at the step edge. In addition to the state at the step edge, an even more pronounced state seems to be present at the kink sites. To understand these observations one should first know what kind of step is imaged.

In Fig. 6.8, the four different configurations which steps in the (112) direction can possibly have are plotted. The two pictures at the top (6.8(a) and (b)), show As-terminated steps, while the two bottom pictures (6.8(c) and (d)) show Ga-terminated steps. All the steps in the (112) direction are occupied by as many Ga (cation) as As (anion) atoms and are therefore non-polar.

From our STM images we cannot directly determine which type of steps are imaged. In principle all configurations are possible. But there is a difference in packing of the different steps. Step (a) (the step in Fig. 6.8(a)) and step (d) are obviously more closely packed than step (b) and (c). We therefore believe that these steps are most likely to occur.

By looking at this configuration we are able in a **rebonding** picture to explain the observations with our STM. At the surface every atom has a dangling bond state. This dangling bond state is pointing out of the surface plane and imaged by STM. At the step edge, however, some extra bonds
Figure 6.8: (a)-(d) Schematic representation of four different step edges extending along the (112) direction on the GaAs(110) surface. (a)-(b) show As-terminated steps. (c)-(d) show Ga-terminated steps. (e) and (f) show the two possible As-terminated steps with one kink site in the step edge. The thick lines near the step edges represent dangling bond states.
are broken. These are given by thick lines in Fig. 6.8. In Fig. 6.8(a), we see only the As atoms at the step edge have an extra dangling bond state. This bond is oriented perpendicular to the direction of the step edge. In Fig. 6.8(d) we see this is the case for the Ga atoms. In Fig. 6.8(b) and (c) the dangling bonds are oriented parallel to the step edge. At the end of each of these dangling bond states another dangling bond state is present from a surface atom positioned in the lower terrace. These bonds are also plotted in Fig. 6.8 and given by a same thick line. If these dangling bonds rebond a dimer is formed at the step edge. The extra state observed in our STM images at the step edge can therefore be explained as the formation of a dimer between an As (Ga) atom in the upper terrace and a As (Ga) atom in the lower terrace.

The formation of such dimers between different terraces is not unlikely. Similar results are obtained for steps at the Si(001) surface [14] and supported theoretically [15]. As far as we know, no calculations have been performed for steps at the GaAs(110) surface. However, some theoretical papers deal with As-vacancies on the GaAs(110) surface. Zhang et al. [10] found using \textit{ab initio} total energy calculations that new chemical bonds can form between the nearest neighbour Ga atoms of the As-vacancy resulting in a Ga-Ga dimer or a Ga-trimer. These rebonded geometries are energetically more favourable than the non-rebonded models. To our knowledge, Ga-vacancies have not been investigated theoretically. Whether the same results hold for As atoms is therefore unclear.

The same model can be used to explain the observed states at the kink sites. In Fig. 6.8(e) and (f) the two types of As-terminated step edges are plotted again, this time with a single kink site. The thick lines, which connect the As atoms at the edge with the As atoms at the lower terrace, again represent the dangling bond states. In Fig. 6.8(e), that a kink site in the close-packed step edge creates three extra dangling bond states. These dangling bond states can rebond to a trimer. This may explain the pronounced state observed at the kink sites. The kink site in the other step edge (Fig. 6.8(f)) induces no extra dangling bonds and therefore no extra states are to be expected. Since the STM images show pronounced states at the kink sites, this supports the hypothesis that the imaged step edges are indeed those schematically plotted in Fig. 6.8(a), (d) and (e).

Steps have also been observed on the p-type sample. In Fig. 6.9(a) and (b) two large scan images are shown, measured on the GaAs(110) surface of a $1 \times 10^{19} \text{cm}^{-3}$ Zn doped sample. Fig. 6.9(a) and (b) were recorded by applying a voltage of -2.5 V and +2.5 V, respectively, to the sample. The set-point current was 24 pA. Two mono-atomic steps are visible. These are
Figure 6.9: Two STM images and two line-profiles measured on the p-GaAs(110) surface. Sample doping concentration: $1 \times 10^{19} \text{cm}^{-3}$ (Zn). Set-point current: 24pA. (a)-(b) Filled and empty state image measured respectively with a sample voltage of -2.5V and +2.5V. Scan size: $200 \times 200 \text{nm}^2$. (c)-(d) Line-profiles measured along the white lines plotted in Fig. 6.9(a) and (b), respectively.

...oriented in the (114) direction. In Fig. 6.9(c) and (d) two line-profiles are plotted which are, respectively, taken along the white lines plotted in Fig. 6.9(a) and (b). Similar to the results on the n-type doped sample, the terraces are bent near the step edges. In the filled state image the terraces are bent downwards, while in the empty state images the terraces are bended upwards. This behaviour can be explained by the presence of a donor state at the step edge, which by definition is positively charged when unoccupied. This positively charged state causes the Fermi level to shift towards the middle of the band gap.
6.4 Summary

In this chapter we presented imperfections near/at the GaAs(110) surface observed by low-temperature STM. We showed that the depressions visible in the empty state images on the n-type doped sample are most probably caused by adsorbed oxygen atoms coming from the tip apex. Oxygen atoms are also observed on the p-type doped sample. On this surface the oxygen atoms do not possess a charge as shown by Stroscio et al. [2, 4] and therefore no band bending effects are visible surrounding the oxygen. In addition to adsorbed oxygen a number of As-vacancies are observed in and below the surface plane. These vacancies possess a positive charge in agreement with earlier observations by Lengel et al. [7]. The density of these kind of features is very low. Cleavage induced steps were also studied at the GaAs(110) surface. The steps on both the n-type and p-type doped GaAs(110) surface are charged and therefore cause local band bending effects. The direction of the band bending is such that the Fermi level is shifted to the middle of the energy band gap. Pronounced states have been observed at the step edges and kink sites along the (112) direction on the n-type doped GaAs(110) surface. The results are explained with a simple rebonding picture.

References


Lett. 72, 836 (1994).


### Appendix A

#### Tabulated values

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<th>Parameter</th>
<th>Value</th>
<th>Description</th>
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<td>effective electron mass in GaAs</td>
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<td>effective hole mass in GaAs</td>
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</tr>
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<td>electron affinity for GaAs</td>
</tr>
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<td>direct band gap for GaAs at 4.2 K</td>
</tr>
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</tr>
<tr>
<td>$N_A$</td>
<td></td>
<td>concentration of acceptor atoms</td>
</tr>
<tr>
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<td>0.0385 eV (at $N_D = 6 \times 10^{17}$ cm$^{-3}$ (Si))</td>
<td>Fermi level position with respect to the edge of the conduction band, calculated using Fermi-Dirac statistics</td>
</tr>
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<tr>
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<td>0.00985 eV (at $N_A = 8 \times 10^{18}$ cm$^{-3}$ (Zn))</td>
<td>Fermi level position with respect to the edge of the valence band, calculated using Fermi-Dirac statistics.</td>
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<td>$E_{CB} - E_D$</td>
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<td>ionisation energy for Si donors in highly doped samples</td>
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<td>$E_A - E_{VB}$</td>
<td>0 eV</td>
<td>ionisation energy for Zn acceptors in highly doped samples</td>
</tr>
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Appendix B

Energy diagrams

In this appendix, we sketched six schematic energy diagrams of a 1-D metal-semiconductor tunnel junction. We make difference between a n-type doped semiconductor for which $\phi_s < \phi_m$ ($\phi_s$ is the semiconductor work function and $\phi_m$ is the metal work function) and a p-type doped semiconductor with $\phi_s > \phi_m$. For the n-type doped material we show the influence on the density of states (dashed lines) of a positive charge positioned near the surface ($\text{Si}_{Ga}$ for instance). For the p-type material the influence of a negative charge is drawn (for example $\text{Zn}_{Ga}$). The situations are sketched with the metal Fermi level above ($V_s = +$), equal to ($V_s = 0$) and below ($V_s = -$) the semiconductor Fermi level, respectively. The flat band condition is reached when a voltage is applied to the sample equal to $-(\phi_m - \phi_s)$. Below this value the energy bands near the surface are bending downwards, above this value the energy bands are bending upwards.
Figure B.1: Six schematic energy diagrams of a 1-D metal-semiconductor tunnel junction. Results are shown for a n-type doped semiconductor (on the left) and a p-type doped semiconductor (on the right), with the metal Fermi level opposite to the empty and filled states of the semiconductor, respectively, and without any voltage applied between tip and sample. The influence on the density of states of a positive charge and negative charge, respectively, positioned near the surface is pointed out by the dashed lines.
Appendix C

Thomas-Fermi screening theory

In this appendix we literally followed the derivations by Ashcroft and Mermin in *Solid State Physics* (Saunders Company, Florida, 1976), page 337-342. The expressions are written in c.g.s. units.

Assume a positively charged particle is positioned in a free electron gas. Due to the presence of this particle charge will be rearranged. To calculate the new distribution of charge two electrostatic potential are introduced $\phi^{\text{ext}}$ and $\phi$. $\phi^{\text{ext}}$ gives the electrostatic potential solely due to the positively charged particle\(^1\), $\phi$ is the full electrostatic potential produced by both the positively charged particle and the cloud of screening electrons. Both electrostatic potentials satisfy Poisson’s equation

\[
-\nabla \phi^{\text{ext}}(r) = 4\pi \rho^{\text{ext}}(r), \quad (C.1)
\]

\[
-\nabla \phi(r) = 4\pi \rho(r), \quad (C.2)
\]

where $\rho^{\text{ext}}$ is the particle’s charge density, $\rho^{\text{ind}}$ the charge density induced in the electron gas by the presence of the external particle and $\rho = \rho^{\text{ext}} + \rho^{\text{ind}}$ the full charge density. By analogy with the theory on dielectric media one may assume a relation between $\phi^{\text{ext}}$ and $\phi$ by an equation of the form

\[
\phi^{\text{ext}}(r) = \int d r' \epsilon(r - r') \phi(r'), \quad (C.3)
\]

\(^1\)The superscript “ext” from the term “external” refers to the origin of the charge from some source of charge external to the system of electrons
where $\epsilon$ can only depend on the separation between the points $r$ and $r'$ since the electron gas is uniform. The corresponding Fourier transform of this equation is

$$\phi^{ext}(q) = \epsilon(q)\phi(q), \quad (C.4)$$

where $\epsilon(q)$ is the wave vector dependent dielectric constant of the material. Assuming that $\rho^{ind}$ and $\phi$ are linearly related by an equation comparable to C.4 their Fourier transforms will satisfy the relation:

$$\rho^{ind}(q) = \chi(q)\phi(q). \quad (C.5)$$

One can calculate now by using the Fourier transforms of the Poisson's equations C.1 and C.2 that $\epsilon(q)$ is related to $\chi(q)$ by the relation:

$$\epsilon(q) = 1 - \frac{4\pi}{q^2}\chi(q). \quad (C.6)$$

In order to calculate the full electrostatic potential $\phi$ one needs to calculate the dielectric constant $\epsilon$ or with help of C.6 the factor $\chi$. In the Thomas-Fermi theory of screening it is assumed that the energy versus wave vector relation for an electron at position $r$ can be described by

$$E(k) = \frac{\hbar^2k^2}{2m} - e\phi(r). \quad (C.7)$$

Since the electrons are described by wave packets with wave vector $k$ this expression only holds if $\phi(r)$ slowly varies on the scale of the Fermi wavelength.

To calculate the induced charge density the expression for the number of electrons per unit volume in a free electron gas with a Fermi-Dirac distribution is used:

$$n(r) = \int \frac{dk}{4\pi^3} \frac{1}{\exp[(E - \mu)/kT] + 1}, \quad (C.8)$$

where the energy $E$ is given by C.7 and $\mu$ is the chemical potential. The induced charge density $\rho^{ind}(r)$ is equal to $-en(r) + e\rho_0$, with $\rho_0$ the charge density of the uniform background which is given by the same expression as C.8 with $E$ equal to the free electron energy $\hbar^2k^2/2m$. One can write:

$$\rho^{ind}(r) = -e[n_0(\mu + \phi(r)) - n_0(\mu)]. \quad (C.9)$$
If one assumes $\phi(r)$ is small enough to be expanded one derives to first order

$$\rho^{\text{ind}}(r) = -e^2 \frac{\partial n_0}{\partial \mu} \phi(r). \quad (C.10)$$

Together with expressions C.5 and C.6 this gives the Thomas-Fermi dielectric constant

$$\epsilon(r) = 1 + \frac{4\pi e^2}{q^2} \frac{\partial n_0}{\partial \mu} = 1 + \frac{k_0^2}{q^2}, \quad (C.11)$$

where $k_0^2 = 4\pi e^2(\partial n_0/\partial \mu)$ and is known as the Thomas-Fermi wave vector.

Using this expression we can now derive the screened Coulomb potential following Thomas-Fermi screening theory. The external potential of a point charge with elementary charge $e$

$$\phi^{\text{ext}}(r) = \frac{e}{r}, \quad (C.12)$$

gives a full potential in a free electron gas given by the relation

$$\phi(r) = \frac{e}{r} e^{-k_0 r}. \quad (C.13)$$

This screened Coulomb potential is also known by the name *Yukawa potential*.

Dingle [1] derived an expression for the screening distance $R (= 1/k_0)$ in a semiconductor by using Thomas-Fermi screening theory and assuming parabolic energy bands. He found\(^2\)

$$R = \frac{(4\pi \epsilon_s \epsilon_0 k_B T F_{1/2}(\eta))^{1/2}}{(4\pi e^2 n F_{-1/2}(\eta))^{1/2}}, \quad (C.14)$$

where $F_{1/2}(\eta)$ and $F_{-1/2}(\eta)$ with $\eta = \mu/kT$ are Fermi-Dirac integrals defined by

$$F_k(\eta) = \frac{1}{k!} \int_0^\infty \frac{x^k dx}{\exp[x - \eta] + 1}. \quad (C.15)$$

$\mu$ is the chemical potential, $\epsilon_s$ the relative dielectric constant, $\epsilon_0$ dielectric constant in vacuum, $k_B$ Boltzmann's constant, $T$ the temperature, $e$ the elementary electron charge and $n$ the average number of electrons (holes) per unit volume in the conduction (valence) band.

\(^2\)This expression is written in S.I. units.
References

Appendix D

Random phase approximation (RPA)

In this appendix we literally followed the derivations by Ashcroft and Mermin in *Solid State Physics* (Saunders Company, Florida, 1976), on page 337-343. The expressions are written in c.g.s. units.

In the random phase approximation (RPA), also known as the Lindhard method, starting point is the expression for the dielectric constant derived in Appendix A:

\[
\epsilon(q) = 1 - \frac{4\pi}{q^2} \chi(q). \tag{D.1}
\]

It is assumed that \(\rho^{\text{ind}}\) and \(\phi\) are linearly related. In order to calculate \(\chi\) the one-electron Schrödinger equation

\[
- \frac{\hbar^2}{2m} \nabla^2 \psi_i(r) - e\phi(r)\psi_i(r) = E\psi_i(r), \tag{D.2}
\]

is solved to linear order by perturbation theory. Knowing the electron wave functions to linear order in \(\phi\) one can calculate the induced charge density by using

\[
\rho(r) = -e \sum_i |\psi_i(r)|^2. \tag{D.3}
\]

In this way the following expression is found for \(\chi\)

\[
\chi(q) = -e^2 \int \frac{dk}{4\pi^3} \frac{f_{k - \frac{1}{2}q} - f_{k + \frac{1}{2}q}}{\hbar^2 k \cdot q/m}, \tag{D.4}
\]
where \( f_k \) denotes the Fermi function

\[
f_k = \frac{1}{\exp[\left(\frac{\hbar^2 k^2}{2m} - \mu\right)/kT] + 1}.
\]

As a result it can be shown that at large distances \( r \to \infty \) the screened Coulomb potential at \( T = 0 \) has the form

\[
\phi(r) \sim \frac{1}{r^3} \cos(2kFr).
\]

The electrostatic potential decays with \( 1/r^3 \) and shows oscillations with a period of \( \lambda_F/2 \), with \( \lambda_F \) the electron Fermi wavelength. These oscillations are known as Friedel oscillations [1].

More calculations have been performed on this problem using different model dielectric functions. The results have been summarised in [2]. All models predict charge density oscillations in the screening of a point charge.

Adawi [3] did calculations on the charge density in 1, 2 and 3 dimensions. He found that at \( T = 0 \) oscillations have the form

\[
\phi(X) \sim X^{-\frac{1}{2}(\nu+3)} \cos(2kFX),
\]

with \( \nu \) the dimensionality and \( X \) the distance to the point charge in 1, 2 or 3 dimensions. At finite temperatures he found the amplitude of the oscillations is reduced approximately by the factor \( \xi/\sinh(\xi) \), where \( \xi = 2\pi kTmX/\hbar^2k_F \). So for large \( X \) the oscillations decay exponentially with \( X \exp(-2\pi kTmX/\hbar^2k_F) \). This reduction is induced by the slightly diffuse Fermi surface at higher temperatures.

References

Appendix E

Tabulated results for model 1

In this appendix the numerically determined results for the displaced charge density (\(\Delta \rho\), in column 5) as a function of distance (\(r\), in column 1) are tabulated in units of \(k_F\) as determined by Langer et al. for an electron density of \(7.5 \times 10^{21} \text{ cm}^{-3}\). From these results \(\Delta \text{LDOS}\) (in column 6) is determined in arbitrary units by multiplying the distance \(r\) in column 1 with the values for \(\Delta \rho\) in column 5, following model 1 (equation 4.12). For point charges at a depth \(d = 0.1/k_F, 1.9/k_F\) and \(3.1/k_F\), \(r_\| = (r^2 - d^2)^{\frac{1}{2}}\) is determined in columns 2, 3 and 4, respectively. One can see that \(r_\| = 0\) if \(r = d\).

![Diagram](image)

**Figure E.1**: In this figure the symbols in the text are explained. The circles in the figure represent spheres of constant displaced charge density (\(\Delta \rho\)).
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Summary

In this thesis scanning tunneling microscopy (STM) measurements on clean GaAs(110) surfaces are described. The influence of different (point) imperfections (Si donors, Zn and Cd acceptors, vacancies and steps) near and at the (110) surface planes is studied. The individual imperfections in semiconductor materials are interesting from a fundamental point of view, and will be of technical importance in new nanometer sized electronic devices in the future.

All the measurements were performed at 4.2 K. This has several advantages in comparison with room temperature measurements. Firstly, at low-temperatures the scan images are not disturbed by thermal drift. Secondly, high spatial resolution in topography and high energy resolution in electronic spectroscopy is obtained. Thirdly, by cleaving our samples at 4.2 K we were able to study clean semiconductor surfaces for prolonged time, more than a week per sample.

In order to compare our low-temperature results with room temperature measurements we start in chapter 2, giving a survey of the STM measurements performed by other research groups on III-V compound semiconductors. This chapter is divided into sections on clean surfaces, doping atoms, vacancies and defects, adsorbates, multilayers and tunneling induced luminescence experiments.

In chapter 3 we describe the home-built low-temperature STM which we have used for our experiments. The STM is equipped with an automatic tip to sample approach facility and an in situ cleaving station at low temperatures.

In chapter 4 we study features visible at the GaAs(110) surface plane induced by subsurface substitutional SiGa donor atoms. In the filled state images charge density oscillations (Friedel oscillations) are observed around the donor atoms. The empty state images show hillock features. The difference between the filled and empty state images is attributed to accumulation respectively to depletion of charge carriers at the surface, due to
tip induced band bending. This is explained theoretically in a simple 1-
dimensional model of the STM junction. The influence of the applied sam-
ples voltage, bias polarity, tunnel current, depth of the donor atom on the
induced feature at the surface is studied experimentally. Two models are
proposed, which describe the experimentally obtained results in a reasonable
way. Spectroscopy measurements on top of the induced features show steps
and peaks in the tunnel current as a function of bias voltage. These fea-
tures are attributed to resonances across the potential wells of the positively
charged Si donor atoms. The results describe the first clear observations of
charge density waves around an impurity potential in a semiconductor.

In chapter 5, the influence of single Zn and Cd atoms on the surface elec-
tronic structure of the GaAs(110) surface is studied. Both elements show
comparable results. In the filled state images, hillock features are visible
around the subsurface substitutional acceptor atoms. In the empty state
images the hillocks are replaced by centro-symmetric depressions. In some
images weak maxima are visible surrounding the depressions. These are
attributed to charge density (Friedel) oscillations. With the tip Fermi level
inside the semiconductor band gap or near the conduction band edge, the
depressions change into triangular elevations and are explained as being an
image of the acceptor state wavefunction. The geometrical orientation of
the triangular features is determined with respect to the GaAs lattice.

In the last chapter, surface features that cannot be attributed to the
influence of substitutional dopants are discussed. We mention the presence
of oxygen and vacancies at and near the GaAs(110) surface. In addition
to point defects, also cleavage induced steps are observed. These steps are
charged and therefore cause a shift of the Fermi level towards the middle
of the semiconductor band gap, as shown in a current-voltage curve. Extra
states are also present at the edges. The formation of these states is ex-
plained in a simple rebonding model.
Samenvatting

In dit proefschrift zijn raster tunnel microscoop (STM) metingen beschreven, die zijn gedaan op het schone GaAs(110) oppervlak. De invloed van verschillende (punt) roosterfouten (Si donoren, Zn en Cd acceptoren, vacatures en stappen) nabij het (110) oppervlak is bestudeerd. De studie aan enkele roosterfouten in halfgeleider materialen is interessant vanuit fundamenteel oogpunt, maar zal in de toekomst ook van technisch belang zijn voor het ontwerp van electronische devices ter grootte van een vierkante nanometer.

Alle metingen zijn verricht bij 4.2K. Dit heeft verscheidene voordelen in vergelijking met metingen die bij kamer temperatuur worden gedaan. Ten eerste, omdat STM metingen bij lage temperatuur niet worden verstoord door temperatuur-drift. Ten tweede, wordt hogere energie resolutie bereikt in spectroscopie metingen. Ten derde, is het mogelijk, door onze preparaten te klieven bij 4.2K, schone halfgeleider-oppervlakken te bestuderen voor langer dan een week.

Om onze lage temperatuur metingen te vergelijken met metingen gedaan bij kamer temperatuur zijn we in hoofdstuk 2 gestart met het geven van een overzicht van de STM metingen die door anderen zijn gedaan op III-V samengestelde halfgeleiders. Dit hoofdstuk is opgedeeld in verschillende secties handelend over schone oppervlakken, doping atomen, missende atomen, defecten, adsorbaten, multilagen and tunnel geïnduceerde luminescentie experimenten.

In hoofdstuk 3 hebben we de lage temperatuur STM beschreven die we voor onze experimenten hebben gebruikt en volledig in eigen huis is gebouwd. We hebben laten zien dat de STM is uitgerust met een faciliteit om automatisch met de tip het preparaat te naderen en een station waarin kan worden gekliefd. Met behulp van dit klief-station kunnen we onze preparaten in situ klieven bij lage temperaturen. Op deze manier worden schone halfgeleider-oppervlakken verkregen bij 4.2K.

In hoofdstuk 4 hebben we de karakteristieke patronen bestudeerd zicht-
baar op het GaAs(110) oppervlak die zijn veroorzaakt door de onder het oppervlak gepositioneerde Si_0 donor atomen. In opnames van de gevulde toestanden zijn rond deze atomen ladingsdichtheids oscillaties (Friedel oscillaties) waargenomen. De opnames van de lege toestanden laten patronen in de vorm van kleine heuveltjes zien. Het verschil tussen deze gevulde en lege toestanden opnames wordt toegeschreven aan de opeenhoping en lediging respectievelijk van ladingsdragers aan het oppervlak veroorzaakt door tip geïnduceerde bandbuiging. Dit is theoretisch verklaard met behulp van een simpel 1-dimensionaal model van de STM junctie. De afhankelijkheid tussen de aangelegde spanning op het preparaat, de polariteit van de spanning, de tunnel stroom, de diepte van het donor atoom en het gevormde patroon aan het oppervlak is experimenteel bevestigd. Twee modellen zijn geponeerd, die deze experimentele resultaten vrij goed beschrijven. Spectroscopie metingen boven de gevormde patronen laten stappen en pieken in de tunnel stroom zien als functie van de preparaat spanning. Deze onregelmatigheden worden toegeschreven aan resonanties over de potentiaalputten die zijn geïsoleerd door de positief geladen Si donoren.

In hoofdstuk 5 is de invloed van enkele Zn en Cd atomen op de electronische oppervlakte structuur van het GaAs(110) oppervlak bestudeerd. Beide elementen vertonen vergelijkbare resultaten. In opnames van de gevulde toestanden zijn patronen in de vorm van kleine heuveltjes zichtbaar rond de onder het oppervlak gepositioneerde acceptor atomen. In de lege toestand opnames zijn deze kleine heuveltjes vervangen door circel symmetrische kuiljes. In enkele opnames zijn maxima zichtbaar rond deze kuiljes, die worden toegeschreven aan ladingsdichtheid (Friedel) oscillaties. Met het Fermi niveau van de tip in de band gap van de halfgeleider of nabij de rand van de geleidingsband veranderen de kuiljes in driehoeksvormige verhogingen wat wordt uitgelegd als een afbeelding van de golffunctie van de acceptor toestand. De unieke oriëntatie van deze driehoekige patronen is bepaald ten opzichte van het GaAs rooster.

In het laatste hoofdstuk worden de verschijnselen aan het oppervlak bediscussieerd die niet kunnen worden toegeschreven aan de invloed van doping atomen. We noemen de aanwezigheid vanoxide en missende atomen op en nabij het GaAs(110) oppervlak. Naast punt defecten zijn ook stappen waargenomen die zijn gecreëerd door het klieven. Deze stappen zijn geladen en veroorzaken daardoor een verschuiving van het Fermi niveau in de richting van het midden van de halfgeleider band gap, wat duidelijk wordt aangeven in een stroom/spannings-curve. Aan de rand zijn ook extra toestanden aanwezig. Deze worden verklaard aan de hand van een simpel model waarin wordt uitgegaan van de vorming van nieuwe chemische bindingen.
Voor niet-natuurkundigen

In dit laatste hoofdstuk, zal ik in simpele bewoordingen proberen uit te leggen waar dit proefschrift over gaat. De titel van dit proefschrift luidt (vertaald in het Nederlands): studie aan onregelmatigheden nabij het GaAs(110) oppervlak (spreek uit: gallium-arseen één-één-nul oppervlak) met behulp van een raster tunnel microscoop (Engelse afkorting: STM) bij lage temperatuur. Kort gezegd beschrijf ik in dit proefschrift de metingen die ik heb gedaan met behulp van een microscoop (genaamd STM) aan enkele onregelmatigheden in het materiaal gallium-arseen. Wat voor soort onregelmatigheden dit zijn, zal ik zometeen behandelen. Ik zal beginnen met iets te vertellen over het materiaal gallium-arseen (afkorting: GaAs).

GaAs is een materiaal dat van groot technologisch belang is. Het wordt o.a. gebruikt voor het maken van LEDs (light-emitting-diodes, dit zijn de kleine licht-indicatoren op je stereo), vaste stof lasers (in je CD-speler zit een dergelijke laser) en zonnecellen. GaAs is opgebouwd uit twee verschillende chemische elementen, gallium en arseen. Het element gallium is in zijn natuurlijke vorm een zacht zilverwit metaal, arseen is in zijn zuivere vorm een staalgrijze, brosses metaalachtige stof en zeer giftig. GaAs zelf komt niet in de natuur voor en moet daarom kunstmatig worden gefabriceerd. Dit kan volgens verschillende methoden. Twee veel gebruikte methoden zijn de zogenaamde horizontale Bridgman en de Czochralski methode. In beide methoden worden de natuurlijke stoffen arseen en gallium gesmolten waarna ze in contact worden gebracht met een zaadje (een klein stukje GaAs). Door de vloeistof te laten stollen aan het grensvlak met het zaadje (volgens een bepaald temperatuurtraject), wordt een kristal gevormd. Op deze manier kunnen grote GaAs kristallen worden gegroeid.
In deze GaAs kristallen hebben de elementen gallium en arseen een vaste positie ten opzichte van elkaar. In Fig. N.1(a) laten we dit zien. De arseen atomen¹ zijn weergegeven met dichte cirkels, de gallium atomen met open cirkels. We zien dat de arseen atomen zijn gepositioneerd op de hoekpunten en in de midden van de vlakken van een kubus. Dit geldt ook voor de gallium atomen, al is dat niet in deze figuur te zien. De beide kubussen zijn een vaste afstand verschoven van elkaar. Deze kristal-structuur wordt in de natuurkunde ook wel diamant-structuur genoemd, omdat diamant precies op dezelfde manier is opgebouwd (maar dan uit koolstof atomen). In deze figuur is maar een heel klein stukje GaAs getekend. De werkelijke grootte van de getekende kubus is ongeveer de helft van een miljoenste millimeter (0.5 × \( \frac{1}{1,000,000} \) mm). In werkelijkheid moet deze structuur naar boven, onder, links, rechts, voor en achter worden doorgedacht.

De schematische weergave in Fig. N.1(a) is een ideale voorstelling van een GaAs kristal. In praktijk zullen er zich altijd onregelmatigheden in het kristal bevinden. Deze worden gevormd tijdens het groeiproces. Typische onregelmatigheden die voorkomen zijn vacatures en onzuiverheden. Vacatures zijn letterlijk niet opgevulde plekken in het kristalrooster. We spreken van onzuiverheden wanneer andere atomen dan gallium en arseen een positie in het rooster hebben ingenomen. In Fig. N.1(b) zijn beide onregelmatigheden getekend. In het midden van het ondervlak van de kubus is een arseen atoom weggelaten. Dit wordt een arseen vacature genoemd. Verder heeft een silicium atoom de positie van een gallium atoom ingenomen. Dit soort onzuiverheden kunnen met opzet of per ongeluk in het materiaal worden gebracht.

In dit proefschrift heb ik soortgelijke onregelmatigheden als hierboven besproken, bestudeerd en beschreven. Om deze onregelmatigheden te kunnen bekijken hebben we een zeer goede microscoop gebruikt. Typische afmetingen die bekeken moeten worden zijn kleiner dan \( \frac{1}{1,000,000} \) mm. Een normale microscoop is hiervoor niet geschikt. We hebben de metingen gedaan met behulp van een raster tunnel microscoop (Engelse afkorting: STM). Om afbeeldingen te maken heeft deze microscoop geen lenzen maar een zeer scherpe naald. Deze naald wordt dichtbij het oppervlak van het te bestuderen materiaal gebracht. Vervolgens wordt deze naald langs het oppervlak gescand. Omdat de microscoop zeer gevoelig is voor veranderingen in de afstand tussen naald en oppervlak kunnen afbeeldingen worden gemaakt met

¹Atomen zijn ongeveer de kleinste deeltjes waaruit een stof is opgebouwd en worden vaak simpelweg voorgesteld als kleine knikkers met een typische diameter van één 10-miljoenste millimeter.
Figure N.1: (a) Schematische weergave van een GaAs kristal. De arseen atomen zijn aangegeven met dichte cirkels, de gallium atomen met open cirkels. Het zogenaamde (110) kristalvlak is gearceerd weergegeven. (b) In deze figuur zijn zowel een arseen vacature als een silicium onzuiverheid getekend.
Figure N.2: Vier afbeeldingen van metingen gedaan met een STM. (a) silicium onzuiverheid, (b) zink onzuiverheid, (c) arseen vacature en (d) atomaire stappen. De periodieke structuren (zichtbaar in alle vier de metingen) zijn afbeeldingen van gallium of arseen atomen in het oppervlak.

een resolutie beter dan \( \frac{1}{1.000.000} \) mm. Deze resolutie is goed genoeg om de onregelmatigheden te kunnen bestuderen.

In Fig. N.2 worden vier STM afbeeldingen getoond van vier verschillende onregelmatigheden die in het proefschrift zijn beschreven. De hoogteverschillen zoals geregistreerd door de STM zijn weergegeven met behulp van grijswaarden: hoog gelegen gebiedjes zijn in wit weergegeven, laag gelegen gebiedjes in zwart. Van (a) naar (d) zijn respectievelijk een silicium onzuiverheid (een silicium atoom heeft hier de plaats van een gallium atoom ingenomen), een zink onzuiverheid (een zink atoom heeft hier de plaats van een gallium atoom ingenomen), een arseen vacature en mono-atomaire stappen (trapjes met treden ter grootte van één enkel atoom) afgebeeld. Deze onregelmatigheden zijn gelegen nabij het GaAs(110) oppervlak. Dit is het vlak dat vrij komt te liggen wanneer het GaAs kristal wordt gebroken (gekliefd) langs de diagonaal die gearceerd is weergegeven in Fig. N.1(a).
We zien dat een silicium onzuiverheid zich manifesteert als een cirkelvormig patroon met ringen. Deze ringen representeren variaties in de dichtheid van lading. Op de kaft van mijn proefschrift zijn veel van dit soort ringpatronen te zien. Deze patronen worden gevormd door de elektronen. Elektronen zijn kleine deeltjes (nog kleiner dan de atomen) met een bepaalde lading. In een GaAs kristal zijn heel veel elektronen aanwezig. In een kubieke centimeter zitten ongeveer $1.000.000 \times 1.000.000 \times 1.000.000$ elektronen. Simpelweg zou je al deze elektronen kunnen beschouwen als een vloeistof, net zoals water. We weten uit ervaring dat wanneer een kei in het water wordt gegooid, er in het wateroppervlak ringen ontstaan. Iets soortgelijks gebeurt rond silicium onzuiverheden. Door reflectie van elektronen aan die onzuiverheden onstaan ringen in de ladingdichtheid. In dit proefschrift laat ik zien dat deze ringen een directe observatie zijn van een reeds eerder (in 1958) door de Fransman J. Friedel theoretisch voorspeld fenomeen. Deze ringen worden daarom ook wel Friedel oscillaties genoemd.

Dergelijke oscillaties zijn ook waar te nemen rond zink onzuiverheden. Wanneer echter enkele experimentele parameters worden aangepast, veranderen deze cirkelvormige patronen in structuren die meer driehoekig zijn. Dit is te zien in Fig. N.2(b). Tot op dit moment is het onduidelijk waarom een zink onzuiverheid deze vorm heeft.

In Fig. N.2(c) is een arseen vacature afgebeeld. Deze manifesteert zich als een cirkelvormig putje. Dit wordt veroorzaakt door de positieve lading van deze onregelmatigheid. Tenslotte laat ik in mijn proefschrift zien dat in de nabijheid van atomaire stappen (Fig. N.2(d)) ook lading aanwezig is.

Wat is de motivatie voor dit onderzoek? Op de eerste plaats levert dit onderzoek een bijdrage aan de fundamentale kennis van het GaAs(110) oppervlak en van enkele onregelmatigheden. Daarnaast is dit onderzoek ook technologisch interessant. Nu we enkele onregelmatigheden kunnen bekijken en herkennen met een STM, is het mogelijk het groeiprocess van GaAs kristallen te optimaliseren. Dit is vooral interessant voor de groei van dunne GaAs lagen, waar bijvoorbeeld opzettelijk gebiedjes met heel veel onzuiverheden worden gemaakt (de zogenaamde delta-gedoteerde lagen). De optimalisatie van dit soort groeitechnieken is van belang voor de ontwikkeling van nieuwe electronische componenten.
List of Publications

- Progress toward spin-sensitive scanning tunneling microscopy using optical orientation in GaAs,
  R. Jansen, M. C. M. M. van der Wielen, M. W. J. Prins, D. L. Abraham, and H. van Kempen,

- Nieuwe methode voor het meten van oppervlaktemagnetisme op subnanometerschaal,
  M. C. M. M. van der Wielen, R. Jansen, M. W. J. Prins, D. L. Abraham en H. van Kempen,

- Photoamperic probes in scanning tunneling microscopy,
  M. W. J. Prins, M. C. M. M. van der Wielen, R. Jansen, D. L. Abraham, and H. van Kempen,
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Curriculum vitae

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