Wavefunctions and carrier-carrier interactions in InAs quantum dots studied by capacitance-voltage spectroscopy

Dissertation

zur Erlangung des Grades eines Doktors der Naturwissenschaften
in der Fakultät für Physik und Astronomie der Ruhr-Universität Bochum

vorgelegt von

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Bochum
- MMVIII -
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Date of submission: 15 October 2008
Date of disputation: 08 January 2009

ISBN 978-3-00-027007-9 (online)
ISBN 978-3-00-027006-2 (print)
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<tr>
<td>$\alpha$</td>
<td>tilt angle (for magnetic field orientation)</td>
</tr>
<tr>
<td>$\beta$</td>
<td>variable direction for $\vec{k}$ vector in the xy-plane</td>
</tr>
<tr>
<td>$\delta(x)$</td>
<td>Dirac function</td>
</tr>
<tr>
<td>$\epsilon_0$</td>
<td>vacuum permittivity</td>
</tr>
<tr>
<td>$\epsilon_r$</td>
<td>relative dielectric constant</td>
</tr>
<tr>
<td>$\lambda_{QD}$</td>
<td>a quantity equivalent with the Wigner-Seitz radius in QDs</td>
</tr>
<tr>
<td>$\mu_B$</td>
<td>Bohr magneton</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>spin</td>
</tr>
<tr>
<td>$\theta(x)$</td>
<td>Heaviside step function</td>
</tr>
<tr>
<td>$\vartheta$</td>
<td>azimuthal angle (for &quot;in-plane&quot; magnetic field measurements)</td>
</tr>
<tr>
<td>$a_B$</td>
<td>Bohr radius</td>
</tr>
<tr>
<td>$d_{QD}$</td>
<td>low-temperature QDs capping height</td>
</tr>
<tr>
<td>$D$</td>
<td>diffusion coefficient</td>
</tr>
<tr>
<td>$D_0$</td>
<td>pre-exponential factor in the diffusion coefficient</td>
</tr>
<tr>
<td>$E_a$</td>
<td>activation energy</td>
</tr>
<tr>
<td>$g^*$</td>
<td>effective gyromagnetic factor</td>
</tr>
<tr>
<td>$k$</td>
<td>reciprocal space vector</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$l$</td>
<td>orbital quantum number</td>
</tr>
<tr>
<td>$l_i$</td>
<td>(with $i = 1,2$) tunneling, respectively blocking barriers in the heterostructure</td>
</tr>
<tr>
<td>$l_B$</td>
<td>characteristic length (2D harmonic oscillator)</td>
</tr>
<tr>
<td>$L_n^{[l]}$</td>
<td>generalized Laguerre polynomials</td>
</tr>
<tr>
<td>$L_D$</td>
<td>diffusion length of atoms</td>
</tr>
<tr>
<td>$M$</td>
<td>tunneling matrix element</td>
</tr>
<tr>
<td>$m^*$</td>
<td>effective mass</td>
</tr>
<tr>
<td>$m_0$</td>
<td>electron rest mass</td>
</tr>
<tr>
<td>$r_s$</td>
<td>Wigner-Seitz radius</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
</tr>
<tr>
<td>$t(B)$</td>
<td>transmission coefficient through the tunneling barrier</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>$T_{Bardeen}$</td>
<td>Bardeen transfer-matrix element between the emitter and the quantum dot states</td>
</tr>
<tr>
<td>$V_{bi}$</td>
<td>built-in potential</td>
</tr>
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<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>AFP</td>
<td>Lehrstuhl für Angewandte Festkörperphysik</td>
</tr>
<tr>
<td>CLCC</td>
<td>Ceramic Lead Chip Carrier</td>
</tr>
<tr>
<td>C(V)</td>
<td>Capacitance - Voltage</td>
</tr>
<tr>
<td>DIP</td>
<td>Dual in-line Package (chip carrier)</td>
</tr>
<tr>
<td>DLTS</td>
<td>Deep Level Transient Spectroscopy</td>
</tr>
<tr>
<td>EMA</td>
<td>Effective Mass Approximation</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full-Width at the Half Maximum</td>
</tr>
<tr>
<td>HFML</td>
<td>High Field Magnet Laboratory</td>
</tr>
<tr>
<td>LCR (~meter)</td>
<td>Inductance-capacitance-resistance measuring equipment</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular Beam Epitaxy</td>
</tr>
<tr>
<td>ML</td>
<td>Monolayer</td>
</tr>
<tr>
<td>nD</td>
<td>n-dimensional ($n = 0, 1, 2, 3$)</td>
</tr>
<tr>
<td>PBN</td>
<td>Pyrolytic Boron Nitride</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>QD(s)</td>
<td>Quantum Dot(s)</td>
</tr>
<tr>
<td>QW</td>
<td>Quantum Well</td>
</tr>
<tr>
<td>QWR</td>
<td>Quantum Wire</td>
</tr>
<tr>
<td>RHEED</td>
<td>Reflection High Energy Electron Diffraction</td>
</tr>
<tr>
<td>RTA</td>
<td>Rapid Thermal Annealing</td>
</tr>
<tr>
<td>RUB</td>
<td>Ruhr-Universität Bochum</td>
</tr>
<tr>
<td>s, p, d, f</td>
<td>Atomic orbital nomenclature (Sharp, Principal, Diffuse, Fundamental)</td>
</tr>
<tr>
<td>SAQD</td>
<td>Self-Assembled Quantum Dot</td>
</tr>
<tr>
<td>S-K</td>
<td>Stranski-Krastanow</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>slm</td>
<td>Standard liter per minute</td>
</tr>
<tr>
<td>SP160</td>
<td>Shipley Photoposit 160</td>
</tr>
<tr>
<td>SPS</td>
<td>Short-Period Superlattice</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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<tr>
<td>UHV</td>
<td>Ultra High Vacuum</td>
</tr>
<tr>
<td>WKS</td>
<td>Worksheet</td>
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<tr>
<td>WL</td>
<td>Wetting Layer</td>
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Chapter 1

Introduction

1.1 Motivation

Materials have been playing a very important role throughout human history, mastering their properties being the backbone of the evolution of humankind. The most important criterion which differentiates hominidae from primates and, in general, from the intelligent mammals is the ability of using and creating tools. There is no better classification, at least for the early stages of our evolution, than the classification made by the materials used for making tools. According to this, the periods in human history are classified as Stone, Bronze and Iron Ages. More recently, since the Industrial Revolution, the civilization has entered a Steel Age; the technological evolution has been accelerated as more and more break-through discoveries were made such that the epochs change more frequently. As a consequence, since the half of the last century most of the world has already entered a new period - a Semiconductor Age. Semiconductors are part of everyday life, as electronic devices have been brought to use in so many tools and equipment we use today.

Different semiconductor materials can be used in the electronics industry. Germanium was initially used for the creation of the first transistor at Bell Labs in 1947 [1]. But due to its unbeatable advantages like abundance, which makes it easy to process, and the fact that its natural oxide is one of the best available insulators, Silicon is by far the most commonly used semiconductor. However, for special applications like high-frequency transistors and most of the optoelectronic devices, Gallium arsenide is preferred. Its main advantage consist in the fact that GaAs has a direct band gap which makes it very efficient in light emitting diodes and lasers but also for infrared detectors and solar cells when combined with Aluminium or Indium [2].

With the invention of the integrated circuit, the evolution of electronics went beyond any imagination. Very large scale integrated circuits today contain several billions transistors on a single chip, capable of performing a huge number of logical operations at great speed, being the core of modern computers. Telecommunications took also advantage of the advances in electronics: vacuum-tube amplifiers and switches used in the 1930’s have been replaced by transistorized ones; more recently, with the development of light emitting diodes (LED’s), laser diodes and photodetectors, fiber-optics communications offered the possibility to increase by several orders the data traffic.

The quest for obtaining increased device performance of the semiconductor lasers used in fiber-optic communications has lead researchers to exploit quantum effects in
heterostructure semiconductor lasers [3]. The quantum well (QW) laser showed improved efficiency and a lower threshold current than bulk semiconductor lasers [4]. The threshold current, i.e. the minimum injection current for which lasing is observed, was found to be less temperature sensitive than that of a conventional double heterostructure [5]. This has been ascribed to the changes in the electrons density of states produced by decreasing the dimensionality from 3D to 2D. Consequently, even more improvements can be obtained by reducing further the dimensionality. The idea was introduced and studied in 1982, when Arakawa and Sakaki have obtained 1D confinement by placing a quantum well laser in a strong magnetic field [6]. From this point of view, the ultimate challenge would be to create 3D carrier confinement in semiconductors. Such regions in a semiconductor, possessing truly 0D properties, are commonly referred as quantum boxes or quantum dots (QDs). They have unique properties, similar to those of atoms, making possible the fabrication of fascinating novel devices [7].

Quantum dots are potential candidates for electronic memories and especially optoelectronic devices. They have been proposed for extremely low threshold current lasers as well as for single photon sources. Quantum computers and quantum cryptography will, maybe, one day benefit of the atom-like properties of the quantum dots [8, 9].

Nevertheless the quantum dots are interesting not only from an application point of view; they are interesting from a fundamental point of view as well. Although they have a quantized spectrum just like atoms, the energy scales are different. Moreover, the dimensions of the quantum dots are much larger than those of atoms. In consequence, some of the experiments which are not possible in atomic physics can be easily performed on quantum dots [10].

For these reasons, quantum dots have been studied intensively in the last two decades. A classification made in 2006 based on a variant of Hirsch’s index showed the quantum dots are one of the hottest topics in physics, after the carbon nanotubes and quantum wires [11].

Quantum dots are also the topic of this thesis. The work is concerned specifically with InAs self-assembled quantum dots grown in a GaAs matrix by molecular beam epitaxy (MBE). Their basic properties will be exploited and tuned in an attempt to acquire new knowledge on the subject. One way to accomplish this is to study the influence of a magnetic field on the quasi-particle wavefunctions for valence band states, knowing the fact that at some point a crossing of the energy levels will occur. It would be interesting to know how the shape of the wavefunctions will change as a consequence of this crossing. This could offer the opportunity of finding a consistent explanation for the charging sequence of holes in self-assembled quantum dots, a question which is still under debate [12, 13, 14]. The second objective of the thesis is to find whether or not the methods used to tune optical properties of the quantum dots have any influence on the carrier-carrier interactions inside. Coulomb blockade energies in the electron ground state will be studied by employing capacitance-voltage spectroscopy ($C(V)$) and discussed in the context of the results obtained from photoluminescence ($PL$) spectroscopy.
1.2 Thesis overview

In the present chapter, the motivation for starting this work was given. The following chapter will introduce the concept of quantum dot as an "artificial atom" and will discuss some of the theoretical aspects which will be needed later on for explanations and interpretation of the results.

The third chapter will discuss in detail the growth of self-assembled quantum dots by MBE. Subsequently, two different methods which have been employed to tune their properties will be discussed: Indium-flushing and rapid thermal annealing (RTA).

Chapter 4 is reserved for details concerning the fabrication of the samples and the methods which have been used for the characterization, namely PL and C(V) spectroscopy. The latter will receive a special attention, as it is also the tool used for the characterization of the samples in a magnetic field.

The following two chapters contain the original contribution of this thesis. The first one of them, Chapter 5, addresses the fundamental properties of the quantum dots. It will present the results obtained for hole wavefunctions in a constant perpendicular magnetic field. Chapter 6 is more application-oriented and deals with energy level engineering of self-assembled quantum dots. The results for the ground state electron-electron interaction energies are compared for the case of Indium-flushing, respectively RTA, in order to find which one of these methods is more suitable for further realization of single-photon sources which desired photon energies. Finally, the results are summarized in the last chapter.

As an integral part of this thesis, supplementary information not contained in the main part are enclosed in several appendices. In Appendix A, the growth recipes of the samples used in this work are provided. They contain important information about the parameters of the MBE growth, for example: substrate and cells temperatures, background pressures, Indium amount and crystal orientation.

In Appendix B, the method used to determine the crystal directions is described. This has been done in order to obtain the correct asymmetry for the plots corresponding to the probability densities presented in Chapter 5.

Given the considerable amount of data which are due to be processed in order to obtain the fan-plots and the wavefunction maps, automatization was indispensable. The code developed for Origin® to facilitate the data processing and handling is provided in Appendix C. This might be helpful for other students which are following the same steps. The code is fully commented and explained, therefore it can be easily adapted to perform different other tasks.
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Chapter 2

Properties of semiconductor quantum dots

The purpose of this chapter is to prepare the ground for the rest of the thesis, making a necessary introduction so that the contents of the following chapters will come in a natural way. Therefore, a description of the basic concepts related with the quantum dots will be presented in the following pages.

The first section of the chapter will answer the questions "What are the quantum dots?" and "How are they obtained?". Different types of quantum dots will be briefly discussed, starting from the methods used for their preparation. The second section is reserved for a theoretical description of the quantum dots with respect to their energy spectra, wavefunctions and carrier interactions.

2.1 Quantum dots

2.1.1 From atoms to "artificial atoms"

The properties of all materials are inherently related with the atoms they are made of and the manner they interact to form more complex structures. The following paragraphs will take the reader in a short journey from atoms to solids and back to a different kind of "atoms".

The concept of atom was developed since antiquity, yet it was not until the 19th century that this concept was elaborated on a scientific basis. The discovery of the electron has led to the planetary model of Rutherford and, after the creation of the quantum theory, the Bohr model was introduced to prevent the collapse of the electron onto the nucleus. However, this model was able to describe only partially the hydrogen atom but failed when applied to more complex ones. The progress came when de Broglie proposed that all moving particles have a wave-like behaviour (the wave-corpuscle duality). The modern atomic theory uses the Schrodinger equation to describe the electrons in terms of probabilities. Now, it is known that the energies of bound electrons are discrete and precisely defined within the limits of the Heisenberg’s uncertainty. However, the Schrödinger equation is impossible to be solved exactly, even numerically, except for the simplest atom [15]. Given the fact the atomic potential has a spherical symmetry of the form 1/r, the Schrödinger equation can be separated in a radial and an angular part. Consequently, the solutions depend on three quantum
numbers \((n, l, m)\), known as the principal, orbital and magnetic quantum numbers respectively.

The results obtained for the hydrogen atom can be extended to describe qualitatively the ground-state electron configuration of heavier atoms. To a first approximation, the individual electrons will occupy the one-particle hydrogenic states \((n, l, m)\) called orbitals which are filled respecting Pauli’s principle and Hund’s rule (see for example [16]). In Figure 2.1 the first atomic orbitals are illustrated, with the usual nomenclature \(s, p, d \cdots\) corresponding to \(l = 0, 1, 2, \cdots\).

![Figure 2.1: The orbitals are particular solutions of the Schrödinger equation for electrons in the atom - wavefunctions with given values of \((n, l, m)\). The orbitals presented here give the spatial region where there is a 95% probability of finding an electron; the blue and red colours highlight the different wave-phases. Reproduced from [17] by permission.](image)

Atoms can interact to form molecules or can arrange themselves in large ensembles extending in all three spatial directions. When atoms are packed close together, they interact strongly which makes the ensemble to become rigid, i.e. the solid state. When the arrangement of the atoms follows a periodic pattern on all the spatial directions, the solid state is called crystalline.

Owing to their small mass compared with the ions in the nodes of the crystal lattice, the valence electrons in the crystal can be treated as a separate system. In the adiabatic approximation the ion rests remain fixed or slowly oscillating, therefore the problem can be reduced to a multi-electronic one. In the expression of the Hamiltonian of this system, the potential energy contains one term describing the Coulomb interaction of the electrons with the fixed ions and another term, \(1/2 \sum_{i \neq j} V(\vec{r}_i - \vec{r}_j)\), describing the interaction between the electrons. In the frame of the uni-electronic approximation the latter is replaced by an effective potential, created by all the other electrons in the crystal acting upon a particular one. Therefore, the Hamiltonian can be written as a sum of single-particle terms

\[
H = \sum_i H_i = \sum_i -\frac{\hbar^2}{2m_0} \nabla^2_i + V_i(\vec{r}) + V_{eff}^i(\vec{r}),
\]

(2.1.1)
where \( V_i \) is the potential energy of the \( i^{th} \) electron in the field of the fixed ions and \( V_{\text{eff}}^i \) is the potential energy of the electron in an effective potential created by all other electrons in the crystal. One has to take into account the periodicity given by the crystal lattice (Bloch theorem) which will result in new concepts like the effective mass and allowed and forbidden energy bands. The fact that the potential \( V(\mathbf{r}) = V + V_{\text{eff}} \) is unknown makes the problem difficult to solve. However, some approximations can be made. For example, in the tight binding approximation [18, 19], the electron energy in the crystal is given by its corresponding energy in the atom plus a supplementary term containing the so-called exchange and overlap integrals. It is this supplementary term, a periodic function of the wave-vector \( \mathbf{k} \), which transforms an atomic level into an energy band.

The existence of allowed and forbidden (quasi-continuous) energy bands is a characteristic of solids, as a signature of the (periodic) potential [16]. Yet, metals semiconductors and insulators have different properties. This is a result of the degree of occupation with electrons in those bands. For metals, at absolute zero temperature, the last occupied level lays inside an allowed energy band while for insulators it coincides with the highest allowed energy in the band. The last permitted band which is filled with electrons (at \( T = 0 \) K) is called the valence band (VB) and the following one the conduction band (CB), the two being separated by a forbidden band (band gap) \( E_g \). If \( E_g \) is not so large (<2.4 eV), at \( T \neq 0 \) K some of the electrons in the valence band have enough energy to jump in the conduction band leaving a hole behind. The introduction of electrons in conduction band or of holes in valence band can be realized also by doping the crystal. These materials are called semiconductors and they possess extraordinary properties which make them essential in the electronic devices today.

The energy spectrum of the carriers in the valence, respectively conduction band, is obtained by solving the Schrödinger equation

\[
\left[ -\frac{\hbar^2}{2m^*} \nabla^2 + V(\mathbf{r}) \right] \Psi(\mathbf{r}) = E \Psi(\mathbf{r}), \tag{2.1.2}
\]

where \( \Psi(\mathbf{r}) \) is the envelope wave-function, \( m^* \) is the carrier effective mass and \( V(\mathbf{r}) \) is the potential energy of the electron (hole) in the crystal.

For a 3D semiconductor crystal, electrons with the mass \( m^* \) behave like free electrons and their energy is quadratic in the wave-vector \( \mathbf{k} = (k_x, k_y, k_z) \):

\[
E_{3D} = \frac{\hbar^2 k^2}{2m^*}. \tag{2.1.3}
\]

Reducing strongly one of the dimensions of the system, \( L_x \) in Figure 2.2 (a), the electrons are no longer free to move along that direction, but are still free to move in a plane (\( y, z \)). This kind of 1D confinement can be realized by embedding a semiconductor material in another one having a wider band gap. For a quantum well (QW), the energy becomes

\[
E_{2D} = \frac{\hbar^2}{2m^*} \left( n_1 \frac{\pi}{L_x} \right)^2 + \frac{\hbar^2 k_y^2}{2m^*} + \frac{\hbar^2 k_z^2}{2m^*}. \tag{2.1.4}
\]

A quantum wire (QWR) represents a system confined along two spatial directions \( L_x \) and \( L_y \), and its energies are in the form

\[
E_{1D} = \frac{\hbar^2 \pi^2}{2m^*} \left( n_1^2 \frac{L_x^2}{L_y^2} + n_2^2 \right) + \frac{\hbar^2 k_z^2}{2m^*}. \tag{2.1.5}
\]
Reducing the third dimension as well, the carriers are confined to a box with dimensions $L_x, L_y, L_z$. Such a 0D structure is called quantum dot (QD). Its energies are written:

$$E_{0D} = \frac{\hbar^2 \pi^2}{2m^*} \left( \frac{n_1^2}{L_x^2} + \frac{n_2^2}{L_y^2} + \frac{n_3^2}{L_z^2} \right).$$  \hspace{1cm} (2.1.6)

In the above expressions of the energies, $n_1, n_2, n_3 \in \mathbb{N}^*$ are the quantum numbers arising from the imposed conditions at the boundaries of the confined regions.

The corresponding densities of states for the first three cases, including the spin degeneracy, are the following:

$$\rho_{3D} = \frac{1}{2\pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{3/2} E^{1/2};$$  \hspace{1cm} (2.1.7)

$$\rho_{2D} = \frac{m^*}{\pi \hbar^2 L_x} \sum_{n_1} \delta(E - E_{n_1});$$  \hspace{1cm} (2.1.8)

$$\rho_{1D} = \frac{(2m^*)^{1/2}}{\pi \hbar L_x L_y} \sum_{n_1, n_2} (E - E_{n_1, n_2})^{-1/2}.$$

Figure 2.2: (a) Schematic comparison of typical dimensions of bulk material, quantum wells, quantum rings, respectively quantum dots. The confinement is realized by embedding a semiconductor into another one with a larger band gap. (b) The corresponding densities of states for the structures shown in (a). Energies are indexed by the corresponding quantum numbers $n_{1,2,3}$ and $E_C$ is the lower margin of the conduction band.
In the particular case of the quantum dot obtained by 3D confinement, there is no dispersion of energy with \( \vec{k} \) (Eq. 2.1.6), thus the density of states depends only on the number of the confined levels [20]. A plot of the density of states would be just a series of \( \delta \) functions

\[
\rho_{0D} = \frac{2}{L_x L_y L_z} \sum_{n_1, n_2, n_3} \delta(E - E_{n_1, n_2, n_3}).
\]  (2.1.10)

(In the expressions above \( \theta(E - E_n) \) and \( \delta(E - E_n) \) are the Heaviside respectively Dirac functions.)

In Figure 2.2 (b), a plot for the densities of states in each possible case of confinement is shown. One can observe the discrete energy spectrum for the quantum dots, a striking similarity with the well-known result for the atom. It is because of this similarity that the quantum dots are often called superatoms or artificial atoms. In Figure 2.3,

![Figure 2.3](image)

*Figure 2.3: The real atom and the quantum dot: artificial structures that confine electrons and holes in all spatial directions give rise to a discrete energy spectrum similar with the case of atoms. A comparison of the (lateral) dimensions and energy scales between quantum dots and atoms reveal nevertheless the differences.*

...the lateral dimensions and the energy scales of such an artificial atom are shown in comparison to the ones of a real atom. Obviously, the QDs are much bigger their real "counterparts". The lateral dimensions for the QDs discussed in the following chapters are in the range of 30 nm, while the Bohr radius is \( a_B \approx 0.5 \text{ Å} \). The experimental results on different types of QDs revealed inter-sublevel energies of the order of several tens of meV while in atoms, these energies are 3 orders of magnitude higher. Because of this fact, the artificial atoms are very sensitive to temperature fluctuations (\( k_B T \approx 26 \text{ meV at room temperature} \)).

### 2.1.2 Semiconductor quantum dots

Owing to their small size, quantum dots have much to offer in the near future technology. As the size decreases, material properties change dramatically due to the quantum effects triggered by the strong confinement of electrons and holes. In the world of
quantum dots, the size is so important that even the addition or removal of a single electron will make a difference.

There are several methods to obtain the 3D carrier confinement, leading to different quantum dots types. A brief description of these quantum dots types will be given in the following.

The colloidal synthesis of small nano-objects dates back from the first half of the 20th century. Initially, they have been used to realize colour filters until mid 1980's when quantum confinement in such systems has been demonstrated. By now, colloidal quantum dots can be produced in large quantities (in the order of grams) and different sizes by chemical synthesis. This method is rather cheap and fast, compared with other methods. Quantum dots with special optical properties inherited from the size of the nano-particles obtained in this way have found uses as dyes in biology (e.g., markers for both in vitro and in vivo) and optics. Recently, LEDs manufactured with polymers incorporating colloidal quantum dots have been realized, yielding amazing colours [21]. Although this type of dots can be fabricated in different sizes and, more than that, can be functionalized by attaching to them different biological receptors, their electrically isolating matrix prohibits electric injections so that their use in optoelectronics is limited.

A second type of quantum dots can be realized by lateral electrostatic confinement of electrons in a 2D electron gas (2DEG) or by lateral patterning followed by vertical mesa etching. By the end of 1980's, the fabrication of quantum dots by patterning of quantum wells was at its peak. It still attracts much attention today due to the fact that it has several advantages [7]:

• quantum dots of almost arbitrary lateral shape can be realized, depending on the resolution of the lithographic technique used;

• easily available and reliable wet or dry etching techniques, combined with optical lithography, electron or focussed ion beam lithography, scanning tunneling microscopy (STM), etc.;

• it is compatible with modern, large-scale integrated semiconductor technology.

In practice, one can create pillars with the radius of about 100 nm by etching a quantum well structure, obtaining in this way a quantum dot inside the pillar. The dot is sandwiched between two non-conducting barrier layers which separate it from the conducting material above and below - the source and drain contacts. The application of a negative voltage to a metal gate around the pillar squeezes the diameter of the dot’s lateral potential. This would reduce the number of the confined electrons, one by one, until the dot is completely empty [10]. A variant of this method consists in the deposition of metal electrodes at the surface of a sample containing a shallow 2DEG region. The application of a voltage on these electrodes will confine the electrons of the 2DEG gas to a small region between the electrodes.

The third method which can be employed to obtain 0D systems is the cleaved-edge overgrowth, which leads to the formation of quantum dots at the junction of three orthogonal quantum wells. This growth method was proposed in 1997 by Grundmann and Bimberg and realized in the same year by Wegscheider in the AlGaAs/GaAs system [7]. Judging from the occurrence in the literature, this is the least used method for QD preparations.
The preparation method which is currently the most widely used is the self-assembly on strained epitaxial layers. By using this method, quantum dots several nanometers high with a diameter around 30 nm can be obtained. Basically, the method consists in a phase transition, from an epitaxial structure (wetting layer) to islands with very similar shapes and high degree size-uniformity. The method allows also stacking of quantum dot layers with the possibility of interaction between these layers. In this way, "artificial molecules" can be created and studied [10]. Another possibility is to obtain quantum rings by allowing the re-evaporation of the central part of a quantum dot.

The island formation in strained heteroepitaxy has been observed in several material systems. Among them InAs/GaAs, InAlAs/AlGaAs, InAs/InP, InP/GaAs, Ge/Si, CdSe/ZnSe and GaN/AlGaN [7]. The most studied of them all is the InAs/GaAs system.

InAs/GaAs self-assembled quantum dots (SAQDs) grown by molecular beam epitaxy (MBE) will be the focus of this work. A detailed description of the quantum dot formation via self-assembly will be given in Section 3.2. For now, only a model which will be used to further describe the InAs QDs is presented in Figure 2.4.

**Figure 2.4:** Model for a lens-shaped self-assembled InAs quantum dot grown on top of the wetting layer, without capping. The model of the quantum dot has circular symmetry, a base diameter of 35 nm and 8 nm height. Darker regions correspond (approximately) to highly strained InAs on GaAs substrate.

The model depicts a spherical cap quantum dot laying on a fully strained wetting layer (WL) representing the remainder of the 2D bed before the island nucleation. Although different shapes can be obtained depending on the growth conditions, here, a lens-shaped quantum dot with circular symmetry has been chosen. The usual dimensions for such islands are a diameter of ≈ 35 nm and a height of ≈ 8 nm. The darker colours represent highly strained InAs on GaAs surface, while lighter colours encode the strain relaxation towards the top of the 3D island.
2.2 Theoretical description of the quantum dots

The properties of semiconductor quantum dots are deduced from a simple theoretical model - the harmonic oscillator. The energy levels, the wavefunctions and the Coulomb interactions will be the focus of the following section.

2.2.1 Two dimensional harmonic oscillator

Because the electrons and holes confined in the quantum dots belong to the constituent semiconductor material, they can still feel the influence of the underlying lattice. It is customary to introduce the effective mass approximation (EMA) which considers that the conduction electrons (valence holes) in the quantum dot form a separate interacting system with an effective mass \( m^*_{el,h} \) and their mutual Coulomb interaction is screened with the static dielectric constant \( \varepsilon_r \) of the semiconductor the dots are made of [22].

For a system of \( N \) electrons or holes, the many-body Hamiltonian can be written as

\[
H = \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m^*} \nabla_i^2 + V(\mathbf{r}_i) \right) + \frac{1}{2} \frac{e^2}{4\pi\varepsilon_0\varepsilon_r} \sum_{i,j=1}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|^2},
\]

where the first term on the right hand side contains the single-particle contribution and the second term accounts for the Coulomb interactions between the carriers confined in the same dot. The interactions between carriers in different dots have been neglected here and this is justified by the fact that the dot spacing is larger than the dot sizes. In the expression above \( m^* = m^*_{el,h} \) and \( e = |e| \) is the elementary charge. Including also the contribution of a magnetic field, the Hamiltonian becomes

\[
H = \sum_{i=1}^{N} \left\{ \frac{1}{2m^*} (-i\hbar \nabla_i + e\mathbf{A}(\mathbf{r}_i))^2 + V(\mathbf{r}_i) \right\} + \frac{1}{2} \frac{e^2}{4\pi\varepsilon_0\varepsilon_r} \sum_{i,j=1}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|^2} + g^* \mu_B \mathbf{\sigma} \cdot \mathbf{B}.
\]

The last term is the Zeeman energy with \( g^* \) being the effective gyromagnetic factor, \( \mu_B \) the Bohr magneton, while \( \mathbf{A} \) is the vector potential generating the magnetic field \( \mathbf{B} \).

Different shapes for the SAQDs have been reported. Usually, pyramidal or lens-shaped quantum dots are considered. The confinement potential \( V(\mathbf{r}_i) \) is not exactly known, but some assumptions can be made based on the fact that the lateral dimensions of the dot are several times larger than the vertical ones. This results in vertical confinement energies almost one order of magnitude larger than the lateral confinement ones, such that the effective confinement potential can be separated into an in-plane and a perpendicular part:

\[
V = V(x,y) + V(z).
\]

The confinement potential along the growth direction, \( V(z) \), can be chosen either as a harmonic potential \( (1/2 \ m^* \omega_z^2 z^2) \), a square well, or a zero-width infinite barrier to describe spherical, cylindrical, or disk-shaped QD structures, respectively [23]. The quantum dot in Figure 2.4 can be taken as a model for the further discussion. Assuming the vertical confinement is so strong that only the ground state is occupied, as it can be
Figure 2.5: Assuming the vertical confinement (along $z$) is so strong that only the ground energy level is occupied, one can take the lateral confinement of the QD as being parabolic. In this figure, the widths of the potential wells representing the vertical confinement are equal with the heights of the lens-shaped quantum dot at the positions indicated by the dotted lines.

seen from Figure 2.5, one can consider the lateral confinement potential to be parabolic [24]:

$$V(x, y) = \frac{1}{2} m^* \omega_0^2 (x^2 + y^2).$$

(2.2.4)

The terms $h\omega_0$ and $h\omega_z$ used above stand for the in-plane, respectively vertical confinement energies.

In an adiabatic approximation, one can separate the in-plane component of the wave function from the one along $z$ direction:

$$\Psi(\vec{r}) = \psi(x, y) \varphi(z).$$

(2.2.5)

The Schrödinger equation $H\Psi = E\Psi$ decouples in this case. Moreover, with the consideration made above, that only the lowest single-particle state perpendicular to the dot plane is occupied, neglecting, for the moment, the Coulomb and Zeeman terms, the problem to be solved reduces to finding the eigenstates of a 2D harmonic oscillator. For an applied magnetic field perpendicular on the dot plane ($\vec{A} = \vec{B} \times \vec{r}/2 = (-y, x)B/2$ in the symmetric gauge), the Schrödinger equation can be solved analytically, leading to a spectrum generally known as Fock-Darwin states [25, 26]:

$$E_{n,l} = (2n + |l| + 1) \hbar \omega + \frac{1}{2} l \hbar \omega_c,$$

(2.2.6)

with

$$\omega_c = \frac{eB}{m^*}$$

(2.2.7)

the cyclotron frequency, and

$$\omega = \sqrt{\omega_0^2 + \left(\frac{\omega_c}{2}\right)^2}$$

(2.2.8)

the effective oscillator frequency. In Eq. 2.2.6, $n$ and $l$ are respectively radial and angular momentum quantum numbers, with $n \in \mathbb{Z}^+$ and $l \in \mathbb{Z}$. In analogy with the atomic physics, the Fock-Darwin states can be indexed by the angular momentum quantum number as being $s$-, $p$-, $d$-like, and so on.
2.2. THEORETICAL DESCRIPTION OF THE QUANTUM DOTS

From the considerations above, the symmetry of the system is cylindrical. This leads to a shell structure with the magic numbers 2, 6, 12, 20, ... with the respective 2, 4, 6, 8, ... fold degeneracies. For atoms, the 3D spherically symmetric potential was responsible for the apparition of shells 1s, 2s, 2p, 3s, 3p, 4s, 3d, ... with the degeneracies 2, 10, 18, 36, ... In this respect, the quantum dots are regarded as being the 2D analogs of real atoms. Due to their larger size and different inter-sublevel energies, they offer the possibility of carrying out experiments which cannot be performed in atomic physics [10].

<table>
<thead>
<tr>
<th>orbital</th>
<th>n</th>
<th>l</th>
<th>energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>0</td>
<td>0</td>
<td>$\hbar \omega$</td>
</tr>
<tr>
<td>$p_-$</td>
<td>0</td>
<td>-1</td>
<td>$2\hbar \omega - \frac{1}{2} \hbar \omega_c$</td>
</tr>
<tr>
<td>$p_+$</td>
<td>0</td>
<td>1</td>
<td>$2\hbar \omega + \frac{1}{2} \hbar \omega_c$</td>
</tr>
<tr>
<td>$d_-$</td>
<td>0</td>
<td>-2</td>
<td>$3\hbar \omega - \hbar \omega_c$</td>
</tr>
<tr>
<td>$d_0$</td>
<td>1</td>
<td>0</td>
<td>$3\hbar \omega$</td>
</tr>
<tr>
<td>$d_+$</td>
<td>0</td>
<td>2</td>
<td>$3\hbar \omega + \hbar \omega_c$</td>
</tr>
</tbody>
</table>

Table 2.1: Eigenenergies for a 2D quantum dot in magnetic field according to Fock-Darwin theory. The shells are indexed with the angular momentum $l$.

Table 2.1 lists the first eigenenergies of a 2D harmonic oscillator which is used as a model for a flat circular dot. The corresponding quantum numbers $(n, l)$ and the convention for the naming of the shells is also given.

Figure 2.6: Fock-Darwin states: dispersion of single-particle energetic states of a 2D quantum harmonic oscillator in magnetic field. Calculations for a parabolic potential with $\hbar \omega_0 = 3$ meV. The field is applied along $z$. Each state is two-fold spin degenerate.

The Fock-Darwin spectrum is shown in Figure 2.6. It gives the magnetic field dependence of the lowest single-particle electron states for a quantum dot calculated with
\( h \omega_0 = 3 \text{ meV} \) and \( m^* = 0.067 m_0 \). At \( B = 0 \text{ T} \), the levels are equally spaced but, as the field increases, they start crossing and shift until they coalesce into the free-electron Landau levels.

From Eq. 2.2.6, one can see the energies are degenerated at \( B = 0 \text{ T} \) and that the degeneracies are partially lifted in magnetic field. A partial lifting of the \((2n + |l| + 1)\)-fold degeneracies can be also obtained by taking the confining potential slightly asymmetric \( V(x, y) = 1/2 m^* \omega_0^2 (\delta x^2 + 1/\delta y^2) \), i.e. breaking the circular symmetry. For very small \( \delta \), however, the Fock-Darwin states of the anisotropic oscillator are very similar with the ones given by Eq. 2.2.6 [27, 28].

Although the energy dispersion in Figure 2.6 depicts exemplarily the Fock-Darwin states of a harmonic oscillator, the parameters used in the simulations were taken for a quantum dot with weak confinement, as in the case of the dots obtained by vertical mesa etching. In Figure 2.7, a simulation for electrons confined with \( h \omega_0 = 50 \text{ meV} \) is made. This energy is more appropriate for the self-assembled InAs quantum dots like the ones used for the experiments in here (for holes \( h \omega_0 \) is smaller due to a larger effective mass). The effective mass \( m^* = 0.067 m_0 \) for electrons in GaAs was used, the reason behind being that they have an essential portion of their wave function extended in the GaAs surrounding matrix [29]. The dispersion of the single-particle energies in the magnetic field, due to the interaction of the orbital angular momentum with the \( B_z \) field, leads to a crossing between \( p_+ \) and \( d_- \) energy levels at a certain critical field, where the \( l = -2 \) orbital has lower energy than the one with \( l = 1 \). This effect will trigger a change in the loading sequence for electrons which can be observed experimentally [30, 31]. In the case of holes, the experimental results show some complications, further details being presented in Chapter 5.

The Eq. 2.2.6 was obtained by neglecting the Coulomb and Zeeman energies in the

![Figure 2.7: Fock-Darwin states for electrons of a MBE-grown InAs quantum dot. For certain critical fields, the levels corresponding to different \( l \) are crossing, resulting in a change of the charging sequence. The parameters used for the calculations are shown on the top of the graphic. The confinement energy \( h \omega \) is representative for electrons in self-assembled InAs/GaAs quantum dots.](image-url)
Hamiltonian from Eq. 2.2.2. Medeiros-Ribeiro et al. have reported a Zeeman splitting of 0.6 meV for electrons at B=12 T [32] which justifies the disregard of the Zeeman term. In the same time, Warburton et al. [31] used a perturbation approach to treat the Coulomb interactions for the electrons. While being illustrative, the description of the quantum dots by a non-interacting electron (or hole) system confined by a harmonic potential is not complete. Different numerical methods were employed to account for the inclusion of the intra-dot Coulomb interactions. A discussion on these diagonalization methods is beyond the scope of this thesis. As an introduction on this subject, the review of Reimann and Mannien [22, 33] and the references therein could be useful.

Apart from neglecting the two terms in the Hamiltonian above, another assumption has been made in this section by considering the quantum dots to be two-dimensional. Different authors [23, 34] have studied the more realistic 3D QD being able to find a better fit for the experimental data. Nevertheless, the 2D harmonic oscillator can still be used as a handy tool for a coarse approach on the problem, being able to predict qualitatively the experimental features.

### 2.2.2 Electrons and holes wavefunctions in quantum dots

The wavefunctions belonging to the Fock-Darwin eigenenergies are given by

\[
\psi_{n,l}(r, \vartheta) = \frac{e^{i l \vartheta}}{\sqrt{2\pi l_B}} \sqrt{\frac{n!}{(n + |l|)!}} e^{-r^2/2l_B^2} \left( \frac{r}{\sqrt{2l_B}} \right)^{|l|} L_n^{|l|} \left( \frac{r^2}{2l_B^2} \right),
\]

with \( L_n^{|l|} \) generalized Laguerre polynomials [35] and the characteristic lengths for the case of electrons and holes:

\[
l_{\text{electrons}} B = \sqrt{\frac{\hbar}{m^* \omega}}; \tag{2.2.10}
\]

\[
l_{\text{holes}} B = \sqrt{\frac{\hbar}{m_n^* \omega}}. \tag{2.2.11}
\]

In Figure 2.8, the square of the single-particle wavefunction \( |\psi_{n,l}(r, \vartheta)|^2 \) is plotted for different values of the quantum numbers \((n, l)\), with the oscillator parameters \( l_{\text{electrons}} B = 7.6 \text{ nm} \) and the effective mass \( m^* = 0.067 m_0 \) taken from [31]. It can be observed the ground state electron probability density has a s-like shape, with a maximum in the center of the dot and decreasing to the edges. Likewise, the probability density for the p-state has a dip in the center of the dot. It is the same for the d-like orbital but here the dip around \( r = 0 \) is larger [10]. The wavefunction corresponding to \((n, \pm l)\) differ only by a phase factor \( e^{i l \vartheta} \), meaning they are somehow orthogonal.

In this model, there is no difference between the electrons and holes wavefunctions, except for their spatial extension. This is because the distinction between electrons and holes is made only by the characteristic lengths \( l_B \). The electron wavefunction is approximatively a factor or two more extended than the corresponding one for a hole [36]. The size of a Fock-Darwin state depends on the quantum numbers \( n \) and \( l \), as well as of the oscillator characteristic length \( l_{\text{electrons}} B \). A convenient measure is the mean square radius, which is given by [37]:

\[
R^2 = 2l_B^2(2n + |l| + 1). \tag{2.2.12}
\]
s-like \((n=0, l=0)\)

p-like \((n=0, l=\pm 1)\)

d-like \((n=0, l=\pm 2)\)

Figure 2.8: The square of the wave functions \(|\psi_{n,l}(r, \theta)|^2\) for a 2D symmetric harmonic oscillator for different orbitals defined by the quantum numbers \((n,l)\). The number of nodes of the wavefunction, starting from the centre is given by the radial quantum number \(n\). For \(l \neq 0\), an additional node appears at \(r = 0\). One can see, the dip in the centre is wider for larger \(|l|\).

With an applied magnetic field (perpendicular to the dot plane), \(l_B\) will decrease as \(B_{\perp}\) increases, being equivalent to an increase of the confinement energy according to Eq. 2.2.8, i.e. magnetic confinement. In Figure 2.9 the decrease in the system size is shown for two quantum dots with different confinement energies of 3 meV (as in the case of electrostatic/vertical-mesa etched QDs) and 25 meV (in the range of hole confinement energies in InAs self-assembled QDs). In (a, d) the variation of \(l_B\) with the magnetic field is presented. This will induce subsequent changes in the s-orbital (b, e) and p-orbital (c, f) wavefunction extension with the magnetic field. It can be observed that the applied magnetic field has a strong influence on the QDs with lower confinement energies (a-c). In this case, two electrons (holes) occupying the same state will be pushed close together, with the result of increasing the Coulomb interactions. On the other hand, Eq. 2.2.12 shows that the system size increases with the angular momentum \(l\). This offers an escape route for the system to compensate for the contraction induced by the magnetic confinement. It is therefore possible to reduce the Coulomb energy by increasing the angular momentum quantum number \(l\) at certain
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Figure 2.9: Magnetic field dependence of system size for two quantum dots with different confinement: (a-c) a vertical mesa etched dot with $\hbar \omega_0 = 3$ meV and $m^* = 0.067 m_0$ corresponding to the electron effective mass in GaAs; (d-f) simulation for a self-assembled quantum dot with $\hbar \omega_0 = 25$ meV and $m^* = 0.51 m_0$ corresponding to the heavy hole in GaAs. In (a,d) the variation of $l_B$ with the magnetic field is presented. The contraction of the $s$- and $p$-orbitals with an increasing magnetic field is simulated in (b,e), respectively (c,f). In these plots, the traces at $B = 0$ T correspond to sections in the wave functions from the previous figure, at $y = 0$.

Critical fields, resulting in oscillations of Coulomb energy [37]. For a quantum dot similar with the ones used in this work, the influence of the magnetic field on the system size, shown in Figure 2.9 (d-f), is negligible even for very strong applied fields.

Returning to the discussion about the localization probability density, in the end of this section, it worths mentioning that the shapes presented in Figure 2.8 will change for an asymmetric 2D harmonic oscillator. In this way, information about the confine-
ment potential can be extracted, provided that the shapes of the wavefunctions can be visualized.

### 2.2.3 The Coulomb blockade

When a quantum dot is separated by a thin barrier from a reservoir, provided that the energy states in the reservoir can be tuned to come into resonance with the quantum dot states, tunneling processes can occur. The first electron (hole) will tunnel into the minimum-energy state of the conduction (valence) band - $E_{0,0}$. In order to differentiate between $E_{n,l}$ for valence and conduction bands the orbitals $s$, $p$, $d$ will be renamed, whenever necessary, to $e_{1,2,3}$ and $hh_{1,2,3}$, where $e$ stands for electrons and $hh$ for (heavy) holes. With the condition that only one type of carriers are tunneling-in, the quantum dot becomes charged. In such a case, the following carrier(s) attempting to enter the dot will be subjected to Coulomb repulsion. Given the small size of the system, it results in a considerable energy cost for adding an extra charge on the dot. It would mean that the tunneling is suppressed unless the extra energy is provided to account for the Coulomb repulsion. This process is known as the Coulomb blockade and it is responsible for the complete lift of the energy levels degeneracy in the tunneling experiments. This situation is depicted in Figure 2.10 for the addition of a third electron. The required energy to increase the number of electrons from 2 to 3 would be the inter-sublevel energy $E_{e_2} - E_{e_1}$ plus the Coulomb energy corresponding to the interaction of the third electron with the ones already in the dot $E_C^{\text{total}}$. The simplest model to include the Coulomb blockade is the constant-interaction model which makes the assumptions that the single-particle energies $E_{n,l}$ are not influenced by the Coulomb interactions and the latter are independent of the occupation of the dot [10]. Described in this way, the Coulomb blockade is an entirely classic effect.

Nevertheless, one has to go beyond the constant-interaction model in order to be rigorous: the Coulomb energy $E_C^{\text{total}}$ is in fact a mix between the classical $E_C^{\text{Coul.}}$ and the exchange $E_C^{\text{ex}}$. Coulomb energies. The latter is a purely quantum interaction effect which resides in the fact the electrons (holes) are indistinguishable [16].

Different than in the case of lithographically-defined quantum dots, where the quantization energies are usually in the range of several meV and the Coulomb blockade can be treated using the constant-interaction model, the quantization energies for self-assembled quantum dots are bigger and quantum effects come into the picture. Using perturbation theory applied to a parabolic 2D-EMA system, Warburton et al. had proposed a method to calculate the Coulomb interaction integrals and have used these results to obtain the addition energies. They had started by making several considerations:

- The quantization energies $\hbar \omega_0$ for electrons and holes were taken to be larger than the Coulomb energies between carriers of the same type inside the dot;
- The quantum dots were considered being 2D ($\hbar \omega_z \gg \hbar \omega_0$) (only the lowest single-particle state in $z$ direction is occupied);
- The confinement potential $V(x, y)$ was parabolic;
- Only intra-dot interactions were taken into account, as the average separation between the quantum dots in the ensemble were larger than the distance to a
highly conductive back contact, with the role of the reservoir, which would screen the influences between the dots.

\[ \text{CB} \quad \text{GaAs} \quad \text{InAs} \quad \text{GaAs} \]

\[ E_g \]

\[ \text{VB} \]

\[ \text{hh}_1 \quad \text{hh}_2 \quad \text{hh}_3 \]

**Figure 2.10:** An electron tunneling into a quantum dot will be subjected to repulsion forces by the charges already present in the dot. Even when resonance conditions are fulfilled, the tunneling is blocked unless the incoming electron pays the extra Coulomb energy. Here, the lateral potential was taken in a form of a square well for simplicity. To differentiate between conduction and valence band energies \( E_{n,l} \) from the previous sections the quantum numbers have been replaced by \( e_i \) and \( hh_i \) respectively.

The interaction between two electrons in the states \( \psi_i^e(\vec{r}_1) \) and \( \psi_j^e(\vec{r}_2) \) is described by the integral [31, 23]

\[
E_{\text{Coul.}} = \frac{e^2}{4\pi \epsilon_0 \epsilon_r} \int \int \frac{|\psi_i^e(\vec{r}_1)|^2 |\psi_j^e(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2, \tag{2.2.13}
\]

for the direct interaction, and

\[
E_{\text{Coul.}}^{\text{ex}} = \frac{e^2}{4\pi \epsilon_0 \epsilon_r} \int \int \frac{\psi_i^e(\vec{r}_1)^* \psi_j^e(\vec{r}_2)^* \psi_i^e(\vec{r}_1) \psi_j^e(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \tag{2.2.14}
\]

for the exchange interaction. In the expressions above, \( \psi_{i,j}^e(\vec{r}) \) are the eigenvectors of a 2D harmonic oscillator (Eq. 2.2.9).

The integrals have been analytically evaluated. The result for the direct interaction energy between the two \( s \) electrons (holes) have the form:

\[
E_{s-s}^{\text{Coul.}} = \frac{e^2}{4\pi \epsilon_0 \epsilon_r} \sqrt{\frac{\pi}{2}} \frac{1}{l_B^2}, \tag{2.2.15}
\]

where \( l_B^2 \) denotes, for each case, \( l_{B,\text{hole}}^2 \) respectively \( l_{B,\text{electron}}^2 \) as defined in Eq. 2.2.10 and Eq. 2.2.11. The second column in Table 2.2 holds the calculated direct and exchange Coulomb contributions in the case of electrons are given as percent from Eq. 2.2.15.

- \( \text{CB} \): Conduction Band
- \( \text{GaAs} \): Gallium Arsenide
- \( \text{InAs} \): Indium Arsenide
- \( \text{VB} \): Valence Band
- \( e \): Electron
- \( hh \): Heavy Hole
CHAPTER 2. PROPERTIES OF QUANTUM DOTS

\[ \psi_i^c - \psi_j^c \]

<table>
<thead>
<tr>
<th>2D-EMA</th>
<th>atomistic</th>
</tr>
</thead>
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<tr>
<td>s - s</td>
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</tr>
<tr>
<td>s - p_+</td>
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</tr>
<tr>
<td>s - p_+</td>
<td>0.59</td>
</tr>
<tr>
<td>s - d_+</td>
<td>0.69</td>
</tr>
<tr>
<td>s - d_0</td>
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</tr>
<tr>
<td>p_+ - p_-</td>
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</tr>
<tr>
<td>p_+ - d_+</td>
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</tr>
<tr>
<td>p_+ - d_0</td>
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</tr>
<tr>
<td>d_+ - d_+</td>
<td>0.60</td>
</tr>
<tr>
<td>d_0 - p_0</td>
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</tr>
<tr>
<td>s - p_+</td>
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<tr>
<td>s - d_0</td>
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<tr>
<td>p_+ - p_-</td>
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</tr>
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<td>p_+ - d_+</td>
<td>0.24</td>
</tr>
<tr>
<td>p_+ - d_0</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Table 2.2: Comparison between direct (upper part) and exchange (lower part) Coulomb energies for two electrons in the states \( \psi_i^c \) and \( \psi_j^c \), obtained with a 2D-EMA model and calculated numerically [38]. The energies are given as percent of \( E_{\text{Coul}}^{s-s} \).

Using these results, the addition energies for the first 6 electrons at B = 0 T are found to be: \( \hbar \omega_0 \), \( E_{\text{Coul}}^{s-s} \), \( \hbar \omega_0 + 1/4 \ E_{\text{Coul}}^{s-s} \), 1/2 \( E_{\text{Coul}}^{s-s} \), 7/8 \( E_{\text{Coul}}^{s-s} \), and 1/2 \( E_{\text{Coul}}^{s-s} \).

The conduction band quantization energies are about 45-50 meV and about half this value for the valence band. The Coulomb interaction energy between two electrons confined in such dots are smaller (\( \approx 20 \) meV), therefore it seems reasonable to be treated using the perturbation theory. Differently, in the case of holes, \( \hbar \omega_0 \) and \( E_{\text{Coul}} \) have approximately the same values such that the analytical method described above is no more justified.

Although a certain qualitative agreement with the experiment has been obtained using the approach of Warburton, as already pointed out in Section 2.2.1, a 2D harmonic oscillator description of the quantum dot over-simplifies the problem and fails to describe certain aspects related with the realistic dots [39], e.g., anisotropy due to the non-equivalent directions in the semiconductor lattices which reduce the symmetry and induce the p-level split; underestimation of direct and exchange Coulomb energies; disregard of the wave-function mixed characters [40].

An atomistic pseudo-potential description to account for all the differences described above was given by He et al [38] who were able to reproduce the many-particle configurations as well as the addition spectra for carriers in SAQDS. A 7 nm high lens-shaped dot with a diameter of 25 nm was considered here. The last column in Table 2.2 contains, for comparison, the Coulomb energies calculated with this method. They differ about 20% from the ones calculated using the perturbation theory. Of course, such an approach requires much effort and specialization. On the other hand, with all its drawbacks, the simplicity of the 2D-EMA model and the possibility of having an "escape route" by adjusting the fitting parameters in a reasonable range (\( \hbar \omega_0 \) and \( m^* \)), makes it useful for a qualitative description of the interaction and addition energies.
2.2.4 Wigner crystallization

In some situations, when the potential energy exceeds their kinetic one, the electrons can undergo a phase change and crystallize forming a Wigner crystal [41]. It means the electrons freeze in certain positions in such a manner that their Coulomb repulsion is minimized. Quantum Monte-Carlo simulations indicate that the uniform electron gas crystallizes when the Wigner-Seitz radius \( r_s = a/a_B^* \) is smaller than 106 in 3D bulk and smaller than 35 for a 2DEG. The parameter \( a \) is the inter-particle average spacing and \( a_B^* = \hbar^2/4\pi\epsilon_0\epsilon_r/a/(m^*e^2) \) is the effective Bohr radius [42].

For the case of the quantum dots, the potential Coulomb to kinetic energy ratio \( \lambda_{QD} = l_B/a_B^* \) is the correspondent of \( r_s \). The condition for Wigner crystallization of the electrons in quantum dots is \( \lambda_{QD} \geq 4 \) [43]. There are two possibilities to artificially drive the quantum dot’s electrons in a crystalized phase by enhancing the strength of the Coulomb interactions over the kinetic energy: to dilute the electron density or to apply a magnetic field.

From Figure 2.9 (b, c), in the case of weakly confined quantum dots, it can be seen it is possible to influence so strongly the system size that the Coulomb interactions increase to a point where it will force the transition of the electrons on levels with greater \( |l| \). This continues, as schematically presented in Figure 2.11, until all the electrons will become spin polarized on the first Landau level [44]. According to Rapisarda [45], the transition to a Wigner crystal is preceded by a spin-polarized phase. When forming a Wigner crystal, the electrons will arrange themselves in such a manner that the Coulomb interactions are minimized. As a consequence, the charge densities (and the wavefunctions) will change accordingly [46, 43].

![Figure 2.11: Electron occupation for the Fock-Darwin energies of a quantum dot with \( \hbar\omega_0 = 5.4 \text{ meV} \) and \( \hbar\omega_z = 540 \text{ meV} \). Reprint from [44]. The magnetic field confinement will force the electrons to occupy states with larger orbital quantum numbers, as a compensation for the increased Coulomb repulsion. This is the mechanism leading to spin polarization which is an intermediate step in the Wigner crystallization.](image-url)
monic confinement will form Wigner molecules consisting of rings of electrons [22]. It has been shown the measured squared modulus of the quasi-particle wavefunction becomes a ring having the same radius as the charge distribution [43].

Differently, for self-assembled quantum dots, as seen from the simulation in Figure 2.9 (e, f), the magnetic field is not able to dwindle the system size even at 20 T. In this case, Rontani and Molinari [43] pointed out that \( \lambda_{QD} \approx 0.5 \), and the Wigner crystallization does not occur.

### 2.2.5 Tunneling in magnetic field

The energies of a quantum dot can be probed by using optical methods, electrical ones or a combination of both. In the case of electrical experiments, electrons or holes from an emitter are tunneling a thin barrier, in the growth direction \( z \), into the dots. Practically, this is done by tuning the emitter states in such a way that they are in resonance with the quasi-particle dot states. The measured quantities can be the current, the differential conductance or the QD capacitance; the emitter can be either a STM tip or a doped contact, while the barrier would be the vacuum or a spacer layer.

In a simplified picture, the tunneling current is given by [47]

\[
I \propto |\mathcal{M}_{\text{Bardeen}}|^2, \tag{2.2.16}
\]

where \( \mathcal{M} \) is the tunneling matrix element and \( T_{\text{Bardeen}} \) is the Bardeen transfer-matrix element [48] between the emitter and the quantum dot states. With the condition that the latter is taken to be constant or slowly varying during the tunneling, for a given barrier thickness, one is interested only in \( \mathcal{M} \).

The matrix \( \mathcal{M} \) is the relevant quantity also for intensities in space-integrated spectroscopies probing the quantum dot addition energy spectrum, i.e. capacitance-voltage spectroscopy which will be used later on in this thesis [43].

Following the calculus of Bester et al. [13], the transition (tunneling) rate of an electron (or hole) form the emitter in state \( \kappa \) to a quantum dot containing \( N \) particles is

\[
T_{\kappa,N} = \frac{1}{\tau} \propto |\mathcal{M}_{\kappa,N}|^2. \tag{2.2.17}
\]

The tunneling matrix elements are given by

\[
\mathcal{M}_{\kappa,N} = \int \psi_\kappa^*(\vec{\phi}) \Psi_{\text{QD}}(\vec{\phi}) d\vec{\phi}, \tag{2.2.18}
\]

where \( \psi_\kappa(\vec{\phi}) \) is the probing (emitter) wavefunction and \( \Psi_{\text{QD}}(\vec{\phi}) \) is the quasi-particle wavefunction in the state \( |N\rangle \). Here it was assumed for convenience, once again, that the quantum dots are two-dimensional. Recasting \( \Psi_{\text{QD}}(x,y) \) from Eq. 2.2.5 into \( \Psi_{\text{QD}}(\vec{\phi}) \) and also considering the emitter state along \( z \) to be evanescent in the barrier, one gets to the expression above.

For a quantum dot evolving from a state \( |N-1\rangle \), with \( N-1 \) electrons (holes), to a state \( |N\rangle \), with \( N \) electrons (holes), the quasi-particle excitation can be expanded on the basis of the single-particle states \( \psi_i(\vec{\phi}) \):

\[
\Psi_{\text{QD}}(\vec{\phi}) = \sum_i \langle N-1| \hat{c}_I |N\rangle \psi_i(\vec{\phi}). \tag{2.2.19}
\]
2.2. THEORETICAL DESCRIPTION OF THE QUANTUM DOTS

Here, the electron (hole) annihilation operator $\hat{c}_i$ has been used.

In the configuration-interaction approximation [49, 50], the many-body states are written as a superposition of different Slater determinants with the weights $C_\gamma$. That is:

$$|N - 1\rangle = \sum_\alpha C_\alpha^{(N-1)} \Phi_\alpha(\vec{q}_1, \vec{q}_2, \cdots, \vec{q}_{N-1}),$$

$$|N\rangle = \sum_\beta C_\beta^{(N)} \Phi_\beta(\vec{q}_1, \vec{q}_2, \cdots, \vec{q}(N - 1), \vec{q}_N).$$

(2.2.20)

Hence, the tunneling matrix becomes

$$\mathcal{M}_{k,N} = \sum_i \langle N - 1 | \hat{c}_i | N \rangle \langle \psi_\kappa | \psi_i \rangle$$

$$= \sum_i \sum_{\alpha,\beta} C_\alpha^{(N-1)} C_\beta^{(N)} \langle \Phi_\alpha^{(N-1)} | \hat{c}_i \Phi_\beta^{(N)} \rangle \langle \psi_\kappa | \psi_i \rangle,$$

(2.2.21)

with

$$\langle \Phi_\alpha^{(N-1)} | \hat{c}_i \Phi_\beta^{(N)} \rangle = \begin{cases} 1 & \text{if } \Phi_\alpha^{(N-1)} = \hat{c}_i \Phi_\beta^{(N)}; \\ -1 & \text{if } \Phi_\alpha^{(N-1)} = -\hat{c}_i \Phi_\beta^{(N)}; \\ 0 & \text{otherwise}. \end{cases}$$

(2.2.22)

The result in Eq. 2.2.21 gives the possibility of obtaining the images for the probability density both in real and reciprocal space, provided the emitter wavefunction $\psi_\kappa(\vec{q})$ generated by the external source is known. Two different scenarios can be considered:

- In STM experiments, where the tunneling is made from a moving tip above the dot, $\psi_\kappa(\vec{q})$ is the localized tip wavefunction [43] and can be ideally approximated with

$$\psi_\kappa(\vec{q}) \approx \delta(\vec{q} - \vec{q}_0).$$

(2.2.23)

Thus, from Eq. 2.2.18,

$$T_{\kappa,N} \propto |\psi_{QD}(\vec{q}_0)|^2,$$

(2.2.24)

i.e. the transition rate $T$ maps out the square of the quasi-particle excitations in real space [51].

- In magneto-tunneling spectroscopy, the probing wave function $\psi_\kappa(\vec{q})$ is not exactly known. In the envelope function approximation, the in-plane emitter wavefunction is assumed to be a plane-wave

$$\psi_\kappa(\vec{q}) = e^{i\vec{k}\vec{q}},$$

(2.2.25)

so that $\langle \psi_\kappa | \psi_i \rangle$ becomes the Fourier transform of the dot single-particle wavefunction of the $i^{th}$ state. It turns out that $T$ will give the square of the quasi-particle momentum space wavefunctions [52].

In the following chapters, the second approach will be used to map the $k$-space quasi-particle probability densities by using $C(V)$ spectroscopy in magnetic field. More details about this method will be given in Section 4.2.2.

*Commonly in the literature, this is referred as "wavefunction mapping"; except several occasions, throughout the rest of this work the term wavefunction will designate the probability density.*
Chapter 3

Growth and processing of quantum dots samples

In this chapter, some of the methods employed for the fabrication and manipulation of InAs/GaAs quantum dots will be introduced. First, the molecular beam epitaxy and the self-assembly of the quantum dots will be described in order to make a smooth link with the in-situ Indium-flush technique, one of the methods used to tune the quantum dots properties. Ex-situ rapid thermal annealing will be presented as an alternative method to In-flushing.

3.1 Molecular beam epitaxy

The advances in micro- and nano-electronics by the end of the 20th century have been possible due to the emerging of precisely controlled crystal growth techniques. MBE is one of the techniques employed on large scale for the growth of single crystals which have created a variety of new opportunities for the fabrication of artificially layered semiconductor structures [53]. The technique was developed and implemented in the early 1970’s at Bell Telephone Laboratories by John R. Arthur, Alfred Y. Cho, and Art C. Gossard [54, 55]. Being a very slow epitaxial process, with usual growth rates of 1 µm/h, extreme control regarding the dimensionality, composition and impurity incorporation can be achieved during the growth by MBE.

The MBE process consists in the simultaneous evaporation of constituting elements of the epitaxial layer which has to be grown onto a heated crystalline substrate where they combine via simple chemical reactions in ultra-high vacuum (UHV) conditions. The term "beam" in MBE means that the evaporated atoms/molecules do not interact with each other or with residual species in the growth chamber until they reach the substrate, due to the long mean free paths of the atoms. The composition of the new epitaxial layer depends on the relative arrival rates of the constituent elements, which, in turn, depend on the evaporation rates of the respective material sources [53]. Attainment of high quality semiconductor structures with excellent optical and electronic properties requires background pressures in the order of $10^{-9}$ Torr. The UHV in the MBE system is obtained and maintained by a combination of turbo-molecular pumps, cryo-pumps, ion pumps, Ti sublimation pumps and liquid-Nitrogen cryo-shrouds.

The materials needed for the MBE growth process are delivered from separate
Knudsen effusion cells which are made from non-reactive refractory materials crucibles, usually pyrolytic boron nitride (PBN). They are filled with ultra-pure elements and each of them is heated with tungsten or tantalum filaments until the contained element begins sublimate/evaporate. The flux of material is regulated solely by the cell temperature which, in turn, is controlled by a feedback loop containing a thermocouple at the bottom of the crucible and a power regulator for the heater. For the growth of arsenides, the group III elements are always supplied as monomers while group V elements can be supplied as tetramers ($\text{As}_4$) or as dimers ($\text{As}_2$) by dissociating the tetrameric molecule in a two-zones furnace (arsenic cracker), for which the flux is regulated by a valve [53]. Effusion cells containing group IV elements are usually also fitted in an MBE system in order to obtain semiconductor doping. Most commonly, Si is used for $n$-type doping of GaAs, as it is incorporated on Ga lattice sites during the growth under As-stabilized conditions [56]. Carbon $p$-type doping is usually chosen because of its high achievable hole concentration and its much lower diffusivity in the layers, compared with Zn or Be [57, 58].

To avoid breaking the UHV condition every time new substrates are loaded or unloaded into the system, a load-lock chamber is connected to the growth-chamber via a transfer chamber which can serve also different built-in facilities. After loading, the enclosure is pumped down to match the pressure in the rest of the system while the substrates are degassed by heating. It is after this step, that the wafers are allowed into the growth chamber.

Reduced to its essentials, a MBE growth chamber consists of an UHV system containing the sources for atomic or molecular beams and a heated support for the substrate wafer. Commonly, other add-ons are fitted-in, e.g., reflection high-energy electron diffraction (RHEED), mass spectrometer. In Figure 3.1, a schematic diagram for the growth chamber of the Riber Epineat III/V MBE system in use at the Lehrstuhl für Angewandte Festkörperphysik (AFP) is presented. A more detailed description of the entire system can be found in [59] and [60]. This is the MBE system employed for the growth of all the samples used in this work. It is equipped with Al, Ga and In solid source cells as well with an arsenic valved cracker cell. For $n$-type doping, a Si cell is available, while the $p$-type doping is done by a solid carbon source based on the electron evaporator principle [57]. The beams are automatically switched on and off with automate shutters in front of each cell, controlled independently by a software following the growth-recipe.

The substrate is laid facing the cells onto a rotating support, in close proximity of a meander heater. The heater temperature is read by a thermocouple which provides input for a regulating power supply. From the construction, the heater and the substrate are not in direct contact, so that there will be always a difference between the set temperature and the substrate temperature. To accurately measure the substrate temperature, a pyrometer is used. In the sample growth-sheets enclosed in Appendix A, both the thermocouple ($T_{\text{set}}$) and the pyrometer ($T_{\text{pyro}}$) temperatures are registered as a reference for obtaining reproducible condition for subsequent growths. To achieve a high degree of temperature uniformity on the wafer and especially to obtain uniform layers (as the cells are tilted with respect to the substrate normal), the substrate is rotated in front of the effusion cells.

During the MBE growth, the stoichiometry of most III-V semiconductors is self-regulated as long as excess group V molecules are impinging on the growth surface. The
sticking coefficient for group V species (As in this case) is zero and their condensation on the surface occurs only if adatoms of group III elements are present. For this reason, an arsenic overpressure can be maintained during the growth, which will control Ga adsorption/desorption from the epi-layer. The temperature plays the most important role in the MBE growth. Reasonably high temperatures assure an increased mobility of the adatoms on the surface, thus reducing the lattice defects.

Depending on the incident flux of group III elements and on the temperature of the substrate, different processes can occur at the surface, as schematically presented in Figure 3.2 (left) [61, 62]. Adatoms or molecules can either adsorb on the surface (a) or desorb at sufficient high temperature (h). They can also migrate on the surface (b) until they link with other atoms and molecules (c) to form islands or to be incorporated into a new layer (g). When islands are already formed new atoms migrating on the surface can be attached (d) or detached (e). In the case (f) when the interaction between the adsorbed species is more intense than the interaction with the substrate, 3D islands start to form.

In-situ surface crystallography and growth kinetics are monitored by RHEED operated at 25 keV with glancing angles < 3°. Because of the small incidence angles, RHEED is very surface-sensitive, sampling only few atomic layers beneath the surface [64]. High energy electrons from an electron gun are focused on the sample surface and the diffracted intensity pattern can be observed on a phosphorus screen. The intensities of individual spots on the RHEED pattern fluctuate in a periodic manner as a
3.2. SELF-ASSEMBLED InAs QUANTUM DOTS

Figure 3.2: Left: Schematic representation of different fundamental surface processes occurring during the epitaxial growth: (a) adsorption, (b) migration on the surface, (c) island formation, (d) attaching to an island, (e) detaching from an island, (f) deposit onto an island, (g) attaching to a step, (h) desorption. After [61, 62]. Right: RHEED oscillations with the period of the monolayer growth rate. Scattering is maximum for surface coverage (%) $\theta = 0$ (completed Ga plane) and $\theta = 1$ (completed As plane). After [62, 63]. Courtesy of Mihai Drăghici.

result of the changing in the relative surface coverage during the growth. Therefore, by monitoring the intensity of the specular spot on the RHEED screen, one can get information on the condition of the surface [64].

The growth GaAs monolayer (ML) consists in the deposition of a complete As layer upon a complete Ga layer. For Figure 3.2 (right), taking by designation $\theta$ the percent of As surface coverage, a maximum intensity for the specular spot on the RHEED screen would be obtained for a complete-grown Ga atomic plane ($\theta = 0$). The roughness of the surface increases as the arsenic begins to nucleate and the intensity of the specular spot continuously fades until a 50 percent As coverage is reached. Further, the roughness of the surface decreases while a new layer is completed so that the RHEED intensity increases again. In this way, the growth rate can be accurately determined from RHEED.

Due to its advantages over low-energy electron diffraction technique, RHEED has become a common tool in almost all modern MBE systems.

3.2 Self-assembled InAs quantum dots

The epitaxial growth of thin films on single crystal surface depends critically on the interaction strength between adatoms and the surface. When the interaction between the substrate and the adatoms is stronger than adatoms’ interaction between themselves, a layer-by-layer growth takes place, with new layers beginning to form only when the layer underneath is completed - a two dimensional growth. The opposite situation, when adatom-adatom interaction is stronger than the interaction between adatom and the surface, will result in the formation of 3D clusters (islands). An intermediate growth mode is also possible for lattice-mismatched systems, with island
structures being self-formed on a 2D wetting layer (WL) when a critical thickness is attained. Such a "layer+island" growth mode is usually referred as Stranski-Krastanow (S-K) growth after I. Stranski and L. von Krastanow have proposed it in 1938 [65]. This distinguishing feature of the Stranski-Krastanow growth mode has been exploited almost half a century later when it was extensively used for new applications. It has been applied for different materials systems, InAs/GaAs being by far the most studied. This work deals with InAs quantum dots in a GaAs matrix, the following paragraphs describing their obtention.

The initial InAs deposition leads to the formation of a strained wetting layer on GaAs (001) due to a 7 percent lattice mismatch between InAs and GaAs. As the thickness of this layer increases, the stress accumulates up to a critical value when the layer becomes energetically unstable and undergoes relaxation. Strain relaxation can be achieved by misfit dislocations or, in certain conditions, by the formation of 3D islands on top of the wetting layer. When appearing, the coherent (defect-free) islands are commonly referred as self-assembled quantum dots (SAQDs) or simply quantum dots.

In Figure 3.3, the basic mechanism leading to the formation of InAs SAQD on GaAs (001) is presented. Here, the orange corresponds to GaAs while blue is for InAs. The 2D InAs wetting layer is "accommodated" on the GaAs (001) surface (b), following the GaAs lattice parameters. After the deposition of 1.5-1.8 ML InAs, the strain is reduced by a sudden, random formation of InAs islands in an attempt to recover the bulk InAs lattice parameters (c).

![Figure 3.3](image_url)

**Figure 3.3:** Schematic drawing showing the growth of the InAs/GaAs quantum dots by the Stranski-Krastanow method: (a) GaAs substrate; (b) growth of the strained InAs WL on GaAs (001); (c) with increasing InAs coverage above a critical thickness, the strained layer undergoes relaxation to minimize its surface energy by spontaneous formation of randomly-distributed 3D islands. Colour coding: orange corresponds to GaAs and blue to InAs. Note the different lattice parameters for the two binary components and the relaxation towards the top of the InAs island.

The transition from 2D to 3D growth mode has a more complex evolution whose description is beyond the scope of this introduction. More details can be found in
As mentioned above, the SAQDs formation is only possible in certain conditions. In fact, the islands assembling is an exception. The initial misfit strain in the InAs layer is independent of substrate orientation and surface reconstruction. Therefore, no dependence of QD formation (whether they appear or not) on these parameters should be observed. Still, it is known that strain relaxation results in QDs formation by S-K growth mode only for GaAs (001) while for other substrate orientations (except GaAs(111)B [67, 68]) a 2D layer-by-layer growth is realized and the strain is relaxed by the formation of misfit dislocations. Even on (001)-oriented substrates, QDs do not form under all conditions, but only on certain surface reconstructions, notably in the presence of excess (above stoichiometry) arsenic. Several possible explanations have been proposed as being the reason of a preferred growth mode which favors the introduction of misfit dislocations in the detriment of 3D QDs. One of them assumes that it is more energetically favorable to introduce the misfit dislocation than to form the islands, except for GaAs (001). Another explanation can be given by considering a strain gradient in an alloyed (In,Ga)As wetting layer [66, 69], which seems reasonable at elevated growth temperatures.

Since Indium is more volatile than Gallium, the growth of InAs is restricted to lower substrate temperatures than for GaAs. The QDs obtained with the Riber machine at AFP were grown at a substrate temperature $T_{pyro} \approx 520$ °C with an arsenic pressure $P_{As} \approx 7 \times 10^{-6}$ Torr. Cf. Joyce et al., for low InAs deposition rates of 0.018 ML/s, as the ones used at AFP [60], a significant (In,Ga)As alloying can be ruled out [66, 70].

The substrate temperature, In flux and the As pressure are of critical importance during the formation of the InAs QDs. In general, for a careful choice of As pressure, the lateral size of the resulting InAs QDs can be controlled by the substrate temperature. For the growth conditions used at AFP, the supplied In amount doesn’t play an important role in the final QDs size. Yet, with an increased InAs deposition, only the island density increases until QDs eventually coalesce. The total InAs coverage of 2.1 ML (for a standard growth) was delivered in consecutive cycles, each consisting of 4 s In deposition followed by 4 s growth interruption at the appropriate substrate temperature under constant arsenic pressure. This allows the diffusion of In atoms at the surface until they find a suitable location for binding. The number of In cycles was adjusted depending on the substrate temperature or the desired quantum dot density, all the growth parameters being registered in the growth sheets enclosed in Appendix A.

From Figure 3.1 it can be seen that due to the construction of the growth chamber, the substrate is tilted with respect to each of the effusion cells. This will result in a non-uniform material flux on the substrate surface. To counter this drawback, the sample holder can be rotated during the growth. But this disadvantage can be exploited in a different way: without rotating the substrate during the last deposition cycles, a quantum dot density gradient will be obtained across the wafer. The substrate region closest to the In cell will exhibit a high island density which will gradually decrease until the complete absence of the 3D features in the substrate regions furthest from the In source. This approach can be particulary interesting for single-dot spectroscopy experiments.

Initially, random nucleation of the InAs QDs will result in a large distribution of island sizes. By continuing the In supply after the critical thickness corresponding to the formation of InAs QDs, the density of randomly nucleated islands increases.
In the same time, a long-range "communication" between the islands is established. Additional to the diffusion due to the temperature, a stress-driven migration of In on the surface is coming into action, which induces a slowing in the growth rate of larger islands [71, 72]. This can be regarded as a self-organization of the InAs quantum dots, leading to a very good uniformity of the coherent island size distribution, as it can be seen from the SEM image in Figure 3.4. This picture was taken for the uncapped quantum dots grown usually at the surface but a narrow distribution can be deduced, from the photoluminescence (PL) spectra, for the buried (inner) ones as well. For the samples used here, InAs islands have lateral dimensions about 20-40 nm, 7-9 nm height and a surface density of $2 \times 10^{10}$ cm$^2$ as determined from SEM measurements [60].

![SEM image of uncapped (outer) self-assembled InAs quantum dots grown on GaAs by molecular beam epitaxy at Angewandte für Festkörperphysik. Courtesy of Minisha Mehta.](image)

Different shapes have been reported and used in the simulations for MBE-grown quantum dots. Most commonly, pyramidal and lenticular dots have been proposed. However, based on RHEED data, Joyce et al. ruled out the possibility of having pyramidal shaped QDs [66]. Further on, it will be assumed QDs being lens-shaped according with the results from AFM and SEM on uncapped dots [60]. The quantum dot shown in Figure 2.4 is usually taken as a model for theoretical calculations [73]. Yet, it is long known that the size, shape, composition and surface density of the SAQDs change significantly during the overgrowth process. Therefore shape anisotropy is expected to arise after the capping of the quantum dots [74], as it would be evidenced in Chapter 5.

To obtain the desired confinement, the quantum dots have to be capped. Although different results can be obtained by choosing various capping materials, for the samples used in this work only GaAs has been used during the quantum dots' overgrowth.
3.3 Size/shape modification of the quantum dots

The optical and electronic properties of the InAs quantum dots are given by their size, shape and composition. Tailoring their properties is an important subject in the current research, as quantum dots are regarded as building blocks for novel optoelectronic devices, quantum cryptography and quantum computing. Moreover, from a fundamental point of view, carriers inside semiconductor QDs can be considered as model systems for studying quantum mechanical interactions between confined electrons and holes. It is therefore interesting to see how the island shape/size and composition will affect the emission properties and electrons/holes energies.

For ensemble measurements, it is of essential importance to achieve a high quantum dots density with a small size distribution and controllable optical and electronic properties. Different methods can be combined in order to achieve this goal. It has been demonstrated that self-assembled growth can be controlled systematically and reproducibly to obtain QDs structures for which manipulation of their energy levels is possible. This allows the tailoring of the number of the confined states as well as their inter-sublevel energies [75].

![Figure 3.5](image-url)

**Figure 3.5:** Manipulation of quantum dot properties by different means: (1) quantum dot size modification is possible during their growth, by growing of the capping layer or by post-growth methods; (2) in-situ or ex-situ thermally-induced In-Ga interdiffusion; (3) changing of the confinement potential by the composition of the overgrowth layer. The upper part of the figure shows the change in dot size induced by these three methods. The lower part shows the corresponding changes in the conduction band energy/confinement potential. After [76].

In Figure 3.5, some of the possible transformations suffered by the quantum dots are shown: (1) an increase/decrease in the dot size will decrease/increase the quantization energy; (2) interdiffusion (alloying) will modify the band gap and smear out the confinement potential; (3) increasing or reducing the confinement potential height by AlAs or (In,Ga)As overgrowth of the quantum dot. These changes are shown schematically in the upper part of the figure. In the lower part, the induced modifications in the conduction band energies are also given.

For InAs/GaAs, several techniques to control the size and exciton levels of the
SAQDs have been demonstrated. Among these, Indium-flushing [77, 78], atomic force microscopy oxidation [79], rapid thermal annealing [80], laser-induced thermal annealing [81], close QDs stacking [82], etc. These techniques add to the previously mentioned ones which have a direct influence on the growth: substrate temperature, Indium amount, overlayer composition or Arsenic pressure [83, 84]. In the following subsections remaining of this chapter, the two most common methods employed for tuning the QDs properties will be presented, namely in-situ Indium-flush technique and ex-situ rapid thermal annealing.

### 3.3.1 Altering QDs in-situ by flush-growth technique

The Indium-flush technique offers a path towards fine-tuning the optical properties of the SAQDs. It was originally developed by Wasilewski and Fafard [77, 78] in an attempt to improve the size uniformity of vertically stacked SAQDs which were intended to be used for fabrication of quantum dot lasers.

As it was already mentioned in the previous subchapter, the capping of the 3D InAs islands has a very important influence on the structural properties of the resulting QDs, with direct consequences on optical and electronic properties of the devices using such structures [85]. In most of the cases, the QDs are completely covered with GaAs, at slightly lower temperature than the one used for the growth of InAs, to avoid the re-evaporation of the QD material. Afterwards, when they are completely buried into the GaAs matrix, the growth is resumed at higher temperatures, more suitable for the deposition of GaAs [53]. The Indium-flush technique is taking advantage of the In sublimation at the surface, to obtain a further control on the size and shape of the SAQDs. The controlled sublimation had been shown to produce the elimination of the eventual incoherent InAs particles, which leads to a further narrowing of island size distribution and to a more precise control of the QDs heights [86].

![Figure 3.6: Quantum dot transformation by the Indium-flush technique. Left: The quantum dot is incomplete capped with low temperature-grown GaAs; Center: Indium flushing in the unprotected regions of the dots; Right: The resulting quantum dots are smaller, flattened and containing less Indium.](image)

The In-flushing is realized in three steps which are schematically presented in Figure 3.6. Once the InAs deposition is terminated and the QDs are completed, the substrate temperature is lowered by ≈ 10 °C to prevent In desorption. The Ga cell shutter is opened and GaAs is deposited until a thickness $d_Q$ is obtained, with $d_Q$ less than...
3.3. SIZE/SHAPE MODIFICATION OF THE QUANTUM DOTS

the height of the 3D InAs islands, as seen in the left part of the figure. At this stage, a short (≈ 60 s) break in the growth process is introduced, to allow In segregation and redistribution at the GaAs surface. Then, the GaAs growth is resumed at substrate temperatures ≈100 °C higher. Because the InAs QDs are not stable against evaporation at such high temperatures [87], this will produce the desorption of the In atoms from the unprotected part of the QDs as in Figure 3.6 (center). While Indium is being removed from the growth-front, the QDs will be completely buried in GaAs. As a result, smaller, truncated dots will be obtained (right), with a slight change in the composition due to Ga diffusion into InAs region. Compared with the normal-grown quantum dots (completely covered), the lateral dimensions of the In-flushed ones are almost unchanged, but their height is significantly reduced. Although the island dimensions are strongly influenced during the overgrowth process, the thickness \( d_{QD} \) of the protective GaAs cap deposited prior to the Indium-flushing can be regarded, in a first approximation, as a measure of their final height. Further on, \( d_{QD} \) would be assimilated with the height of the QDs, as the most important parameter which offers the opportunity of obtaining a good control of the resulting ensemble properties.

With Figure 3.6, the basic of this method can be explained. However, this is only a simplistic description of what is actually happening during the capping and the In-flushing. Of course, the growth kinetics will play an important role as well as the thickness of the low-temperature protective capping layer. Furthermore, Figure 3.7 presents a model of the material redistribution during the overgrowth and Indium-flush step is presented, as it was proposed by Wasilewski et al. [77].

![Figure 3.7](image-url)

**Figure 3.7**: Detailed picture for Indium flushing: (a) InAs quantum dots of different sizes nucleated on top of a wetting layer; here, InAs is shown in black and GaAs substrate in grey; (b) the dots are partially covered with a GaAs over-layer; (c) Indium segregation at the GaAs surface; (d) redistribution on GaAs surface and formation of a partial wetting layer; (e) Indium flushing from the growth front with a subsequent increase of the growth temperature. Reprinted from [77] by permission.

Figure 3.7 (a) shows the situation immediately after the nucleation of the 3D InAs quantum dots on top of the 2D wetting layer. The GaAs substrate is pictured in grey,
while the InAs is in black. Figure 3.7 (b) shows the processes occurring during the GaAs overgrowth. As already explained, the InAs is relaxed at the top of the dot, with a lattice spacing approaching that of the bulk InAs crystal, making energetically unfavorable the binding of Ga there. On the contrary, the wetting layer is fully strained and retains the GaAs lattice parameters. It is therefore expected the GaAs will start to grow preferentially on the wetting layer if the adatoms have sufficient surface mobility and the growth is much slower towards the top of the dot [88]. The quantum dots were formed initially by relaxing the strain induced by the GaAs substrate and now, they are subjected to additional strain from the surrounding GaAs. To cope with this, Indium from the yet uncovered region will migrate away from the dot, to form a new partial wetting layer on top of the overgrown GaAs layer, as in Figure 3.7 (c). In this situation, a redistribution of the strain in the dot will take place [86] until there is no mismatch to prevent the deposition of the GaAs on the remaining part, resulting in a complete overgrowth as shown in Figure 3.7 (d). At this point, the temperature is increased by \(\approx 100\, ^\circ\text{C}\) resulting in the desorption (flushing) of all the Indium from the growth-front (Figure 3.7 (e)).

A variant of this method consists in "flushing" the Indium at the growth-temperature of the InAs, as proposed by Sasakura et al. [89]. They have performed a 3 minutes In-flush at QDs growth temperature, which is \(\approx 90\, ^\circ\text{C}\) lower than usual. This method is less effective in removing the surface remanent Indium but resulted also in reduction of the height of the islands. By comparing different sets of samples obtained using their modified variant or using standard flushing method, they have calculated that the latter is accompanied by an In/Ga interdiffusion, the composition of the QDs changing to \(\text{In}_{1-x}\text{Ga}_x\text{As}\) with \(x\) ranging between 0.16 and 0.2.

![Figure 3.8](image)

**Figure 3.8:** Changes in the quantum dot confinement potential induced by the In-flush method. Lateral and in-growth directions are depicted.

Apart from obtaining Ga-rich discs, a decrease in island density and an increased homogeneity was also reported after flushing [86]. It can be observed from Figure 3.7 (c) the QDs of different sizes will end by having all approximately the same height.
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Such size/shape modified quantum dots will exhibit different properties than the normal-grown ones, mainly due to the modification of the confinement potential in the growth direction. This offers the opportunity of manipulating the energies and also improve the quality of the devices obtained by In-flushing. The changes induced by the differences in the confinement potential for normal and In-flushed quantum dots are schematically presented in Figure 3.8. Here, the valence and conduction band energies are shown for in-plane and in-growth directions, before and after annealing. There is only a minor change in the lateral confinement, coming from the Ga/In intermixing, as discussed above. For the growth directions however, the changes are much stronger: the height of the QDs is connected with the thickness of the protective GaAs layer, the confinement increasing accordingly with the decrease of $d_{QD}$.

3.3.2 Altering QDs ex-situ by rapid thermal annealing

Besides in-situ Indium-flush technique, post-growth tuning of the QDs emission energy has been also widely used. Methods like RTA [90, 80], laser-induced thermal annealing [81] or ion-implantation induced intermixing [91, 92, 93] can be employed to achieve this goal. For this work, thermal induced alloy intermixing on quantum dots samples have been obtained by an ex-situ RTA process.

The RTA is a special method used in semiconductor manufacturing process consisting in a high temperature treatment on timescales in the range of tens of seconds. This technique had been commonly used in semiconductor device technology for the activation of dopants or as a mean to repair the damages resulted from ion implantation, but it has proven to be useful in the tuning of the quantum dots optical properties.

RTA is performed in special machines, usually industrial robots, which follow pre-designed recipes containing instructions regarding the temperature profiles and the desired atmosphere conditions during the annealing. The main part of such a machine is the reactor chamber, schematically represented in Figure 3.9. A Silicon wafer which lays on a quartz frame serves as a support for the sample to be annealed. RTA systems use a variety of heating configurations, energy sources and temperature control methods. The most widespread approach involves heating the wafer using banks of tungsten-halogen lamps because they provide a convenient, efficient and fast-reacting thermal source which can be easily controlled. In the RTA system which has been used at AFP (SHS100 made by AST GmbH), the Si wafer and the sample are heated by two arrays of lamps - one above and one below the support wafer. The lamp-arrays are further subdivided into groups or zones that can be individually programmed with various powers to maximize temperature uniformity [94]. The temperature control is made by a closed-loop circuit which contains a pyrometer, previously calibrated with the output of a thermocouple on the back-side of the Si wafer, and power regulators. The cooling at the end of the process is assured by water running through pipelines embracing the reactor unit. The environmental conditions in the reactor chamber can be also controlled precisely: prior the heating step, the enclosure is pumped to remove any trace of oxygen and water vapours which can give undesired reactions with the sample under treatment; during the thermal processing, inert or reaction gases can be delivered from high purity gas bottles via electro-mechanical valves.

Structures containing InAs QDs in GaAs matrix were annealed with GaAs proximity capping, i.e. the sample surface was covered to prevent As loss and reduce the defects.
Figure 3.9: Schematic drawing of the reactor chamber of a RTA machine (after [95]).

The sample lays on a support in the reaction chamber, surrendered by halogen lamps having the role of thermal sources.

inside the structure which would result otherwise in poor optical quality [96, 97, 98, 99]. The proximity capping was realized by simply covering the sample with a GaAs piece, having a 2-3 times larger area, cleaved from a blind polished wafer. This small detail plays an important role during the RTA process, as it provides a supplementary interface which can break the As diffusion out of the sample.

Small pieces with $3.5 \times 5$ mm, cleaved from the as-grown samples, were placed in the middle of the Si support in the reactor chamber to make sure they are in the zone with an uniform temperature distribution, away from regions where the temperatures are more difficult to control due to edge effects. Prior to annealing, both the sample and the GaAs cover piece have been carefully cleaned with acetone and isopropanol before they were introduced in the RTA machine.

In the frame of this work the samples were annealed for 30 s at temperatures between 800 and 900 °C in a N$_2$ flow (5 slm). First, a base-temperature was set, at an inferior value compared with the maximum temperature attained during MBE growth. From this point, the ramp-up to the desired annealing temperature was performed in 5 s as it can be seen in the left part of Figure 3.10. Here, the relevant range of the pyrometer data for an annealing at 820 °C is presented as an example. After the annealing, it takes approximately one minute to ramp-down to the base-temperature and cool down the sample. The right side of Figure 3.10 shows a zoom-in on the recorded pyrometer data during the annealing step. It can be seen the lamp power control assures a high accuracy of the temperature during the processing, resulting in less than 0.3 percent variations for 83% of the total annealing time.

Subjected to RTA, the InAs islands suffer major transformations, the responsible mechanism being the diffusion of atoms inside the system [100, 101]. The reason behind consists in the fact that In atoms diffuse out of the quantum dot while Ga ones diffuse into the dot, as it is schematically presented in Figure 3.11 [102]. In the left part of the figure, the as-grown situation is depicted, with an InAs quantum dot on top.
3.3. SIZE/SHAPE MODIFICATION OF THE QUANTUM DOTS

Figure 3.10: Temperature profile for RTA step. Left: Pyrometer temperature for the RTA process. The rising time from 450 to 820 °C is shorter than 5 seconds; Right: Detailed view of pyrometer temperature during the annealing step. The actual temperatures differ from the intended ones by less than 0.3% for at least 25 seconds.

of the wetting layer, completely overgrown with intrinsic GaAs. During the RTA step (center), due to increased temperatures, atoms will start diffusing in and out of the dot. This will result an increase in the dot size, both in lateral and growth direction. Moreover, a change in island composition - which is referred as intermixing - occurs. The resulting Ga rich InAs island is shown in the right part of the figure.

Because of the small aspect ratio of the quantum dots the principal effects of the intermixing are expected to come mainly from the diffusion in the vertical (in-growth) direction. Consequently, the changes in the island dimension along the growth direction will be more pronounced than the ones in the lateral size. Finally, the InAs quantum dots will have an asymmetric biconcave lens-shape, a bigger volume compared with the initial situation and a significant Ga content.

Figure 3.11: Quantum dot transformation during RTA. Left: Lens-shaped as grown InAs quantum dot in an GaAs matrix; Center: In and Ga diffusion; intermixing in the quantum dot during thermal treatment; Right: The resulting dot is bigger, contains less Indium and has a different shape. Colour coding: GaAs in blue and InAs in orange.

The effect of the RTA on the quantum dot valence and conduction band states, including the change in size and composition, is presented in Figure 3.12 both for
lateral and along growth directions. Incorporation of Ga into the InAs islands will increase the band gap and will produce a shift of the valence and conduction bands energy states closer to the GaAs band edges. An opposite effect is expected due to the increased quantum dot dimensions, hence a competition between these effects will take place.

Figure 3.12: Valence and conduction bands after RTA. An increased size and a modified quantum dot composition arise from the diffusion of Indium and Gallium at elevated temperatures. The transformations induce a modification in the confinement potential. Lateral and in-growth directions are depicted.

To conclude this section, it results that the quantum dots’ properties can be tuned by modifying their size and composition after the island nucleation. The two methods presented in this chapter offer such opportunities. RTA leads to a significant change in the island dimensions but also to a strong In/Ga intermixing. On the other side, with the Indium-flush method, the dot height can be reduced very much while the intermixing process can be even hindered. To this moment, both these methods have been used to shift the emission wavelengths of the SAQDs. In Chapter 6 it will be shown this is not the only advantage given by these two methods.
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Chapter 4

Experimental techniques used for the characterization of the quantum dots

The following pages will introduce the experimental techniques employed in the characterization of InAs quantum dots. The starting point for the discussion will be the actual structure of the samples as resulting from the MBE growth. Further, the optical and electrical properties for large quantum dots ensembles will be studied. The energetic configuration of the quantum dots will be accessed via PL and capacitance-voltage \( C(V) \) spectroscopy. While PL gives information on the inter-band energies, with \( C(V) \) spectroscopy it is possible to obtain information about levels in the valence and conduction bands separately. Moreover, sequential charging of the quantum dots becomes possible and carrier-carrier interactions can be studied. From the \( C(V) \) measurements in magnetic fields interesting aspects related with the nature of the capacitance charging peaks are revealed. In the end of the chapter it will be shown how the \( C(V) \) spectroscopy can be used for the visualization of the valence and conduction band \( k \)-space projections of the quasi-particle probability densities.

4.1 Heterostructure design

This section deals with the details related with the layer sequence and the MBE growth parameters. Because the samples are due to be characterized by \( C(V) \) spectroscopy, they have to be contacted. The preparation of the electrical contacts is therefore presented.

4.1.1 Layer sequence

The MBE growth begins with a 50 nm GaAs layer, deposited at 650 °C on the (100) face of a 2 inches epi-ready GaAs wafer supplied by CrysTec GmbH. A 20 to 30 periods 2 nm AlAs / 2 nm GaAs superlattice is grown, followed by another 50 nm GaAs layer having the role of smoothing the surface. The relevant part of the layer sequence starts with a 300 nm thick Silicon or Carbon doped GaAs which will play the role of the back contact in the final structure. The deposition is made at the same temperature as before. To ensure that no traces of Carbon remain in the growth chamber after the \( p \)-type doping,
the growth process is temporarily suspended for an overnight pumping of the system. In the case of Si doping, no such step is required. The growth is resumed in both cases with the deposition of 5 nm GaAs at slightly lower temperatures to avoid the diffusion of the dopant into the subsequent layers. Then, the substrate temperature is increased again at 600 °C and the growth continues until a total thickness $l_1$ is obtained for the undoped GaAs region, which will serve as a tunneling barrier in the final structure. For the $n$-type samples, $l_1$ is usually in the range of 25 nm although it can be as much as 45 nm when the tunneling time is to be controlled. In the case of $p$-type samples, typical values for $l_1$ are in the range of 17 nm to 19 nm.

Afterwards, the substrate temperature is reduced down to 520 °C and a single layer of SAQDs is formed in the manner described in Section 3.2. The conditions used result in a homogenous ensemble of quantum dots with several (3-4) bound electron and hole states. The dots are then overgrown (capped) usually with 8 nm GaAs at $\approx 500$ °C to ensure their protection but partial capping was employed as well, in order to tune the quantum dots properties (see Section 3.3.1). After the capping layer, the normal temperature (600 °C ) was restored to continue the growth of the GaAs layer until a total thickness of 30 nm. It is followed by an AlAs/GaAs (3 nm/1 nm) short-period superlattice (SPS) and a 10 nm GaAs cap layer. Most of the times, another InAs quantum dot layer is grown at the surface (outer QDs) for microscopy measurements (AFM, SEM, etc.). Although the growth conditions are the same as for the inner dots, the surface ones are uncapped and differ drastically from the buried ones. Regardless this dissimilarity, the outer quantum dots can be studied for different samples, offering the possibility to compare them and to adjust accordingly the growth conditions, in order to obtain similar results.

Figure 4.1: Sketch of typical heterostructure employed for conduction band $C(V)$ spectroscopy (a) and the corresponding energy band diagram (b).
A typical $n$-type heterostructure employed for charging spectroscopy on quantum dots conduction band states is schematically presented in Figure 4.1. The SPS below the surface is intended to block the current flow to the top gate of the final device [103]. The number of the periods in the SPS is adjusted in such a way the total distance $l_2$ from the quantum dots layer to the surface will be 5 to 11 times larger than $l_1$.

### 4.1.2 Sample preparations

Immediately after the growth, the wafers were covered with a thick photoresist layer and baked at 100 °C in order to ensure their protection during storage. Whenever needed, small pieces were cut from the central region of the wafers by using a diamond tip. After cleaving the samples, they were cleaned with acetone and isopropanol on a spinner and underwent further processing to obtain Schottky diodes suitable for $C(V)$ measurements. Although this is the least important part of the sample preparation, an error in the recording and retrieval of the alignment of the edges of the cleaved piece with respect to the wafer flats would have major influences later, leading to erroneous interpretations for the results of measurements.

The cleaved pieces were further provided with Ohmic and Schottky contacts. The Ohmic contacts and the gates have been prepared differently for samples with an $n$- or a $p$-type back contact. First, the Ohmic contacts were soldered at the corners or along the edges of the cleaved piece: in the case of $n$-type $C(V)$ samples, Indium was used followed by alloying for 5 minutes at 370 °C to assure the diffusion down to the doped region; for the $p$-type $C(V)$ samples In-Zn contacts were provided without further alloying, the thermal energy during the soldering being sufficient for the diffusion to the C-doped back contact.

The preparation of the top contacts (gates) was done by evaporation of thin metallic layers in a vacuum chamber, the area to be evaporated being defined by a photolithographic step. Again, differences between $n$-type and $p$-type $C(V)$ samples existed. The exact recipes used for obtaining the Schottky gates can be found in Table 4.1.

<table>
<thead>
<tr>
<th>Evaporation of Schottky diodes</th>
<th>$n$-type diode</th>
<th>$p$-type diode</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 nm Au</td>
<td>15 nm Cr</td>
<td>10 nm Ni</td>
</tr>
<tr>
<td></td>
<td>300 nm Au</td>
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</tbody>
</table>

**Table 4.1:** *Evaporation recipes for the preparation of the Schottky diodes designed for $C(V)$ measurements.*

In order to have sufficient quantum dots under the gates that a signal could be registered by our set-up, contacts of 300 $\mu$m $\times$ 300 $\mu$m were used for the preparation of the $C(V)$ samples. At an usual dot density of $(1-2) \times 10^{10}$ cm$^{-2}$, an ensemble with $10^7$ quantum dots would be probed.

Finally, the samples were mounted in 16-pin (DIP), 20-pin or 32-pin (CLCC) carriers and contacted with 25 $\mu$m Al wire in a wedge bounder. The choice for the chip carrier to be used is dependent of the requirements of the measurement type: in most of the cases, 16-pin carriers have been used for regular $C(V)$ measurements, while rectangular
32-pin carriers were used for measurements in magnetic field; for measurements in a tilted magnetic field, square-shaped 20-pin carriers were used because, in this configuration, it was possible to mount the sample in such a way that the in-plane component of the magnetic field could be aligned to either of the principal crystal directions [011] and [0-11], as it will be detailed later.

4.2 Characterization

This section introduces the two experimental methods which have been employed for the characterization of the samples used in this work: photoluminescence spectroscopy and capacitance-voltage spectroscopy.

4.2.1 Photoluminescence

Usually, room temperature PL spectroscopy is the preferred technique employed to characterize the newly-grown samples as soon as they are taken out from the growth chamber, in order to confirm the quality of the contained quantum dots. PL is well-suited for a rapid characterization because no special preparations are required to perform it, provided the availability of a simple optical setup.

The 3D confinement of carriers in a small region cause a discrete energy spectrum for electrons and holes. A Coulomb-correlated photo-generated electron-hole pair (exciton) in a quantum dot can recombine with the emission of a photon with the energy

\[ E_i = E_g - E_{e_{i+1}} - E_{hh_{i+1}} - E_{X_i} \]  

(4.2.1)

where, with the conventions in Figure 4.2, \( i \in \mathbb{N} \). Here, \( E_g \) is the band gap energy of the matrix material, \( E_{X_i} \) are the exciton binding energies, while \( E_{e_1} \) and \( E_{hh_1} \) are the energetic distances between the single-particle energy states in the conduction, respectively valence band, measured from the edges of the GaAs band. The allowed optical transitions for a single quantum dot consist of a series of \( \delta \) function lines whose positions depend on the energy levels in the 3D confined region [7].

The Stransi-Krastanow growth mode results in an ensemble which consists of individual quantum dots with slightly different sizes, shapes, strains or compositions, such that the energy spectrum varies from dot to dot. This leads to the inhomogeneous broadening of the ensemble properties. Typical inhomogeneous broadened line-widths of several tens of meV have been experimentally observed from PL measurements. In most of the cases, the broadening comes from the size distribution of the randomly-formed individual 3D islands. It is reasonable to assume a Gaussian distribution of dot compositions, giving the same widths for all peaks [7]. When both these effects come into action, the resulting PL spectrum will show broader peaks at higher energies.

In Figure 4.2, the processes leading to the typically observed PL spectrum of an InAs/GaAs quantum dots ensemble are illustrated. First, electron and hole pairs are obtained by the absorption of photons having higher energy than the band gap of the matrix material. The electrons and holes are then captured by the quantum dots
and relax into the ground state from where they can recombine with the emission of a photon. The relaxation in the quantum dot is made by emitting one or several phonons while the photon emission follows selection rules which allow recombination mainly from electrons and holes belonging to the levels with same quantum numbers ($e_i \leftrightarrow hh_i$) whose wavefunctions have sufficient overlapping [104]. Increasing the excitation power, saturation might occur and the excited levels become also populated one by one, enriching the PL spectrum. This can be exploited by state filling spectroscopy which allows the schematic representation of the processes leading to PL: (1) formation of electron-hole pairs in bulk GaAs by laser excitation; (2) capture into the QD by phonon emission; (3) electron (hole) relaxation onto the QD ground-state or lowest (highest) unoccupied excited state; (4) recombination and emission of the photons. Inset shows a corresponding room temperature PL spectrum for an annealed quantum dot sample (#12948).

The experimental setup in use at AFP, sketched in Figure 4.3, contains of a modulated laser diode, a monochromator and a detector. The employed laser diode emits at 635 nm (1.95 eV), well above the GaAs band gap (1.42 eV), with a power density of $\approx 5$ mW. The beam is focused with a system of lenses, down to a spot of $\approx 10^{-5}$ cm$^2$.

Figure 4.2: Schematic representation of the processes leading to PL: (1) formation of electron-hole pairs in bulk GaAs by laser excitation; (2) capture into the QD by phonon emission; (3) electron (hole) relaxation onto the QD ground-state or lowest (highest) unoccupied excited state; (4) recombination and emission of the photons. Inset shows a corresponding room temperature PL spectrum for an annealed quantum dot sample (#12948).
such that an ensemble of \( \approx 10^{5-6} \) quantum dots is probed at a time. The quantum dots’ emission is spectrally resolved by a 0.5 m Spex500M monochromator which disperses the radiation on a diffraction grating with blaze wavelength of 750 or 1000 nm. The spectrally dispersed photons are then detected with a liquid-Nitrogen-cooled InGaAs photodiode by using lock-in technique to filter the signal.

**Figure 4.3:** Experimental set-up used for PL spectroscopy. A laser spot is focused on the sample surface creating electron-hole pairs which relax into the quantum dot states from where they recombine. The radiation emitted by the quantum dot ensemble is dispersed by the grating of a monochromator and detected by a liquid-Nitrogen-cooled photodetector by lock-in technique.

For the same exciting power and same focusing area, the intensity of the PL signal depends on the ratio between electron-hole recombination time and their relaxation time into the quantum dots as well as on the number of excited quantum dots (surface density), the number of the confined levels in the dot (given by the sizes of the dots) and on the presence of capturing centers (defects). Therefore, PL spectroscopy gives information on the optical quality of the sample. More important information regarding the ensemble homogeneity is given by the widths of the peaks. The inter-sublevel energies and the localization energies with respect to the wetting layer can be also obtained, making PL a valuable tool in the study of the properties of the quantum dots.

### 4.2.2 Capacitance-Voltage spectroscopy

In addition to the optical measurements, a wealth of information regarding the QD’s energy level structure can be obtained from electrical measurements. Several methods had been widely used to characterize QD systems. Among them, one can mention tunneling spectroscopy, deep-level transient spectroscopy (DLTS) or \( C(V) \) spectroscopy [7]. The latter has been the main tool employed to gather the results presented throughout this work, its principle and applications being presented in this section. For a concise comparison with the other characterization methods mentioned above the work of
Reuter [103] can be a starting point.

Different from PL, which probes valence and conduction band states simultaneously, \( C(V) \) can access these bands separately. Moreover, information about carrier-carrier interactions inside the quantum dots can easily be extracted.

The \( C(V) \) spectroscopy consists in tunneling electrons (or holes) through a thin barrier, from a reservoir into the quantum dots embedded in a Schottky diode, and registering the changes in the capacitance of the structure as a function of the applied voltage.

As it was the case in the previous section, the method will be introduced starting from the energy band diagrams. In Figure 4.4, the conduction band energies are obtained by solving the Poisson equation for the entire structure; a representative sample containing quantum dots was considered. For the calculations the quantum dots layer was treated as a thin quantum well. The energy levels inside quantum confined region are put just for exemplification, without solving the Schrodinger equation there. The simulations have been carried out using G. Snider's 1D Poisson solver [105].

By applying a voltage between the back contact and the top gate of the structure sketched in Figure 4.4 (a), the energy bands can be tilted in respect with the Fermi level \( E_F \) which is pinned by the high doping level in the back contact. With the variation of the gate voltage, the discrete energy levels in the quantum dot shift relatively to \( E_F \), coming one by one in resonance with it. When this is happening, carriers can tunnel through the thin barrier and localize in the dot, as the thick AlAs/GaAs SPS prevents
4.2. CHARACTERIZATION

them of reaching the surface. Because the tunneling is realized when the Fermi level in the back contact is aligned with the levels in the quantum dots, it results only one type of carriers (either electrons or holes) can be loaded into the dots, depending on the doping type of the back contact. Besides, due to their different effective masses, electrons can tunnel through thicker barriers than holes. To account for these differences, distinct heterostructure design was needed for studying the valence and conduction band states (see Appendix A).

The differential capacitance is derived from the charging current and can be measured by lock-in or with a precision LCR meter as long as a small AC modulation signal is superimposed on the sweeping DC bias. Superimposing an additional small AC component on the DC bias, makes the carriers tunnel forth and back into the dots, resulting in a periodic charging/decharging which leads to an increase in the device capacitance. All the $C(V)$ measurements presented in here were performed with an Agilent 4284A precision LCR-meter, with special attention being given to minimize parasitic signals. The measurement setup comprising the LCR meter is presented in Figure 4.5. The AC amplitude was 10 mV and the frequency was chosen, as it will be explained below, between 1 kHz and 1 MHz. All measurements were performed at low enough temperatures (4.2 K) so that $k_B T$ would be much smaller than relevant energies in the quantum dot system and thermal broadening of the $C(V)$ spectra would be avoided.

Initially, the dot had been depleted of carriers by applying a sufficiently high reverse potential on the structure, so that all their discrete conduction band energy levels would be above (below, in the case of valence band) the $E_F$ in the back contact. With the reduction of the inverse-voltage applied on the gate, the quantum dots’ energies come in resonance with $E_F$ and carriers can tunnel at well-defined gate voltages, any tunneling being suppressed in between. At large negative bias, the background capacitance reflects the geometrical capacitance between the back contact and the top gate

Figure 4.5: Sketch of the $C(V)$ measurement setup. The Schottky diode containing the quantum dots is biased with a small amplitude AC signal. Capacitance is read in a four points configuration by an LCR-meter (lock-in might also be used). After [106].
(dependent on gate area and $l_2$). The QDs-related capacitance peaks are superimposed on a rather large linearly-varying background which resides in the voltage dependance of the capacitance of the Schottky diode. To obtain only the information related with the charging of the dots, the linear part has to be extracted.

A characteristic $C(V)$ spectrum for the conduction band states is presented in Figure 4.6 to provide support for the explanation. The charging peaks corresponding to the first six electrons are clearly resolved. With a gate area of 300 $\mu$m $\times$ 300 $\mu$m and an island density obtained from the growth process described in Section 3.2, $\approx 10^7$ quantum dots are simultaneously probed. This can be verified by calculating the area of the first peak in the $C(V)$ spectrum, considering only one charge per dot. Similarly to the broadening of the PL spectrum, the size distribution of the SAQDs will produce also a finite width of the peaks in the $C(V)$ spectrum. The difference is that the spreading in energy is smaller for $C(V)$ because the broadening is given by the contribution only from conduction band (or from the valence band in the case of charging spectra for holes).

With each peak corresponding to approximately one supplementary charge per dot, in most of the cases, up to six electrons can be loaded for an $n$-type standard-grown quantum dots sample. Likewise, the number of holes could reach eight for a standard $p$-type sample, due to the smaller Coulomb energies. Increasing the gate voltage after all the quantum dot’s bound-states are occupied will produce the charging of the quantum well formed by the remainder InAs wetting layer. The exponential rise in the capacitance at $V \approx 0.8$ V in Figure 4.6 will account for that (see also the inset). At even
higher gate voltages, close to flat-band conditions, the carriers will escape from the dot to the GaAs region just below the AlAs blocking barrier, forming a 2DEG (2DHG) [29].

The voltage scale can be easily converted into an energy one by employing a geometrical argument. From Figure 4.4 it can be seen that the lever-arm rule can give the energetic distance between the dot states and the GaAs band-edges, as a function of the gate voltages $V_{gate}$. In this case, the QD energies will appear negative for the conduction band and positive for the valence band. Taking into account the diode is reverse-biased, the following relation can be used:

$$E_{C(V)} = e l_1 (V_{bi} - V_{gate}) - l_2.$$  \hspace{1cm} (4.2.2)

The lever-arm $l_1 / (l_1 + l_2)$ can easily be obtained from the sample growth-sheet. Its usual values are $\approx 1/7$ for normal n-type samples and $\approx 1/11$ for p-type ones. For the built-in potential $V_{bi}$, different values can be found in the literature [59, 107, 108].

This is only a coarse approach to obtain the energy scale, but it has the advantage it is fast and does not rely on supplementary measurements and simulations. More precision can be attained by considering the charge image in the back contact, different permittivities in the SPS and the voltage-dependent spill-over from the back contact which reduces $l_1$. All these are studied in detail in [103], the calculations showing a 7 percent underestimation for the electron-electron interaction energies when only the lever-arm rule was used. Considering this, it seems reasonable to use the lever-arm rule for energy-scale conversion when presenting the results in Chapter 6, which deals only with the tuning of the Coulomb energies for electrons in the ground state. For sake of completeness, it is worth to mention that in the case of holes the errors are more significant, accounting up to 20 percent.

As already explained, by changing the gate voltage, the ladder of the dot states is shifted through the Fermi energy of the back contact. With the degeneracies of the QD energy levels (see Section 2.2.1), two peaks should arise from the tunneling into the conduction band ground state and another four peaks corresponding to the tunneling in the excited p-state, with a separation given by the Coulomb interactions (see for example [10]). Indeed, in the plot from Figure 4.6, it can be seen that the electrons charging peaks are coming in two groups, comprising two and four peaks respectively. The energy separation between the first two peaks gives exactly the direct Coulomb energy interaction in the ground state $E_{Coul}$. For more than two electrons, exchange interactions can account for up to 25 percent from the direct Coulomb energy. This has been discussed in detail by Warburton et al. [31] and introduced in Chapter 2.2.3.

In Figure 4.7, a sketch of the influence of the Coulomb blockade on the barrier height is presented. It can be seen the charge in the dot locally modifies the band structure (conduction band in this case). Assuming the quantum dot as a disc, homogeneously charged with a single electron, Luyken et al. have estimated the potential along the growth direction [109]. This potential adds to the triangular potential (left) with the result of lifting the dot levels (center) by the Coulomb blockade. With the increase of the gate voltage, the dot's ground state matches again the Fermi energy and the dot is filled with the second electron (right). Because the degeneracies are lifted by the Coulomb interactions and because all the levels below $E_F$ remain occupied, it results $C(V)$ spectroscopy does not probe the single particle energies but gives the so-called addition spectrum, i.e. the sum between the energy due to quantization and the Coulomb energies.
Another parameter extracted from the $C(V)$ spectrum, the height of the $N^{th}$ capacitance peak, is given by the number of the dots being charged. By increasing the measurement frequency, less dots can be charged during one AC cycle, resulting, eventually, in a successive suppression of the peaks, starting with $s_1$, as seen in Figure 4.8. This can be put on the fact that the barrier height is smaller for higher states than for the deeper ones. The frequency dependence of the addition spectra for electrons is presented here for exemplification. Luyken et al. have demonstrated it is possible to tune

\[
\begin{align*}
\text{Figure 4.7: Sketch of the quantum dot’s conduction band ground state while the dot is charged. The effect of the Coulomb blockade on the tunneling barrier. After [109].}
\end{align*}
\]

\[
\text{Figure 4.8: Frequency dependence of the conduction band } C(V) \text{ spectra. By increasing the frequency, less quantum dots can be charged during one AC cycle, resulting in a decrease of the capacitance peak height and, eventually, to a complete disappearance. The frequency at which the height of the peak is half of the value at } \nu \rightarrow 0 \text{ gives the tunneling time into the state corresponding to the respective charging peak.}
\end{align*}
\]

the charging dynamics in a wide range either by a combination between measurement frequency and the thickness of the tunneling barrier or by the application of a magnetic field perpendicular to the tunneling direction [109]. Reuter et al. have shown that the tunneling time $\tau$ into a quantum dot state can be reasonably found from $\nu^{1/2}$, the frequency at which the height of the corresponding capacitance peak had decreased to
the half of the value measured at very low frequencies (\(\nu \to 0\)) [110]

\[
\tau = \frac{1}{2\pi\nu^2}.
\]

(4.2.3)

This is a very important result which will be exploited in the wavefunction mapping, as it will be described later on in this chapter.

**C(V) spectroscopy in magnetic field**

From C(V) spectroscopy, information on the energies in the valence or conduction band are easily obtained. Moreover, carrier-carrier interactions energies can be also determined. Supplementary knowledge can be obtained by performing C(V) spectroscopy in magnetic field.

Attempts to explain the differences observed in the charging spectra for electrons and for holes have been made by studying the dispersion of the energy levels with a magnetic field applied perpendicular to the base-plane of the dots [111]. With a magnetic field rotated into the growth plane, k-space projections of the probability density corresponding to the individual charging peaks can be visualized [111, 112]. Although these methods have been already employed for the study of quantum dot ensemble properties, in the Chapter 5 new results will be presented as obtained, for the first time, by a combination of the two approaches mentioned in the paragraph above.

All the measurements have been performed in the same conditions as described before, by using an LCR-meter to measure the capacitance of the devices at 4.2 K, with a 10 mV AC modulation.

Throughout this work, the direction of the magnetic field will be assigned with respect to the quantum dot layer such that an applied perpendicular field will be directed in the growth direction. Likewise, a parallel field will lay in the quantum dot's plane.

The remainder of this chapter deals with the practical details concerning the magneto capacitance measurements and the expected outcome of this kind of experiments.

**C(V) in perpendicular magnetic field**

There are no essential differences from a standard C(V) measurement setup in the case of an applied perpendicular magnetic field. The only requirement is that the cryostat has to be provided with a coil to produce the desired magnetic field. In our case, the design of the sample holder required the sample to be mounted in a CLCC type carrier. For the measurements performed at the Oxford-Cryo facility at AFP, the sample was directly immersed in the cryogenic liquid because the bore diameter of the variable-temperature insert fitted-in didn't allow enough space for the encasement of the sample holder.

**C(V) in parallel magnetic field**

Following the approach of Patanè [47], Wibbelhoff et al. have suggested the possibility of mapping the k-space quasi-particle probability density of the electrons in the quantum dot by applying a magnetic field perpendicular to the growth direction, i.e. in-plane (parallel) field [112]. The same method has been applied then for the hole system and differences between the hole and electron wavefunctions have been disclosed [103, 111, 113].
The essential principle underlying this type of experiment is related with the changes induced by the presence of the magnetic field on the overlap of electron (hole) wavefunctions in the back contact and the quantum dot. More exactly, the applied magnetic field will influence the tunneling matrix $M^{k,N}$ defined by Eq. 2.2.21 which is depending by the overlap of the wavefunctions.

When carriers tunnel from the reservoir to the dot in the presence of a magnetic field perpendicular to the tunneling direction, they acquire an additional in-plane momentum \[52, 114\] whose magnitude is given by
\[
|\vec{k}_\beta| = \frac{l_1 e |\vec{B}|}{\hbar},
\]
(4.2.4)
with $l_1$ being the thickness of the tunneling barrier and $e$ the elementary charge.

A sketch of the geometry of the tunneling process for holes in Figure 4.9 (left) shows the action of the Lorentz force causing the additional momentum $\vec{K}_\beta$.

Figure 4.9: Left: Sketch of the geometry of the tunneling process with $\vec{B}_\parallel$: the carrier tunneling to the quantum dot is subjected to the Lorentz force, gaining additional momentum $k_\beta$. The direction of the magnetic field, electric field and $k_\beta$ are orthogonal, forming a trihedron. Right: the superposition of the carrier wavefunctions in the emitter (blue) and quantum dot (red) - $k$-space representation. The tunneling rate is influenced by this superposition which can be controlled, via $k_\beta$, by the application of an in-plane magnetic field. After [47].

In Figure 4.9 (right), the overlap between the Fourier transforms of an electron (or hole) wavefunctions in the back contact $\phi_E(\vec{k} - \vec{k}_\beta)$ (blue) and in the quantum dot $\phi_{QD}(\vec{k})$ (red) is shown for a given magnetic field [47]. The strong spatial (real space) confinement in the dot corresponds to a broad wavefunction in $k$-space. Differently, the weak spatial confinement in the back contact gives a sharp distribution which can be displaced with $\vec{k}_\beta$ by the applied field [115]. Consequently, the overlap between tunneling carrier wavefunctions in the back contact and in the quantum dot can be altered by applying an in-plane magnetic field, which in turn, will modify the tunneling rate $1/\tau$. Furthermore, if $\phi_E(\vec{k} - \vec{k}_\beta)$ is approximated by a $\delta$ function, the tunneling rate $1/\tau$ will be proportional to the momentum space projection of the probability density $|\phi_{QD}(\vec{k}_\beta)|^2$ (refer to Section 2.2.5).

But in $C(V)$ spectroscopy, at appropriate frequencies (according to Eq. 4.2.3), the height of the capacitance peak $C_{QD}$ is directly proportional with the tunneling rate, as
it was explained by Reuter [103]. It follows that:

$$C_{QD}(\vec{B}_{||}) \propto \frac{1}{\tau(k_{\beta})} \propto |\phi_{QD}(\vec{k}_{\beta})|^2. \quad (4.2.5)$$

By rotating $\vec{B}_{||}$ in the quantum dot’s plane, it is possible to obtain the full spatial profile of $|\phi_{QD}(\vec{k}_x, \vec{k}_y)|^2$ representing the k-space projection of the probability density of a given quasi-electronic state confined in the quantum dot. Because the capacitance peaks arise by subsequently filling the dots with electrons or holes, with this method, multi-carrier states are probed, the issue being discussed by Rontani and Molinari from a theoretical point of view [43, 116].

The charging dynamics of the quantum dots can be tuned in a wide range by the AC frequency [109]. It has been proposed that the tunneling time can be calculated from frequencies at which the height of each capacitance peak had decreased to half of its corresponding value at very low measurement frequencies [110]. The band tilting makes so that the height of the tunneling barrier is different for higher states than for the ground state. This will be reflected in the tunneling time, requiring different frequencies for s- and p-states. Also, the thickness of the tunnel barrier $l_1$ should be bigger for the samples used in wavefunction mapping, otherwise the required AC frequencies would be impracticable high [111]. Whereas for n-doped samples, the thickness of the tunnel barrier should be increased from the usual value of 25 nm to around 40 nm, for holes, due to their larger effective mass and lower tunneling rates, a value of about 19 nm is sufficient for $l_1$. Taking all these things into account, prior to measurements with applied parallel magnetic field, a frequency dependence should be recorded so that the required measurement frequencies would be settled.

Returning to Figure 4.9 (left), it can be seen that the directions of the magnetic field, electric field and $\vec{k}_{\beta}$ are orthogonal, forming a trihedron. It is important to stress here that $\vec{B}_{||}$ and $\vec{k}_{\beta}$ are orthogonal such that the k-space directions are rotated by 90° with respect to the real-space directions. The latter are taken as reference when applying the in-plane field. This small detail produced some trouble in the past, resulting in an erroneous labeling of the asymmetry directions for probability density contour-plots [117, 118] due to some errors in handling the samples during contact processing. By now, the issue has been solved and the directions confirmed for further reference, the correct assignation being made using the method described in Appendix B.

The $C(V)$ measurements with applied parallel magnetic field were performed at the AFP facility by using the standard measuring equipment (LCR-meter) and conditions (4.2 K). Magnetic fields up to 13 T were obtained with a superconducting coil fitted into an Oxford Instruments bath-cryostat. The samples were mounted in CLCC chip carriers on a rotating sample holder, making possible the application of the magnetic field at different azimuthal angles ($\vartheta$) in the quantum dot’s plane. By varying the magnetic field strength and orientation, 3D plots (or 2D contour-plots) of the tunneling probability in k-space can be obtained from the height of the peaks in the $C(V)$ spectra [112]. For each spectrum, a Gaussian multi-fit procedure was employed using a Levenberg-Marquardt algorithm [119, 120]. During the fitting, constraints were imposed on the peak positions and on the peak widths. After the fitting, the peak heights were extracted and associated with the field and the angular parameters. Further, the peak heights were normalized to their corresponding values at 0 T. A transformation from polar ($\vec{B}_{||}, \vartheta$) to cartesian coordinates ($\vec{k}_x, \vec{k}_y$) and a matrix transformation of the dataset
were the last steps required to obtain the plots. A detailed description of the entire procedure is given in Appendix C, including the programming code to implement it in Origin (OriginLab Corp.).

As an exemplification, the momentum space projection of the probability density distribution corresponding to a second electron entering the dot is given in Figure 4.10, with red encoding a higher probability density. This map has been obtained with a 1 T step for the magnetic field sweep and a 22.5° in-plane rotation step. It can be seen that the contours are asymmetric, having an elliptical shape for this particular case. The two black curves on the side-graphs represent sections into $|\phi_{QD}(\vec{k}_x, \vec{k}_y)|^2$ along $\vec{k}_x$ and $\vec{k}_y$ directions, corresponding to the major and the minor ellipsis axes (grey reticle). Accordingly, enough information regarding the asymmetry of the electron (hole) wavefunctions can be obtained only by applying the magnetic field along two orthogonal directions. This would reduce considerably the time needed for completing the measurements, while still obtaining valuable results.

**C(V) in tilted magnetic field** In Section 2.2.1 it has been shown that the dispersion of the quantum dot energies in a perpendicular magnetic field will result in a level crossing at certain critical fields. It had been experimentally shown that the filling sequence is changed upon the critical field, with different behaviour for electrons and for holes [103]. It would be therefore interesting to see how this will affect the shape of the
wavefunctions. Yet, the \( k \)-space wavefunction mapping is performed with a parallel magnetic field by rotating it at different azimuth angles in the growth plane. Hence, a combination of an in-plane field and a perpendicular one will be required to obtain the plots of \(|\psi_{QD}(\vec{k}_x, \vec{k}_y)|^2\) before and after induced level-crossings, i.e. \( C(V) \) in tilted magnetic fields.

By controlling the sample orientation and the total strength, the tilted field was applied in such a manner that a perpendicular component was kept constant at different values in order to obtain the energy shifts, while the in-plane component was swept from 0 T to \( \approx 25 \) T in order to map the wavefunctions. Due to the sample-holder design and to a limited measurement time, the in-plane \( C(V) \) was measured only for two azimuthal angles, i.e. two orthogonal directions aligned with the edges of the sample ([011] and [0-11] GaAs (100)). This was done by taking the sample out of the cryostat and re-mounting the chip carrier into the sample holder. In Figure 4.11 (left), the field orientation with respect to the sample is schematically shown. In the table to the right, the total field and the tilt are given as an example for the case when a 18 T perpendicular component is to be applied. The last two columns in the table show the calculated shift from the desired values, when a 2° uncertainty in setting the tilt-angle is introduced, due to the construction of the experimental setup. It can be seen from here that the error induced would be in the range of mT for the perpendicular component but close to 1 T for the in-plane field. However, an eventual error in setting the correct angles would influence only the measurements at extremely high fields, i.e. only the tails of the wavefunctions will be affected and only in the case of 18 T perpendicular field series. To tackle this problem, the rotating mechanism was adjusted by using a Hall-bar probe prior to the actual measurements.

From the simulations in Figure 2.7 and the results reported earlier [121], the ex-

<table>
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<th>( B_{\text{total}} ) [T]</th>
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<th>( B_\perp ) [T]</th>
<th>( B_\parallel ) [T]</th>
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expected crossing appears when the perpendicular magnetic field strength is somewhere between 12 T to 15 T. On the other hand, the wavefunction are known to be extended up to $|\vec{k}| = 8 \times 10^8$ m$^{-1}$ [117], which corresponds to an equivalent magnetic field of $\approx 25$ T. In these conditions, the experimental particularities require high magnetic fields with effective strengths up to 30 T. Such experimental conditions are not available at

![Flowchart](image.png)

**Figure 4.12:** Flowchart for tilted magnetic field measurements: quantum dot energy dispersion in magnetic field was studied first to get the critical fields $B_c$ for which the level crossing is expected. Sections along two orthogonal directions into the plots of the probability density distribution were taken by sweeping the in-plane magnetic field component while a constant perpendicular component was applied.

AFP and an application for magnet time at the High-Field Magnet Laboratory (HFML) in Nijmegen, the Netherlands, was submitted. However, the 40 h magnet-time obtained would have not been sufficient for a complete wavefunction mapping with high azimuthal resolution. Instead, sections into the wavefunction were taken as it was shown to provide enough information on the quasi-particle probability densities (see Figure 4.10).

The flowchart in Figure 4.12 describes the successive steps taken to obtain the results of Chapter 5. First, $C(V)$ spectra for different values of an applied pure perpendicular magnetic field were recorded and deconvolved by a multiple-peak procedure. An array with the peak positions $V_i$ was formed for each of $|B_\perp|$ applied. Next, the tilted field was applied so that the in-plane component could be varied in 1 T steps along [011] while keeping a constant perpendicular component of 0, 4, 8, 12 respectively 18 T. The procedure was repeated with the in-plane magnetic field along [0-11] direction in GaAs (100). After finishing the measurements, the $C(V)$ spectra were fitted with multiple Gaussian curves, this time keeping the peak-positions fixed at their respective values from the $V_i$ arrays corresponding to the constant pure-perpendicular fields initially measured. After the last fit, the heights of the peaks were extracted and the datasets were further processed in order to obtain the profiles of $|\phi_{QD}(\vec{k}_x, \vec{k}_y)|^2$.

The measurements in tilted magnetic field were performed at HFML under identical conditions with the ones at AFP. The magnet used was a Bitter type coil with a maximal field of 30.2 T.
Chapter 5

Carrier wavefunctions in InAs quantum dots

To understand and exploit the unique properties of quantum dots, their discrete energy structure was intensively studied in the last two decades. Due to their properties, quantum dots are candidates for the further development of quantum computers and cryptography, therefore tuning and controlling the quantum interactions are of great importance. This requires the so-called engineering of the electronic wavefunctions in order to obtain the desired behaviour. The wavefunction engineering will allow, for example, to alter the overlap of the wavefunctions of electrons and holes so that the optical transition probabilities can be enhanced. Knowledge of the carrier wavefunctions in the quantum dot is the starting point to accomplish all of these.

The possibility of mapping the quasi-particle probability density by performing $C(V)$ spectroscopy in magnetic field was explained in Sections 2.2.5 and 4.2.2. The results obtained in this way are presented in the following chapter. An overview of the current knowledge on the shape/extension of the momentum space projections of the electrons and holes quasi-particle probability density distributions will be given first. The second half of the chapter will present how the wavefunctions change in the presence of a magnetic field component perpendicular on the quantum dots plane, which would influence also the conduction and valence band energies as described by the Fock-Darwin model (Section 2.2.1). The results presented here concern only the hole system whereas the electron system has been investigated recently [122].

5.1 State of the research

$C(V)$ spectroscopy on InAs self-assembled quantum dots allows the charging of the quantum dots with individual carriers, either electrons or holes, depending on the type of sample which is used.

As discussed before, the Coulomb interactions lead to a partial lift of the degeneracies of the energy levels so that the peaks in the $C(V)$ spectra appear grouped as shown exemplarily in Figure 4.6 for conduction band states. The first two peaks in the figure correspond to electrons tunneling into the s-like ground state, having opposite spins according to Pauli principle. The following group should consist in four peaks, corresponding to the four-fold degenerated p-like states. While this is true for the case of conduction band, in the case of valence band $C(V)$ spectroscopy the peaks appear
in pairs as it was shown by Reuter et al. [12]. In consequence, a legitimate question would be to establish the charging sequence of the quantum dots.

In analogy with the atomic physics, for a perfect rotation symmetry of the confining potential, the filling with electrons or holes should happen according to the Hund’s first rule, i.e. the total spin is maximized. This implies that the third carrier will enter into a $p_-$ shell ($l = -1$) and that the fourth carrier will belong to $p_+$ ($l = +1$) having the same spin as the previous one. The following carriers will have opposite spins and will populate $p_-$ and $p_+$, respectively. However, for an asymmetric potential, the $p$-level would be split, favoring the filling in the order $p_- p_+ p_+ p_+$ (Aufbau principle). A strong $p$-shell splitting could also explain why the $C(V)$ peaks are coming in pairs in the case of holes.

By performing $C(V)$ spectroscopy with an applied magnetic field directed along the growth direction, the Fock-Darwin spectrum can be obtained from the shifts in the capacitance peaks, as the dispersion of the energies are given mainly by the dispersions of the single particle levels (Table 2.1). This is a consequence of the fact that the Coulomb energies depend only weakly on $B_\perp$, for the case of the quantum dots studied here, when the magnetic confinement is very small (see Figure 2.9 (e-f)).

The magnetic field dispersions of the individual charging peaks are presented in Figure 5.1 for electrons (a) and for holes (b) as resulted from conduction, respectively valence band $C(V)$ spectroscopy [103].

![Figure 5.1](image_url)

**Figure 5.1:** Dispersion of individual charging peaks for electrons (a) and holes (b) as resulted from $C(V)$ spectroscopy for conduction and valence bands with a magnetic field directed along growth direction. The lines are guide to the eye. After [103] by courtesy of Dirk Reuter.

Although the energies for the first two charging peaks for electrons (holes) show no shift with the magnetic field, which is consistent with the charging of a two-fold degenerate $s$-state of the conduction (valence) band, the situation is more complicated for the excited states. Major differences in the Fock-Darwin spectra for the conduction and valence bands have been found:

- **electrons:**
  - peaks 3 and 4 shift downwards in energy while peaks 5 and 6 shift upwards with increasing $B_\perp$;
slopes for the peaks 3 and 4 are almost equal with the slopes for 5th and 6th peaks (absolute value).

- **holes:**
  - the peaks 3 to 6 shift downwards and upwards in energy in an alternating manner;
  - the slopes of the 5th and 6th peaks are almost double (in absolute value) compared to the slopes of peaks 3 and 4;
  - there is a large separation in energy between 4th and 5th peak at $B_{\perp} = 0$ T.

The results obtained in this way clearly indicate that the filling sequence for electrons is $p^-p^-p^+p^+$ when considering an asymmetric (elongated) quantum dot. Yet, for a symmetric dot, the filling can be still made according to Hund’s rule at $B_{\perp} = 0$ T, but the magnetic field would change this, forcing the filling sequence to $p^-p^-p^+p^-$. The violation of the Hund’s rule occurs when the energy $\hbar \omega_c$ becomes larger than the exchange interaction between electrons with parallel spins [10]. The calculations of Warburton et al. [31] have shown that the critical field at which this change occurs should be around 1 T so that such a detail would not appear in the figure above.

The results in Figure 5.1 (b) point to a filling of the valence band states according to the Hund’s rule, but this would not explain the significant energy separation between the 4th and the 5th peaks at $B_{\perp} = 0$ T. Even more, if the energies correspond to levels having the same orbital angular momentum $|l| = \pm 1$, it is not possible to explain why the peaks 5 and 6 shift twice more than peaks 3 and 4. To account for this, Reuter et al. had proposed an *ad hoc* non-sequential filling for holes, breaking the Hund’s rule and the Aufbau principle [12]. According to them, the d-states would be filled before the p-level is completed in the case Coulomb blockade energy is larger than the separation between p and d levels. The incomplete shell filling was further confirmed by theoretical calculations taking into account hole correlation effects [123]. Climente and coworkers have challenged this proposal, being able to reproduce the Fock-Darwin spectrum, following Aufbau principle, by employing a multi-band k·p Hamiltonian, which considers the interaction between heavy hole and light hole subbands explicitly [14].

Recently, Bester and coworkers [13] have settled the issue of the charging sequence at $B_{\perp} = 0$ T by studying the quasi-particle wavefunctions. The k-space probability density images were obtained from $C(V)$ spectroscopy by rotating a magnetic field $B_{\parallel}$ in the plane of the quantum dots.

The experimental quasi-particle probability densities for electrons and holes are presented in Figure 5.2 (a) and (c), respectively. Here, the normalized $C(V)$ amplitudes of the different charging peaks are plotted as a function of $k_{ij}$ (Eq. 4.2.4) which spans a range from $-6 \times 10^8$ to $+6 \times 10^8$ m$^{-1}$ for the electrons and from $-7 \times 10^8$ to $+7 \times 10^8$ m$^{-1}$ for holes. The arrows at the bottom of the figure indicate the corresponding real-space crystallographic directions. The labels of the form "(i) e ⇒ (i+1) e" indicate the wavefunctions correspond to the tunneling of the $(i+1)^{th}$ electron in a quantum dot ensemble already filled with $N = i$ electrons per dot, i.e. the $(i+1)^{th}$ peak in $C(V)$. The indexing of the holes is done accordingly. It should be noted that the experimental resolution for the case of the electrons was not sufficient to resolve all the peaks. In
these conditions, the 4th and 6th peaks in Figure 5.2 (a) are just duplications of the 3rd and the 5th ones.

<table>
<thead>
<tr>
<th>Electrons</th>
<th>Holes</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Experiment</td>
<td>b) Theory</td>
</tr>
<tr>
<td>c) Experiment</td>
<td>d) Theory</td>
</tr>
<tr>
<td>0e ⇄ 1e</td>
<td>0h ⇄ 1h</td>
</tr>
<tr>
<td>1e ⇄ 2e</td>
<td>1h ⇄ 2h</td>
</tr>
<tr>
<td>2e ⇄ 3e</td>
<td>2h ⇄ 3h</td>
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<td>4e ⇄ 5e</td>
<td>4h ⇄ 5h</td>
</tr>
<tr>
<td>5e ⇄ 6e</td>
<td>5h ⇄ 6h</td>
</tr>
</tbody>
</table>

**Figure 5.2:** Experimental and, respectively, theoretical quasi-particle probability densities for electrons (a-b) and holes (c-d). The directions given by arrows and labeled as [110] and [1-10] are real-space crystallographic directions while the plots are in k-space. The calculations are performed on a single quantum dot, while the experiment probes an ensemble of quantum dots. For the electrons (holes), the reciprocal lattice vectors span a range from -6 x 10^6 to +6 x 10^6 m⁻¹ (from -7 x 10^6 to +7 x 10^6 m⁻¹). Reprinted from [13].

The corresponding quasi-particle probability densities for a single quantum dot have been calculated theoretically using an atomistic empirical pseudopotential approach which takes into account the multiband, multivalley and spin-orbit effects [13]. The results for electrons and for holes are given in Figure 5.2 (b) and, respectively, (d). The calculations for the electrons quasi-particle probability densities were performed for a circular quantum dot, while the holes probability densities were obtained for
an asymmetric dot. The agreement with the experimentally determined quasi-particle probability densities is remarkable. A closer inspection reveals important details:

- **electrons**
  - The wavefunctions for the first two electrons are $s$-like and slightly elongated on the [110] direction in $k$-space which corresponds to a [1-10] elongation in real space.
  - The wavefunctions for $N = 3, 4$ have a bone-like shape with a node at $\vec{k}_{3} = 0$ and two maxima along [1-10] in real space; for the states with $N = 5, 6$ the bone-like shape is preserved except the maxima are along [110]. The fact that the probability densities for $N = 3, 4$ and $N = 5, 6$ are orthogonal indicates that they belong to states with $l = -1$, respectively $l = 1$. Therefore the charging sequence is conform with the Aufbau principle as it was concluded from the energy dispersion in a perpendicular magnetic field (for an asymmetric dot).
  - The theoretical results presented here for a symmetrical quantum dot differ from the expected circular shape presented in Figure 2.8. The argument of Bester et al. is that this reveals an atomistic and not necessarily only a shape asymmetry. The observed orientation of the $p$-like states in Figure 5.2 (b) is a result of the "atomistic nature of the underlying zinc blende crystal lattice in contradiction with effective-mass models that lead to degenerate and isotropic $p$-states" [13].

- **holes**
  - The transitions $0h \Rightarrow 1h$ and $1h \Rightarrow 2h$ resemble the case of electrons. As concluded also from the Fock-Darwin spectrum, they belong to a $s$-like shell. It is important to stress-out here, the asymmetry is the same as for the electrons. This points out to an asymmetric potential with structural (geometrical/atomistic) cause and not to a strong piezoelectric effect as it was believed initially [113].
  - Different from the case of electrons, the probability densities extracted from the peaks 3 and 4 on one side, and peaks 5 and 6 on the other side show clear differences both in the experimental and theoretical results. Based on these results, the authors argue in favor of an incomplete shell filling model as the ones proposed by Reuter [12] and He [123].
  - The interparticle correlation effects play an important role in the case of valence band states [124]. Comparing the theoretical results for the transitions $2e \Rightarrow 3e$ and $2h \Rightarrow 3h$ in Figure 5.2 (b) and (d), it can be seen the third tunneling hole has not a pure $p$-orbital character. The same is valid for the fourth hole. Accordingly, the 5th and 6th holes have mixed $d$- and $p$-characters, the $p$-like character being about 12%, respectively 23% [13].

To emphasize the nodes along the two orthogonal directions giving the high symmetry crystal axes, a contour plot for the hole probability densities is presented in Figure 5.3 [103]. Different from [121], the correct orientation (here in $k$-space) was obtained using the procedure described in Appendix B. Although it might seem redundant, this will make more intuitive the figures in the next section.
Figure 5.3: Contour-plots for the holes quasi-particle probability densities obtained by C(V) spectroscopy on sample #11618. Different from [121], the correct orientation (here in $k$-space) was obtained using the procedure described in Appendix B. The contour-plots correspond to the 3D plots in Figure 5.2 (c), although for a different sample, are presented here to emphasize the probability density nodes along the $k$-space directions which were taken as reference.
5.2 Wavefunctions in magnetic field

By employing an in-plane magnetic field, the capacitance-voltage spectroscopy on InAs/GaAs quantum dots allows the mapping of the in-plane momentum space probability densities corresponding to the individual electron/hole charging peaks. This approach has given new insight into the quantum dot confinement potential and the charging behaviour as it permitted the direct visualization of wavefunctions anisotropy and, more important, it helped in the establishing the loading sequence for valence band states.

It is well known that a perpendicular magnetic field will shift the quantum dot energy levels [12, 31] which would eventually result in a level crossing at certain critical fields, as it can be seen in the simulation in Figure 2.7. An open question is how the probability density distribution will change due to the presence of the perpendicular magnetic field, especially after the crossing.

In order to answer this question, the mapping of hole probability densities was realized by applying a tilted field chosen in such a way that, by varying the tilt angle and the field strength, the in-plane field component could be swept to map the wave function while keeping the perpendicular component constant. For experimental reasons, only sections along the two principal axes and no full two-dimensional maps have been obtained but, as already shown in Figure 4.10, this is sufficient to get most of the valuable information regarding the probability density distributions. From Figure 5.3 it can be seen that the $k$-space sections along $[01\bar{1}]$ and $[0-1\bar{1}]$ into the probability density distributions corresponding to each $C(V)$ peak with no applied perpendicular component have several characteristic features which are summarized in Table 5.1:

<table>
<thead>
<tr>
<th>peak No.</th>
<th>orbital</th>
<th>wavefunction $@k_{\beta} = 0$</th>
<th>shape</th>
<th>mixed with:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>[011]</td>
<td>[0-11]</td>
<td></td>
</tr>
<tr>
<td>peak 1</td>
<td>s</td>
<td>max</td>
<td>max</td>
<td>bell</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>none</td>
</tr>
<tr>
<td>peak 2</td>
<td>s</td>
<td>max</td>
<td>max</td>
<td>bell</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>none</td>
</tr>
<tr>
<td>peak 3</td>
<td>p</td>
<td>local max</td>
<td>node</td>
<td>bone</td>
</tr>
<tr>
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<td></td>
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<td></td>
<td>s</td>
</tr>
<tr>
<td>peak 4</td>
<td>p</td>
<td>local max</td>
<td>node</td>
<td>bone</td>
</tr>
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<td>peak 6</td>
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<td>node</td>
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</tr>
<tr>
<td></td>
<td></td>
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<td>p</td>
</tr>
</tbody>
</table>

Table 5.1: Particularities of the hole probability density distribution in InAs self-assembled quantum dots as extracted from Figure 5.3 ($B_{\perp} = 0$ T). The second column lists the wavefunction (dominant) character, while the last one gives the wavefunction mixing. The columns in the middle provide information about the existence of nodes or (local) maxima on the two orthogonal directions and the shape of the probability density distribution plot.

The probability densities corresponding to each of the charging peaks are further described by the number of the nodes on the orthogonal directions used for the sampling. Their shapes will be ascribed accordingly:

- **s-like**: bell-shaped with a maximum at $\vec{k}_{\beta} = 0$;
- **p-like**: bone-shaped with a node at $\vec{k}_{\beta} = 0$ along [0-11] direction in reciprocal space;
- **d-like**: ring-shaped with nodes at $\vec{k}_{\beta} = 0$ on both directions.
5.2. WAVEFUNCTIONS IN MAGNETIC FIELD

The experiments in a tilted magnetic field were performed on the sample #11618, similar with #11599 which was used to obtain the plots in Figure 5.1 (b). The lever-arm \((l_1 + l - 2)/l_1\) was 9.8 while it had a tunneling barrier \(l_1 = 19\) nm, a little smaller than in the one in the previous case \((l_1 = 17\) nm), allowing a larger range for \(|\vec{k}_\beta|\) at the same value of \(B\). Another consequence of using a sample with a slightly larger barrier thickness was that the frequencies required for the mapping were lower.

According to Eq. 4.2.3 and 4.2.5, the frequencies for which the capacitance signal drops by 50% have to be used for the wavefunctions mapping. The frequency dependence of the \(C(V)\) spectrum for the sample #11618 is presented in Figure 5.4. The reference frequency \((\nu \to 0)\) was taken the lowest frequency for which the signal could still be measured with acceptable noise. From the decrease of the second capacitance peak, a frequency of 8 kHz has been chosen to map the \(s\)-state wavefunctions, while the proper frequency for the mapping of the excited states was 20 kHz.

Prior to the mounting of the sample for the \(C(V)\) measurements, the offset in the rotation mechanism of the holder had been verified by using a Hall-bar probe. From the Hall voltage, a compensation of 1° was found as being necessary at the start of the experiment.

First, a measurement in pure perpendicular field has been carried out in order to obtain the dispersion of energies with the magnetic field. The applied field was increased to sufficiently high fields so that the expected levels crossings could be observed. From the shift of the capacitance peaks (not shown here), the hole addition energies were extracted and plotted against \(B\). The resulting Fock-Darwin spectrum is presented in Figure 5.5 (a). The energies are measured from the edge of the GaAs valence band and were calculated by using Eq. 4.2.2 with a built-in potential \(V_{bi} = 0.65\) V. It can be seen

![Figure 5.4: The frequency dependence of the sample #11618. The lowest frequency for which the capacitance could be measured without considerable noise was taken as a reference. The frequency for which the second capacitance peak decreased to half its reference value has been used for the mapping of the \(s\)-states. This frequency was then further considered as a reference when choosing the frequency for the mapping of \(p\)- and \(d\)-states.](image-url)
the first two peaks (\(0\hbar \Rightarrow 1\hbar\) and \(1\hbar \Rightarrow 2\hbar\)) show almost no shift with the magnetic field, while the other peaks are slightly shifting in an alternating fashion as previously discussed. In the figure, the lines showing the shifts are added only as guides to the eye. Although the feeble variations make difficult to see it, the crossings of the levels take place somewhere around 15 T and are visible as a change in the slope of the energies for peaks 4, 5 and 6.

In order to enhance the resolution and to make the level crossing more visible, the fan-plot in Figure 5.5 (b) shows the individual peak energies relative to their value at \(B_{\perp} = 0\) T. The different slopes are clearly observed along with their sudden change above \(B_{\perp} = 13\) T. This indicates a change in the holes loading sequence into the quantum dots from \(s-s-p-p-d-d\) onto \(s-s-p-d-p-d\) at \(B_{\perp} = 18\) T which should be observed also in the shapes of the wavefunctions.

Before moving to the main results of this chapter, it is worth to mention that all the points in Figure 5.5 were obtained by performing a multiple Gaussian fit on each measured \(C(V)\) spectrum, a difficult task especially at very high fields. For this, a special Labtalk code had been developed and used in Origin\textsuperscript{®}; a comprehensive description of the code and the approach used to handle the measured data are given in Appendix C. The code was tested in different conditions for different tasks and was has been proven as reliable before employing it to fit the measured data. However, it is not likely any fit can give good results when the Gaussian peaks are nearly flat\(^*\). This was the case for the first two peaks of the \(C(V)\) spectra taken at extremely-high fields (above 20 T). This can be seen in Figure 5.5 (b) for the peak corresponding to \(1\hbar \Rightarrow 2\hbar\). Further in the processing, the unusually shifted points were just ignored as no reliable information could be obtained from the vanishing s-peaks. However, the errors in the calculation would not influence the fitting of the following peak as long as these errors are one order of magnitude smaller than the energetic separation due to the confinement and the Coulomb blockade.

The remainder of this chapter contains the results concerning the changes in hole wavefunctions induced by the presence of a magnetic field directed perpendicular to the quantum dot base plane.

The sections into momentum space probability density plots along two main crystallographic directions were taken with a constant perpendicular magnetic field component of 0, 4, 8, 12 and 18 T. The results for each of the \(C(V)\) peaks corresponding to the transitions \((i)h \Rightarrow (i+1)h\) are presented on the following pages. Owing to the axial symmetry of the wavefunctions, the points corresponding to the negative fields in the figures were obtained by simply mirroring the ones corresponding to the "positive" magnetic field orientation. All the capacitance peaks were normalized to their corresponding value measured without magnetic field. In this way, the probability densities are relative to the one obtained for \(B_{\perp} = 0\) T.

\(^*\)Although only shifts in the gate voltages are expected for \(C(V)\) spectroscopy in a perpendicular magnetic field, without an apparent reason, a decrease of the capacitance peak heights is also observed with increasing \(B_{\perp}\) (see for example [121]).
5.2. WAVEFUNCTIONS IN MAGNETIC FIELD

Figure 5.5: Influence of a perpendicular magnetic field on valence band energies of the quantum dots. (a): Fock-Darwin states of valence band states for sample #11618; the energies are measured from the edge of GaAs valence band by assuming a built-in voltage $V_{bi} = 0.65$ V. The crossings of energy levels around $B_\perp = 15$ T are visible for peaks 4, 5 and 6. The lines are guides to the eye. (b): The variation of individual peak energies from their corresponding value when no magnetic field was applied. In this display mode, the variations are more clear.
Figure 5.6: Sections along [0-11] (above) and [011] (below) into the probability density distribution of the first hole inside the quantum dots, taken for different values of the perpendicular component of the magnetic field. The height of the capacitance signal associated to the individual $C(V)$ charging peaks is normalized to its corresponding value at $B = 0$ T ($\vec{k} = 0$ in Figure 5.3).
Figure 5.7: Sections along [0-11] (above) and [011] (below) into the probability density distribution of the second hole inside the quantum dots, taken for different values of the perpendicular component of the magnetic field. The height of the capacitance signal associated to the individual $C(V)$ charging peaks is normalized to its corresponding value at $B = 0$ T ($k = 0$ in Figure 5.3).
Figure 5.8: Sections along [0-11] (above) and [011] (below) into the probability density distribution of the third hole inside the quantum dots, taken for different values of the perpendicular component of the magnetic field. The height of the capacitance signal associated to the individual $C(V)$ charging peaks is normalized to its corresponding value at $B = 0$ T ($k = 0$ in Figure 5.3).
Figure 5.9: Sections along [0-11] (above) and [011] (below) into the probability density distribution of the fourth hole inside the quantum dots, taken for different values of the perpendicular component of the magnetic field. The height of the capacitance signal associated to the individual \( C(V) \) charging peaks is normalized to its corresponding value at \( B = 0 \, \text{T} \) (\( \vec{k} = 0 \) in Figure 5.3).
Figure 5.10: Sections along [0-11] (above) and [011] (below) into the probability density distribution of the fifth hole inside the quantum dots, taken for different values of the perpendicular component of the magnetic field. The height of the capacitance signal associated to the individual $C(V)$ charging peaks is normalized to its corresponding value at $B = 0 \, T$ ($\vec{k} = 0$ in Figure 5.3).
5.2. WAVEFUNCTIONS IN MAGNETIC FIELD

Figure 5.11: Sections along [0-11] (above) and [011] (below) into the probability density distribution of the sixth hole inside the quantum dots, taken for different values of the perpendicular component of the magnetic field. The height of the capacitance signal associated to the individual $C(V)$ charging peaks is normalized to its corresponding value at $B = 0$ T ($\vec{k} = 0$ in Figure 5.3).
The remarkable and unexpected changes in the probability densities sections along the two orthogonal directions are summarized in Table 5.2. The features at $\vec{k} = 0$ in each direction, either a maximum, a local maximum or a node are recorded. From this, according to the assignment made in Table 5.1, the alleged shape and the wavefunction character are roughly predicted whenever possible. The last column shows the trend the radius of the probability density ($k$-space) has with respect to the estimated radius at a lower $B_\perp$. For the $s$-like probability densities the FWHM was considered as a measure for their extension while, for bone and ring shaped ones, the $|\vec{k}|$ value at which $C/C(0 \text{ T})$ had a maximum was considered.

<table>
<thead>
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<th>peak No.</th>
<th>$B_\perp$ [T]</th>
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<th>shape</th>
<th>$k$-space radius variation</th>
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<td></td>
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</tr>
<tr>
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<td>4 max max s bell →</td>
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<td></td>
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<tr>
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<td></td>
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<td></td>
<td>12 max max s bell ←</td>
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Table 5.2: Summary of the changes induced by the presence of $B_\perp$ on the valence band wavefunctions. For each constant perpendicular field applied, the distinguishing feature at $k_\beta = 0$ is given (maximum, local maximum or node). From this, the shapes of the probability densities are deduced and associated with the ones in Table 5.1. The last column shows the trend the radius of the probability density ($k$-space) has with respect to the estimated radius at a lower $B_\perp$ (→ for constant, ↓ for decreasing, ↑ for increasing and ↑ for strongly increasing probability density radius).
5.2. WAVEFUNCTIONS IN MAGNETIC FIELD

To be more explicit, the results show the following:

- The $s$-state probability density corresponding to a single hole per dot retains its shape but its real space extension decreases for $B_\perp > 4$ T, which points to an additional confinement due to the magnetic field.

- For two holes per dot (peak 2) there is a striking change: the probability density plot changes dramatically from the bell shape corresponding to an $s$-like state to a ring shape which is characteristic to a $d$-like state, while passing to an intermediate bone shape at $B_\perp = 8$ T. Even more, the resulting ring at $B_\perp = 18$ T has a larger extension in $k$-space (smaller in real space) than the corresponding one of a $d$-state at $B_\perp = 0$ T. This is not justified by Eq. 2.2.12 taking into account also the variation of $l_{\text{hole}}$ in Figure 2.9 (d).

- The changes of the probability density’s features corresponding to the third peak seem to be linked with the evolution of the previous one but in an opposite manner, the initial bone shape changing to a bell shape at $B_\perp = 8$ T.

- The following wavefunction is behaving even more strange. For $4$ T < $B_\perp < 18$ T, the maximum at $\vec{k}_{[011]} = 0$ is accompanied by two satellites at finite $\vec{k}_{[011]}$. In the end, at $B_\perp = 18$ T, when the level crossing should have already occurred, the shape of the probability density distribution evolves into a ring one, indeed corresponding to the expected $d$-state.

- The fifth peak has been assigned initially to a $d$-like state. From the dispersion in a pure perpendicular field, a transformation into a $p$-like state had been predicted for $B_\perp \approx 15$ T. Yet, the only change is the strong increase of $k$-space extension of a ring-shaped wavefunction.

- For the sixth hole, the reverse effect is observed when increasing $B_\perp$, namely, the probability distribution retains its shape but there is a shrink of the $k$-space extension.

These results are extremely interesting and exciting, but they cannot be explained in the framework of the model presented here.

To be sure the plots in Figures 5.6 to 5.11 really correspond to the actual quasiparticle probability densities, one has to verify whether something has not been overlooked. Two possible causes might be discussed here. The first one of them would be an erroneous fitting procedure. This can be easily ruled-out on several reasons. One reason is that the fitting at $B_\perp = 0$ T could reproduce the results obtained by other methods. Another reason would be the fact that the script used for the automated fitting was verified by comparing its output with the results of a standard fit procedure in Origin for randomly-chosen datasets. The third argument is that there is no need to fit the $C(V)$ spectra to obtain the $s$-like distributions, as the capacitance peaks are well separated due to the Coulomb blockade and they do not influence one another. Taking this into account, at least the results in Figure 5.7 will be valid.

The second cause which would compromise the results is an assumption which makes the wavefunction mapping possible. This has been made in Eq. 2.2.16 by considering that the Bardeen transfer-matrix element between the emitter and the quantum dot states $T_{\text{Bardeen}}$ is slowly dependent on $B_\parallel$. To be sure this condition holds for
the actual sample which has been used, the behaviour of $T_{\text{Bardeen}}$ with the magnetic field has to be verified. Following the approach of Patanè et al. [47], the transmission coefficient through the tunneling barrier $t(B) = |T_{\text{Bardeen}}|^2$ was calculated.

Within the Wentzel-Kramer-Brillouin (WKB) approximation, the transmission coefficient can be expressed as

$$ t(B) = \exp\left[ -\frac{2}{\hbar} \int_0^{l_1} \sqrt{2m^*U(z)} \, dz \right], \quad (5.2.1) $$

with

$$ U(z) = \hbar \omega_0 + \frac{1}{2} m^* \omega_c^2 (z - Z), \quad (5.2.2) $$

and

$$ Z = t_B^{\text{holes}}(B) k_\beta(B). \quad (5.2.3) $$

Figure 5.12 shows the $B_\parallel$ dependence of $t(B)$ calculated for the barrier parameters of sample #11618. The normalized transmission coefficients are shown in red and green for the first, respectively the third tunneling hole. A hole effective mass $m^* = 0.51 m_0$ corresponding to a heavy hole in GaAs was considered, while the energies $\hbar \omega_0$ were extracted from Figure 5.5 (a).

**Figure 5.12:** Magnetic-field dependence of the transmission coefficient $t(B)$ of the tunneling barrier between the occupied emitter states and the quantum dot layer. The transmission coefficient in the WKB approximation was calculated for the first hole (in red) and the third one (in green), using the model of Patanè [47]. This would correspond to the C(V) measurement performed in order to obtain the plots in Figure 5.3. The barrier thickness was taken $l_1 = 19$ nm and the hole effective mass was assumed $m^* = 0.51 m_0$.

From Figures 5.6 to 5.11, it can be seen that all the information regarding the asymmetry and the nodes of the wavefunctions are not beyond $\pm 4 \times 10^8$ m$^{-1}$ which corresponds to a magnetic field up to $\approx 14$ T. It means the variations in the transmission
coefficient $|T_{\text{Bardeen}}|^2$ are less than 25 percent except for the highest parallel field components which would influence only the tails of the wavefunctions. Moreover, even when the Bardeen matrix element would have changed more than 25 percent, the change is monotonous, therefore the shape character of the wavefunctions will still be given correctly [125].

A more problematic issue, which has been usually ignored, resides in the observed decrease of the capacitance peak height $C(V_i)$ with $B_{\perp}$. The cause of such a behaviour is still unclear as long as only the peak capacitance are affected but not the diode background capacitance.

It is obvious the level crossings of the Fock-Darwin states cannot justify the results obtained for the hole wavefunctions in a perpendicular magnetic field: the expected changes from a $p$-like to a $d$-like wavefunction for the transition $3h \Rightarrow 4h$ and from a $d$-like to a $p$-like wavefunction for the transition $4h \Rightarrow 5h$ are not observed. Yet, the probability density corresponding to peak 2 is changing drastically which rises a huge question mark. N.B.: The findings presented here cannot be interpreted regardless if the incomplete shell filling or Aufbau principle are considered.

Attempts to explain these findings have been unsuccessful until the time of writing this thesis was due. A first idea was to attribute them to a Wigner crystallization of the hole system, knowing the fact that this phase transition would change the shape of the wavefunctions as it was demonstrated in the case of electrons [43]. However, it was shown that the Wigner crystallization is not possible for MBE-grown self-assembled quantum dots (see discussion in Section 2.2.4 and Figure 2.9).

Another approach was to simulate the structure with an applied tilted field and calculate numerically the quasi-particle probability densities. Two different methods were/are employed by two groups at the Walter Schottky Institute in München and Max Planck Institute for Solid State Research in Stuttgart, respectively.

The first method employed was a full quantum mechanical simulation based on the 8-band $k \cdot p$ model within a high precision finite differences grid, using Nextnano$^3$ [126], but the results couldn't reproduce the ones presented here [127]. The simulations made in this way have shown no major changes in the shape of the quasi-particle probability densities for different $B$ up to 30 T applied at different tilt-angles $\alpha \in \{0^\circ, 45^\circ, 90^\circ\}$.

The second method will use an atomistic pseudo-potential formalism. For the moment, calculations are being performed for the more simpler case of electrons. In this case, preliminary results have shown that the quasi-particle wavefunctions for the conduction band states would change in the presence of a pure perpendicular field, even before the expected level crossing. In Figure 5.13 these results are presented. It can be seen the quasi-particle probability densities for the $s$-like electron states are not influenced by the magnetic field, while the $p_{1p2}$ and $p_{3p4}$ would change from a bone shape to a ring (doughnut) shape. However, these results which correspond to calculations for an InAs quantum dot having a base diameter of 25 nm and a height of 3.5 nm [128] differ from the probability density images obtained experimentally at University Duisburg. The latter show the bone-shaped $p_{1p2}$ distribution (wavefunction having a $p_-$ character) changes into a bell shape one at $B_{\perp} = 9$ T [122]. One possible explanation is that there is a strong correlations between the $s$- and $p$-states even at $B_{\perp} = 0$ T [129]$^7$. Such a correlation has been observed by Rontani et al. [131] for their electron

$^7$ A different interpretation for $p_{3p4}$, which shows a different behaviour when compared with $p_{1p2}$,
probability densities maps without a perpendicular field component. This might also explain the behaviour of the $p$-like wavefunctions at $\vec{k}_\beta = 0$, for which $|\psi(\vec{k})|^2$ should be zero but the experiments had failed to show this.

So far, only speculations could be made on the possible causes of the odd behaviour of the hole probability densities with an applied perpendicular field. At a first sight it seems there is no connection with the Fock-Darwin states which would have been expected. The results presented here are even more strange than the ones obtained for electrons in the same conditions.

Results of theoretical calculations which take in consideration the real 3D nature of the quantum dots and suitable materials parameters might give a reasonable explanation for the experimentally-obtained quasi-particle probability densities.
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Chapter 6

Tuning of the Coulomb blockade in the quantum dot ground state

The control of energy levels inside quantum dots is important both for basic research and for device applications. As shown before in Chapter 3, the growth conditions play an important role in obtaining quantum dots with desired properties. There are different methods to fine tune their properties which can be categorized as in-situ or ex-situ ones. Among them, Indium-flush technique and post-growth RTA were intensively studied for more than a decade. Although these methods are not new, to present, they have been used mainly for adjusting the optical properties (emission wavelength, ensemble uniformity) of the quantum dots. Up to now no studies were performed on carrier tunneling or carrier-carrier interactions inside quantum dots subjected to these manipulation techniques. The goal of this chapter is to obtain information on the behaviour of modified quantum dots, with the main objective of showing the direct influence of the Indium-flush step and RTA on the Coulomb blockade in the ground state. This will open new possibilities for future electronic devices, like single-photon or single-electron turnstile devices, which take advantage of the carrier interactions inside quantum dots.

Throughout this chapter energy manipulation, via the two different available methods mentioned above, will be studied by means of PL spectroscopy and $C(V)$ spectroscopy for conduction band. The shift in the emission and Coulomb blockade energies will be extracted and compared for the two techniques, in an attempt to decide which method is more appropriate to be used for different desired applications. A potential application of such modified quantum dots will be discussed in the end of this chapter.

6.1 Manipulation by Indium-flush technique

A series of samples containing InAs quantum dots with different heights was grown by solid-source MBE on (100)-oriented GaAs substrates by employing a flush-growth technique (see Section 3.3.1). Each sample consisted of a single InAs/GaAs quantum dots layer embedded in the intrinsic region of a Schottky diode. An $n$-type back contact was formed by growing a Si-doped GaAs layer ($\approx 2 \times 10^{18}$ cm$^{-3}$). The quantum dots were separated from the back contact by an intrinsic GaAs layer with a thickness of 25 nm having the role of a tunneling barrier for electrons in $C(V)$ experiments. The InAs quantum dots were grown at a substrate temperature of 520 °C and overgrown
with a GaAs layer of thickness $d_{QD}$ at 511 °C, followed, after a 60 s break, by $(30 - d_{QD})$ nm GaAs at the normal growth temperature of 600 °C. This was followed by 34 periods of a 3 nm AlAs/1 nm GaAs superlattice having the role to reduce the leakage current in $C(V)$ experiments. The whole layer sequence was terminated by a 10 nm GaAs cap layer. For our standard samples, which served as base material also for the annealing experiments, the typical value for $d_{QD}$ had been 8 nm whereas for the samples grown with an In-flush, $d_{QD}$ was reduced, in several steps, down to 2.2 nm. More details about the layer sequence and growth parameters can be found in Appendix A.

Room temperature PL spectroscopy was employed to find the effect of the Indium flush growth on the optical properties of the quantum dots. The normalized spectra in the Figure 6.1 show the expected blue-shift due to the increased confinement in the growth direction as a consequence of the shape/size modifications during the in-situ processing (refer to Section 3.3.1 and other works [77, 100]). It can be seen that the total number of resolved bound zero dimensional states changes from three, for the reference sample, to two, when $d_{QD} = 2.2$ nm. Further decreasing the protection GaAs capping would result in the wiping of the quantum dots, as most of the Indium will be flushed [75]. The ground-state emission peak $E_0$ ($e_1 \leftrightarrow h h_1$) is shifting from 1260 nm, in the case of the reference sample with $d_{QD} = 8$ nm, down to 1026 nm when the overgrown GaAs protection cap has a thickness of 2.2 nm. There is also a certain decrease in the inter-sublevel energies ($E_1 - E_0$) with the decrease of $d_{QD}$. Apparently, the widths of the quantum dots PL lines remain unchanged but a further careful analysis shows that, in fact, the ground-state peak line-width increases slightly by 3.4 meV with reducing $d_{QD}$ down to 2.7 nm and by 14 meV for $d_{QD} = 2.2$ nm. This

![Figure 6.1: Blue-shift of the emission spectra for samples with different capping thickness $d_{QD}$. PL signal is normalized for each spectrum to the ground-state peak intensity. Spectra were taken at room temperature.](image-url)

\[\text{Figure 6.1: Blue-shift of the emission spectra for samples with different capping thickness } d_{QD}. \text{ PL signal is normalized for each spectrum to the ground-state peak intensity. Spectra were taken at room temperature.}\]
is somehow in contradiction with the results reported earlier [102] for a different set of samples and with several other reports in the literature [75, 78]. Most probable this is related with the considerations made in decomposing the spectra in order to explain some particularities of the quantum dots ensembles in the studied samples and/or with a certain In/Ga intermixing.

According to the results which will be presented later in this section, it was considered that the particular conditions during In-flush growth resulted in the appearance of bimodal quantum dots. The decomposition of the PL spectra for samples with $d_{QD} < 8$ nm was made by considering the low-energy peak as a superposition of two Gaussians, centered at $E_0$ and $E'_0$, which had to be determined by fitting each spectrum. The energies of these two peaks, together with the energy of the first excited state $E_1$

![Figure 6.2](image)

**Figure 6.2:** Influence of the quantum dots capping thickness $d_{QD}$ on PL. **Left:** PL energies ($E_0$ and $E_1$) as extracted from fitting the spectra. $E'_0$ corresponds to a different quantum dot population and it will be further ignored. **Right:** ground-state relative shift and the decrease in inter-sublevel energies as described in the text. The lines are guides to the eye.

$(e_2 \leftrightarrow \hbar h_2)$ are plotted against the quantum dots capping thickness $d_{QD}$ in Figure 6.2 (left). The plot to the right shows the shift of the ground-state energy $E_0$ from its corresponding value in the case of the reference sample with $d_{QD} = 8$ nm. By using the In-flush method during the growth of the quantum dots, a 180 meV blue-shift of the ground PL emission could be achieved. In the same time, the separation in energy between the ground-state and first excited state is decreasing from 63 meV in the case of reference sample $d_{QD} = 8$ nm to $\approx 40$ meV when $d_{QD} = 2.2$ nm, as it can be observed in Figure 6.2 (right).

Decreasing the thickness $d_{QD}$ of the protection capping layer is equivalent with decreasing the height of the quantum dots which leads to an increased confinement in the growth direction. The quantum dots energy levels move closer and closer to the edges of the corresponding GaAs valence and conduction bands, increasing the electron-hole energy separation, hence $E_0$, in agreement with the PL results presented here. When this is the case, more carriers can escape from the quantum dots and recombine from the quantum well formed by the InAs wetting layer or even directly from bulk GaAs.
This explains increased intensity for the non-shifting peaks at 870 nm and 912 nm. On the other hand, the lateral dimensions remain almost constant after the In-flush step but as $d_{QD}$ decreases In/Ga interdiffusion could induce alloy fluctuation and reduce the uniformity of quantum dot emission. Moreover, the inter-sublevel spacing is influenced also by this intermixing process [89].

Further, the samples were provided with contacts in order to be characterized by $C(V)$ spectroscopy at 4.2 K, the results being presented in Figure 6.3 after the extraction of a linear background. The gate voltage for which the quantum dots are charged with the first electron ($s_1$) shifts towards more positive values when decreasing the overgrowth thickness $d_{QD}$ (the heights of the quantum dots). This indicates that the electron ground state shifts energetically towards the GaAs conduction band edge which is consistent with the blue-shift observed in the PL measurements. The observed PL decrease in the inter-sublevel spacing is present in the $C(V)$ spectra also, meaning the distance between the conduction band energy levels is smaller as $d_{QD}$ is smaller. The same is valid also for valence band (not shown here).

![Figure 6.3: Comparison of the $C(V)$ spectra for the as-grown and Indium-flushed quantum dots embedded in an n-type Schottky diode. All the peaks are shifted to more positive voltages for smaller $d_{QD}$; the charging of the wetting layer occurs at lower energies for the flushed quantum dots. $C(V)$ performed at 4.2 K and energies are measured from the edge of the conduction band.](image)

From the voltage separation between the first two peaks ($s_1$ and $s_2$), the Coulomb blockade in the ground state can be calculated using the lever-arm argument. According to the simple model in Section 4.2.2, one can transform the gate voltages in an energy scale. Although this requires the built-in potential $V_{bi}$ to be known, provided the Coulomb blockade is given as a difference in energies, the built-in potential is irrelevant for the moment. The gate voltages for which electrons are subsequently tunneling into the dots have to be accurately determined via fitting. With the considerations in Section 4.2.2, the $C(V)$ should contain two group of peaks - one group, consisting of
two peaks ($s_1$ and $s_2$), for the two electrons in the ground state and a second group of four peaks, for the $p$-like states ($p_{1,2,3,4}$). Eventually, with decreasing $d_{QD}$, the latter merges into the wetting layer charging peak and this aspect should be considered during the fitting. One interesting aspect is observed in the $C(V)$ traces corresponding to samples with flushed quantum dots, especially for $d_{QD} = 4.1$ and $3.2$ nm: although the separation between the two groups of peaks ($s$ and $p$) is much bigger than the FWHM of the $s_2$ and $p_1$, the capacitance does not drop to zero before loading the third electron into the dot as it would be normally expected. Provided a linear background was subtracted correctly, this is an evidence for a bimodal size distribution of the quantum dots [132, 133]. It means the electrons are loaded onto the ground-state of another quantum dot population before higher levels of the main quantum dots distribution are populated. The datasets were fitted accordingly and the gate voltages corresponding to the peak centers were used to obtain an energy scale. In Figure 6.4 for example, the $C(V)$ spectrum for the sample with $d_{QD} = 4.1$ nm was deconvolved taking into account a bimodal quantum dots distribution. The peaks centered at -0.6 and -0.44 V ($s_1$ and $s_2$) were considered further for calculating the Coulomb blockade energies; the origin of the other two $s$-like peaks centered at -0.33 and -0.2 V ($s'_1$ and $s'_2$) was considered to be a different population of smaller-size quantum dots with only one bound zero dimensional state and a lower density. This is suggested by a smaller amplitude of the peaks. Even in the case of two bounded 0D states for the second population, the results presented here would not be affected. However, at the moment of writing, this is only a speculation as long as no microscopy picture for the inner quantum dots has been taken yet to confirm this assumption.

The small-size population was disregarded because the aim of the current chapter is to compare (as much as possible) the properties of similar dots with the ones in the as-grown sample. For the same reason, the $E'_0$ peak in PL was considered irrelevant.
to the discussion. However, the signature of the second population of InAs islands is present in the broadening of the spectra (Figure 6.5). \textit{N.B.:} The bimodal growth of the quantum dots is not generally related with the Indium-flush technique. This outcome was unintentional, but more a peculiar event.

After fitting the spectra, when more details are obtained, one can also compare the FWHM of the peaks. This is an important parameter from an application point of view, its decrease in the case of PL spectroscopy being an indicator of an increased size-uniformity in the quantum dots ensemble. However, a surprising result is obtained here: the widths of the peaks appear to increase as $d_{QD}$ becomes smaller. This is in contradiction with the findings of other authors and, as before argued, can be justified by the existence of a second size quantum dots population, whose signature is more difficult to extract. In consequence, an even more careful approach for the fitting is needed; again, the results discussed here focus on the energies of the main population quantum dots which, in turn, are obtained from the locations of higher intensity peaks, with a higher aspect-ratio, which are prone to more efficient localization during the fit. From the results in Figure 6.5, one can observe the line-widths for the PL are almost double as for the $C(V)$ (see also Table 6.3). The difference in the broadening of the peaks comes from fluctuations in dots sizes which will give a Gaussian distribution for the ground state energies for electrons and holes. Thus, the $C(V)$ peaks are broadened only by the distribution of electron ground-state energies with respect to the Fermi energy, while in PL the lines are broadened also by the hole energy distribution [31].

The Coulomb blockade for the electrons in the ground state was extracted from the $C(V)$ spectra taking into account the two quantum dots populations. The results for the main quantum dots population are plotted in Figure 6.6. It can be easily seen the intra-dot electron-electron interaction energy for the quantum dots obtained with the Indium-flush growth technique stays almost constant. In fact, there is a tendency of

\begin{figure}[h]
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\includegraphics[width=0.5\textwidth]{figure6.5.png}
\caption{FWHM for the ground-state peaks as resulting from PL and C(V) spectra. The results are obtained from fitting for the main population. The lines are only guides to the eye.}
\end{figure}
increasing the carrier-carrier interaction energy but the differences are less than 1 meV for $d_{QD} < 4.1$ nm. This is, again, related with the size: the trimmed quantum dots have a smaller volume but the lateral sizes remain almost unchanged, which means the spatial separation between the two electrons accommodated inside is not drastically influenced by the changes resulted from the flushing step. This can explain the evolution of the Coulomb blockade depicted in Figure 6.6.

![Figure 6.6: Decrease of the electron-electron interaction in the quantum dots' ground-state via in-situ processing of the capping layer, relative to the value obtained for the as-grown sample. Absolute values for the Coulomb blockade are linked to the right-hand scale of the figure. To make the comparison easier, the same range as for Figure 6.11 has been kept.](image)

Regarding the initial decrease in the Coulomb blockade energy when comparing the reference sample ($d_{QD} = 8$ nm) with the one subjected to the flushing step ($d_{QD} = 4.1$ nm), unintentional variations in the general growth conditions with time are the most likely to be the cause.

In the next section, the same study is presented for quantum dots ensembles manipulated with a different method.

### 6.2 Manipulation by RTA

Starting from a reference as-grown sample (#12948), a series of samples was prepared in order to study the effect of the ex-situ thermal treatments on quantum dots. The series consisted in small pieces $3.5 \times 5$ mm cleaved from the wafer along [011] and [0-11] directions which were subjected to a $t = 30$ s RTA step in $N_2$ atmosphere with GaAs proximity capping. The annealing was performed in a temperature range between 820 and 900 °C. A description of the method has been given in Section 3.3.2.

PL spectra shown in Figure 6.7 were taken at room temperature for all the samples in the series and compared with the reference (as-grown) PL. Although the intensities are different from sample to sample, mainly due to appearance of dislocations in the
annealing process [134, 135], for the matter in hand, it is more convenient to normalize the spectra to the intensity value of the ground peak $E_0$.

![Figure 6.7: Blue-shift of the emission spectra with respect to the un-annealed reference sample. Spectra are taken at 300 K. PL signal is normalized for each spectrum to the ground-state peak intensity.](image)

The RTA on quantum dots produces a significant blue-shift in the $PL$ emission, a decrease in the energy spacing between quantum dots energy levels and the narrowing of the spectral lines [102]. These changes depend mainly on the annealing temperature, the properties of the starting quantum dot ensemble and the proximity capping used during the annealing step. In general, the modifications induced through RTA are reproducible to a certain extent.

In order to extract more detailed information on these changes, the $PL$ spectra were decomposed by fitting the data, the compiled results being presented throughout this section. The positions of the fitted $PL$ peaks as a function of the annealing temperature are presented in Figure 6.8 (left). A pronounced shift towards higher energies of all the quantum dots levels is observed. The peak corresponding to the wetting layer is only slightly affected when the annealing temperature is increased. The non-shifting peak around 870 nm (1.424 eV), which is common for all spectra, is associated with the bulk GaAs emission [136]. The right part of Figure 6.8 contains the plots corresponding to the shift of the ground-state emission $E_0$ from its value before the thermal processing, as well as the decrease in the separation between the ground and the first excited state emission $E_1 - E_0$. The ground-state peak is blue-shifted up to 343 meV with respect to the as-grown sample, due to the annealing at 900 °C. In the same time, the inter-sublevel energy decreases form 63 meV to a value of 19 meV, being in the same range with the values reported by different groups. Recalling the similar picture obtained in
the case of flushed quantum dots, one can remark the influences of the RTA method are more severe. A comparison between the results of the two methods will be made in Table 6.3.

As it can bee seen in the figures above, the quantum dot intermixing has three main effects on the optical properties of the samples:

- a pronounced blue-shift of the energy levels
- a decrease of the inter-sublevel energies
- a reduction of the in-homogeneously broadened emission

These results obtained for the annealed samples can be explained taking into account the transformations suffered by the InAs quantum dots during the RTA process:

- change in composition
- change in size and shape
- increased ensemble uniformity

Thermally induced alloy intermixing is responsible for the changes mentioned above. The strong blue-shift of the spectra can be explained by a simple model of a Fickian diffusion which considers Gallium diffuses into and Indium diffuses out of the quantum dots. This results in Ga-rich quantum dots with increased band-gap which will give a stronger blue-shift of the PL spectra as the anneal temperature increases. This overcompensates the effect of the reduced confinement (both lateral and in the growth direction) due to the size-increase of the quantum dot.

With these considerations, it would be interesting to know how the RTA process affects the carrier-carrier interactions inside the dots. In order to obtain the Coulomb
blockade in the ground state, $C(V)$ spectroscopy was again employed for annealed samples having an $n$-type doped back contact (Si:GaAs).

The available samples were provided with contacts and the measurements were performed, as usual, at liquid helium temperature. In Figure 6.9, the $C(V)$ spectrum of the as-grown sample is plotted after the extraction of a linear background, together with the one of the sample annealed at 820°C.

![Image of Figure 6.9](image-url)

**Figure 6.9:** The electrons charging peaks for the annealed sample are shifted to more positive gate voltage. The energy scale is valid in this case only for the reference sample (see text). The $C(V)$ measurements were performed under the conditions specified in the frame.

The shift of the $C(V)$ spectra is similar with the one observed in PL measurements, the charging peaks move closer to the one corresponding to the charging of the wetting layer, i.e. towards the GaAs conduction band edge. The similarity with the PL results goes further as one can observe the post-growth annealing decrease in the separation between the two groups of charging peaks corresponding to the filling of $s$- and $p$-like quantum dots states. In Figure 6.10 it can be seen that the line-widths exhibit a significant decrease which points to a higher degree of size-uniformity for the quantum dots subjected to annealing.

As in the previous section, the gate voltages corresponding to the charging peaks have to be determined. By considering only two bound states in the as-grown quantum dots conduction band, taking into account that the Coulomb blockade will lift the level degeneracy, one needs six Gaussian peaks to fit the $C(V)$ traces. Eventually, the number of the peaks decreases for the spectra of the annealed samples. This is happening because of the energy shifting caused by the intermixing process, which will push some of the energy levels into the wetting layer region. However, another effect should be considered also at this point, as it will be described in the next paragraphs.

Sequential charging of the quantum dots is made by tunneling electrons from a reservoir through the tunneling barrier (details have been given in Section 4.2.2). Dur-
CHAPTER 6. TUNING OF THE COULOMB BLOCKADE

Figure 6.10: FWHM for the ground-state peaks as resulting from PL and C(V) spectra. This points to a higher size-uniformity for the quantum dots subjected to annealing.

Table 6.1: The length of the tunneling barrier is reduced due to the Si diffusion from the back contact. The details for the calculations are given in the text.

<table>
<thead>
<tr>
<th>Anneal temperature [°C]</th>
<th>Si diffusion length [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>1.28</td>
</tr>
<tr>
<td>800</td>
<td>1.93</td>
</tr>
<tr>
<td>820</td>
<td>2.47</td>
</tr>
<tr>
<td>840</td>
<td>3.11</td>
</tr>
<tr>
<td>860</td>
<td>3.90</td>
</tr>
<tr>
<td>880</td>
<td>4.85</td>
</tr>
<tr>
<td>900</td>
<td>5.98</td>
</tr>
</tbody>
</table>

As already mentioned, the energy scale is calculated using a geometrical argument. As a consequence of the Si diffusing into the tunneling barrier, the lever arm is changed for samples annealed at different temperatures. In Table 6.2 the actual values for this parameter as well as the energy for the ground-electron with respect to the GaAs conduction band are given. It is worth to mention that the results in Table 6.2 are taking into account a built-in potential of $V_{bi} = 1$ V as in [59]; although one might think this value is a little over-estimate compared with the one given by Sze [107], it would not influence the results presented in this chapter, which take into account only differences in energies of the peaks, $V_{bi}$ canceling out when calculating the Coulomb energy (with Eq. 4.2.2).
Table 6.2: Lever arm and the energy of the ground-state electron, measured from the GaAs conduction band edge, considering the Si-diffusion from the back contact.

With the gates voltages corresponding to the charging peaks being known and the corrected value of the lever arm, it is now possible to determine the energies in the electrons system. In Figure 6.11 electron-electron interaction energies in the ground state are calculated from $C(V)$ spectra, for all the annealing temperatures. The absolute value and the percentage from the Coulomb energy of the as-grown sample are given. An almost 50% decrease of the Coulomb blockade energy is obtained after 30 s RTA at 900 °C, providing a method to manipulate in a wide range the carrier-carrier interactions inside quantum dots. This finding seems interesting and might find some applications in the future, although at this moment it is desirable, at least for single photon turnstiles devices [140], to have a constant or increased Coulomb blockade.

![Figure 6.11](image-url)

The explanation for the significant decrease of the electron-electron interaction after annealing can be given in terms of the increased volume of the quantum dots as
a consequence of the intermixing process; in this case one can imagine a larger spatial separation between the charges inside the dot and consequently a decrease in the Coulomb energy.

Different from the situation of the Indium-flushed quantum dots, the increased average size of the Ga-rich InAs islands allows a spreading of the electron wavefunction in the dots. This will increase even further the spatial extension of the electrons wavefunctions which should be already more extended because of the lowering of the barrier as the levels move closer to GaAs conduction band. The latter effect becomes more clear if the confinement $\hbar \omega_0$ is lowered in Eq. 2.2.10 and Eq. 2.2.9. Further investigations on the electron probability density distribution for an annealed quantum dots system are presented in the following sub-section.

### 6.2.1 RTA influence on ground-electron probability density

To examine the effects of RTA on the shape and the extent of the electron probability density distribution in the quantum dots, the approach of Patanè and coworkers has been used to map the probability density in $k$-space. The method was already described in the Section 4.2.2. It requires a larger separation between the reservoir and the quantum dots layer, otherwise the optimal measurement frequencies would be impracticable high. Usually, the tunneling barrier is between 37 and 40 nm [111], but slightly larger values are needed in this case to account for Si diffusion from the back contact.

The sample chosen for this task was grown with a 45 nm tunnel barrier (#12969), otherwise identical with the as-grown reference in Section 6.2. A different reference sample with a tunneling barrier of 37 nm was also used (#11210). A 3.5×5 mm piece was annealed at 840 °C, in the same conditions as previously described, and provided with electrical contacts for $C(V)$ measurements in magnetic field. The annealing temperature was chosen arbitrary and there is no reason to expect qualitatively different results for higher annealing temperatures (at least in a reasonable temperature range) other than the ones described in this section. In order to be consistent with the previous approach, the ground-electron probability density will be compared with the one of an un-annealed reference sample.

As shown before (see Section 4.2.2), by performing $C(V)$ spectroscopy in parallel magnetic field, information on the shape and the extent of the carrier probability density in $k$-space can be obtained. On the other hand, the results presented throughout this chapter were explained and interpreted in connection with the size of the quantum dots, i.e. the real space.

In Figure 6.12, the $k$-space ground-state electron probability density inside as-grown quantum dots (b) and quantum dots subjected to RTA at 820 °C (d) are shown. The corresponding contour plots ((a), respectively (c)) show more clear how the quasi-particle probability density is changed after the annealing. This represents the $k$-space projection of the probability density of the electronic state confined in the quantum dot. Here, red corresponds to a higher and blue for a lower value of the capacitance signal which is proportional to $|\phi_{QD}(k_x, k_y)|^2$.

Compared with as-grown quantum dots, the electron probability density is qualitatively the same (shape, asymmetry). The asymmetry is preserved so that the elongation in $k$-space is observed in the direction [011] as in the case of as-grown quantum
Figure 6.12: Colour plots for the ground-state electron probability density in $k$-space: (a) Representative contour-plot for the electron probability density inside a reference quantum dot; (c) Contour-plot for the electron probability density in a quantum dot subjected to RTA @840 °C; (b) and (d) 3D representation of the electron wavefunction for the reference, respectively annealed quantum dots. Red colour corresponds to a higher quasi-particle probability density.

dots [103]. Quantitatively, the $k$-space wavefunction extension in the case of the annealed quantum dots is less than for the as-grown dots. Sections in the contour-plots presented above, along high-symmetry directions [011] and [0-11] are made in Figure 6.13. Here, only positive $|\vec{k}_\beta|$ are presented, the profile being quite symmetrical. The contraction of the $k$-space ground electron wavefunction accounts up to 22 percent from the extension corresponding to the as-grown sample. This signifies an extension of the wavefunctions in the real space after the annealing, which is consistent with the interpretation of the results in the Section 6.2 and Section 3.3.2, made on the basis of an increased volume of the quantum dots after the thermal processing.

Presented in this way, the results can be regarded with suspicion. It is the case to
remind that the dependence of the capacitance peaks extracted from $C(V)$ spectroscopy by the applied magnetic field gives a quantity which is proportional with the electron probability density function in momentum space (Section 4.2.2). Therefore, any com-
comparison between probability density distributions is questionable in the absence of their normalization. The Figure 6.13 will be the starting point to achieve this. In order to perform the normalization of the wavefunctions, the results obtained from the annealed sample were multiplied by a constant which would give the same area under the curve as for the as-grown sample. Figure 6.14 displays the normalized probability density function in momentum space for a direction parallel to [011] before and after annealing. The data-points for negative $|\vec{k}\beta|$ values were just mirrored and a 2-points adjacent averaging was employed to smoothen the profiles. After normalization, the extension of the momentum space wavefunction is reduced by 31 percent subsequent to annealing at 840 °C.

### 6.3 Coulomb blockade vs. emission energy for modified InAs quantum dots

With the results presented in Section 6.1 and 6.2, it is possible to construct a new image of the influences produced by the in- and ex-situ processing on the InAs/GaAs quantum dots, enriching the knowledge on the effects of flush-growth technique and RTA on this system. In Figure 6.15 the variation of the Coulomb blockade and the blue-shift of the ground state PL emission with the annealing temperature and quantum dots’ low-temperature GaAs capping height are plotted.

**Figure 6.15:** Changes in the properties of the quantum dots for different annealing temperatures and different GaAs capping thicknesses: Coulomb blockade (left scale) and inter-level spacing (right scale) are plotted against the ground-state energies.

The similarities and the differences can be easily seen:

- Regarding the PL, both In-flush technique and RTA processing produce qualitatively the same results, namely a blue-shift of the PL emission wavelength, a decrease in the inter-sublevel energies and a better size-uniformity of the quantum dots. Quantitatively, blue-shifting realized through the RTA is much stronger
than the one obtained with flushing technique (almost double), the latter being limited by the fact that InAs islands are washed out without a suitable protection. In reference [75], for example, the minimum height of the quantum dots capping was reported to be $d_{QD} = 2$ nm;

- The possibility of manipulating at will the Coulomb blockade is one of the novelties of this work. With respect to the variation of the Coulomb blockade, there are no similarities between the results of the two methods used for altering the quantum dots properties. The differences are both qualitative and quantitative. Post-growth annealing of the quantum dots gives a strong decrease in the ground-state Coulomb blockade, as much as 50 percent, while for the Indium flushing, the electron-electron interaction is almost constant (to be more precise, it even increases by 0.5 meV after an initial slight decrease).

For convenience, all these findings are summarized in Table 6.3. The shifts in the ground and 1st excited states are listed as taken from PL measurements. The FWHM for both PL and $C(V)$ peaks corresponding to the ground levels are also included.

<table>
<thead>
<tr>
<th>Results from PL</th>
<th>Δ PL</th>
<th>Results from C(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground state</td>
<td>FWHM PL</td>
<td>1st excited state</td>
</tr>
<tr>
<td>[eV]</td>
<td>[meV]</td>
<td>[eV]</td>
</tr>
<tr>
<td>as-grown 650 °C</td>
<td>0.98</td>
<td>35.54</td>
</tr>
<tr>
<td>RTA 820 °C</td>
<td>1.16</td>
<td>27.73</td>
</tr>
<tr>
<td>840 °C</td>
<td>1.20</td>
<td>27.71</td>
</tr>
<tr>
<td>860 °C</td>
<td>1.25</td>
<td>25.09</td>
</tr>
<tr>
<td>880 °C</td>
<td>1.28</td>
<td>24.52</td>
</tr>
<tr>
<td>900 °C</td>
<td>1.32</td>
<td>23.12</td>
</tr>
<tr>
<td>as-grown 8.0 [nm]</td>
<td>0.98</td>
<td>35.54</td>
</tr>
<tr>
<td>RTA 4.1 [nm]</td>
<td>1.07</td>
<td>32.77</td>
</tr>
<tr>
<td>3.2 [nm]</td>
<td>1.13</td>
<td>36.96</td>
</tr>
<tr>
<td>2.7 [nm]</td>
<td>1.16</td>
<td>38.93</td>
</tr>
<tr>
<td>2.2 [nm]</td>
<td>1.21</td>
<td>49.81</td>
</tr>
</tbody>
</table>

Table 6.3: PL energies (ground and first excited states), inter-level spacing and broadening for the ground PL emission together with Coulomb blockade energies for electrons.

Further applications in optoelectronic devices

The results presented in this chapter might find applications in the further development of optoelectronic devices for quantum communications, quantum computing and quantum cryptography.

Applications in the quantum information science require optical sources with strong quantum correlations between single photons [141]. Single photon generation has been so far demonstrated using emission from single atoms, molecules and defects, as well as with single photon turnstiles and electroluminescence from single quantum dots [142]. Each of these approaches has its own advantages and drawbacks, therefore new improvements and developments are needed. Advanced processing technologies for III-V materials allow the fabrication of complex structures with single quantum dots as the active region. Taking advantage of these technologies, it is possible to design, for example, single photon turnstiles - devices which are able to emit single photons...
by precisely controlling the tunneling of individual carriers into a quantum dot. In this type of devices, single carriers can be injected into the quantum dot, any second electron or hole being prevented to enter the dot by the Coulomb blockade [143]. Such a single-photon turnstile was realized with a single InAs/GaAs quantum dot embedded in the intrinsic part of a p-i-n diode [140, 144].

When better single-photon sources will be available, numerous applications and experiments will be explored. By that time, reliable methods for spectral tuning of such single photon sources would be needed. For single quantum dot based turnstile devices the tuning can be achieved either by changing the growth parameters (e.g., materials, substrate temperature) or by manipulations using the Indium-flush technique and RTA. As it was previously demonstrated in the current chapter, these manipulations can influence dramatically the Coulomb blockade which, eventually, can compromise the device operation. Consequently, in order to prevent this from happening, it is necessary to use a suitable method for fine tuning the optical properties of the quantum dot while keeping the Coulomb interaction energy above a certain value.

Referring to the Figure 6.15 and Table 6.3, it can be concluded one has the possibility of tuning the quantum dots emission energy in such a way to minimize the change in the Coulomb blockade energy. It can be seen the Indium-flush technique is the appropriate method to be used in order to obtain a shift up to 200 meV for the energy of the emitted photon at the expense of decreasing the Coulomb energy by less than 3 meV. Applying this method for the growth of several low-density quantum dots layers with different overgrowth thicknesses $d_{QD}$, each of them embedded in the intrinsic part of a p-i-n structure, it is possible to obtain on the same chip single photon turnstiles operating at different wavelengths. These devices, stacked one on top of the other, can be separately contacted after several etching steps. Further work will be required to realize this as it might prove to be a challenging task considering also the difficulties in extracting the photon from the stacked structures.
Chapter 7

Conclusions

7.1 Summary and outlook

The purpose of this thesis was to study the impact of a modified confinement on the quantum dots ensemble properties, specifically on the hole wave functions and the Coulomb interactions in the conduction band ground state. In order to achieve this goal, the confinement was modified either reversibly, by applying an external magnetic field, or irreversibly by changing the size, shape and composition of the quantum dots.

The capacitance-voltage spectroscopy is a powerful method which gives insight on the energy level structure and the Coulomb interactions in InAs/GaAs self-assembled quantum dots. In combination with an in-plane magnetic field, it allows also the direct visualization of the in-plane momentum space quasi-particle probability densities corresponding to the carriers producing individual $C(V)$ charging peaks.

The application of a magnetic field perpendicular to the base plane of the quantum dots results in an additional confinement which produces the dispersion of the quantum confined energy levels, similar to the Fock-Darwin spectrum of a two dimensional harmonic oscillator. In consequence, at sufficiently high fields, some of the energy levels would cross, resulting in a modified energetic configuration. The first objective of the thesis was to find in which manner the hole wavefunctions evolve when the magnetic confinement is modified and how they change after the expected level crossings. In order to attain this goal, $C(V)$ spectroscopy in a tilted magnetic field was employed. The direction and the tilt angle of the magnetic field with respect to the quantum dots plane were chosen in such a way that a perpendicular component remains constant at different values, while the in-plane component can be swept to perform the wavefunction mapping. The shapes of the quasi-particle probability densities have been "predicted" from their profiles taken along two orthogonal directions.

The results obtained in this way are quite surprising: not only that the probability densities seem not to change according to the supposed new configuration resulted after the levels crossing at certain critical perpendicular field strength, but there are drastic changes of the probability densities corresponding to the non-crossing levels.

Although no changes were expected for the $s$-like wavefunctions corresponding to the first two holes in the dot, the second one of them suffered a drastic modification, changing, with increasing $B_\perp$, first from a bell shape to a bone shape and then to a ring shape which is rather characteristic to a $d$-like state. The third hole should have
retained a p-like character for all the perpendicular field strength used, yet it was found to change to a bell-like shape which is characteristic to a lower s-state. The fourth hole wavefunction has a p-character at $B_{\perp} = 0$ T and should change to a ring-shaped figure subsequent to the crossing at $B_{\perp} \approx 15$ T. This is happening indeed, but at intermediate fields the shape looks nothing in between. From the measurements in a pure perpendicular field, a cusp in the energy evolution with the magnetic field is observed, which indicates a level crossing. The same is also valid for the sixth capacitance peak. However, the only changes in the corresponding wavefunctions for different $B_{\perp}$ are their spatial extensions.

These findings are entirely unexpected as they are not supported by the simple theory in which the quantum dot is treated as a 2D harmonic oscillator. They can rise questions whether the results correspond to the actual hole probability density distribution in the magnetic-confined InAs quantum dots. In attempt to answer this question, the transmission coefficients to the tunneling barrier have been calculated for different system energies and were found to change by less than 25 percent for the relevant $k$-space range of interest. According to the model used to access the $k$-space probability densities, the transmission coefficient should not depend on the magnetic field, or at least to be slowly varying. Its monotonous variation with $B_{\parallel}$ constitutes a good reason to support the fact the wavefunctions are actually probed according to the methods presented in the literature.

Future theoretical calculations which would consider more realistic models and situations are expected to shine more light onto these experimental results.

Permanent changes in the confinement potential of the quantum dots are obtained by modifying their structural properties either during the growth or by post-growth processes. The resulting modifications of the size, shape and composition of the quantum dots trigger a shift in their emission energies. Not only a manipulation of the optical properties can be achieved in this way, but also the strength of the carrier-carrier interaction inside the quantum dots can be controlled by altering their structure. This can be particularly important for the realization of novel optoelectronic devices based on self-assembled quantum dots, e.g., single photon turnstiles.

Given its significance, the Coulomb blockade energy of ground state electrons has been studied for quantum dots ensembles obtained by Indium-flush growth technique or subjected to a post-growth rapid thermal annealing (RTA). It has been found that, despite the fact that changes in the optical properties of the resulting quantum dots ensemble exhibit the same tendency (blue-shift) regardless of the method used to manipulate them, the Coulomb energies behave differently depending on the employed method. More exactly, for the case of the In-flushed dots, the Coulomb blockade in the electron ground state changes only about 15 percent from the corresponding value measured on a normal-grown quantum dots ensemble and even increases slightly after an initial drop. Differently, the electron-electron interactions energies are decreasing strongly for the quantum dot samples subjected to a RTA process, accounting up to 50 percent from the as-grown reference sample in the case of the highest annealing temperature. Putting together these results, by taking into account also the well-known blue-shift of the emission spectrum, an enhanced picture of the possible degree of manipulation of the quantum dot properties via In-flushing and RTA processing is obtained. This can be particularly useful to decide which of these two methods should be
employed to achieve desired properties in order to make the self-assembled quantum dots more suitable for a specific purpose.

This work can be continued with the study of the effects of Indium flushing and RTA on the hole-hole interaction energies. It would be also interesting to see whether the Coulomb blockade energy increases subsequent to an AlAs overgrowth of the quantum dots.

Regarding the wavefunction mapping, supplementary investigations should be made in order to establish the nature of the observed effects. As a first step, the probing emitter wavefunctions can be changed by performing magneto-capacitance-voltage spectroscopy on samples having a two dimensional electron (hole) gas back contact. The possible influence of the magnetoresistance of the back contact upon the tunneling dynamic should be also verified.

In conclusion, this thesis reveals new interesting and intriguing properties of self-assembled InAs/GaAs quantum dots which have relevance both from fundamental and practical point of view.

7.2 Deutsche Zusammenfassung

Das Ziel der hier vorgelegten Arbeit ist es, Modifikationen des Ladungsträgereinschlusses an InAs-Quantenpunkten zu untersuchen. Insbesondere die resultierende Veränderung der Löcherwellenfunktion und die Coulomb-Wechselwirkungen im Leitungsband Grundzustand sind Bestandteil dieser Arbeit. Um dieses Ziel zu erreichen, wurde der Ladungsträgereinschluss zum einen reversibel durch Anlegen eines externen Magnetfelds und zum anderen irreversibel durch Ändern der Größe, Form und Zusammensetzung der Quantenpunkte variiert.

Die Kapazitäts-Spannungs-Spektroskopie ist eine leistungsstarke Messmethode, welche Einsicht in die Energieniveaustruktur und Coulomb-Wechselwirkungen in selbstorganisierten InAs/GaAs Quantenpunkten gewährt. Sie ermöglicht in Kombination mit einem senkrecht zur Wachstumsrichtung angelegten Magnetfeld die direkte Visualisierung des lateralen Impulsraum-Wellenfunktions-Betragsquadrates, korrespondierend mit den einzelnen C(V) Ladungspeaks.

Das Anlegen eines Magnetfeldes senkrecht zur Quantenpunkt-Ebene bewirkt einen zusätzlichen Ladungsträgereinschluss, welcher eine Dispersion der Quantenpunkterniveaus verursacht, vergleichbar mit dem Fock-Darwin-Spektrum eines zweidimensionalen harmonischen Oszillators. Als Konsequenz werden sich, bei ausreichend hohen Feldern, bestimmte Energieniveaus kreuzen, was eine modifizierte Energiekonfiguration zur Folge hat. Das erste Ziel dieser Arbeit war es, herauszufinden, auf welche Weise die Lochwellenfunktionen sich entwickeln, wenn der Ladungsträgereinschluss magnetisch modifiziert wird und wie sich die Wellenfunktionen nach dem erwarteten Kreuzen der Energieniveaus verändern. Um dieses Ziel zu erreichen, wurde C(V)-Spektroskopie im verkippten Magnetfeld durchgeführt. Die Richtung und der Neigungswinkel des Magnetfelds relativ zur Quantenpunkt-Ebene wurde so gewählt, dass die vertikale Komponente konstant blieb, während die laterale Komponente durchgeführt werden konnte, um das Wellenfunktions-Betragsquadrat-Mapping durchzuführen. Die Formen der
Quasi-Partikel-Wellenfunktions-Betragsquadraten wurden mit Hilfe der entlang zweier orthogonalen Richtungen gemessenen Profile rekonstruiert.

Die so erhaltenen Ergebnisse sind ziemlich überraschend, nicht nur, weil das Wellenfunktions-Betragsquadrat (die Aufenthaltswahrscheinlichkeitsdichte nach Max Born) sich scheinbar nicht aufgrund der angenommen neuen Konfiguration (welche aus der Energie niveaukreuzung resultiert) ändert, sondern auch weil drastische Änderungen in den mit den nicht-kreuzenden Energieneiveaus verknüpften Wellenfunktions-Betragsquadraten auftreten.

Obgleich keine Änderungen an den s-artigen-Wellenfunktionen erwartet wurden, welche den ersten beiden Löchern im Quantenpunkt entsprechen, zeigte die zweite der Beiden drastische Änderungen. Mit zunehmendem Magnetfeld $B_{\perp}$ änderte sich die Wellenfunktion, zunächst von einer Glockenform zu einer Knochenform und dann zu einer Ringform, welche eigentlich charakteristisch für d-artige-Zustände ist. Das dritte Loch sollte einen p-artigen-Charakter für alle verwendeten senkrechten Magnetfeldstärken beibehalten, jedoch wurde eine Änderung zu einer Glockenform beobachtet, welche für tiefere s-artige-Zustände charakteristisch ist. Das vierte Löcherwellenfunktions-Betragsquadrat hat bei $B_{\perp} = 0 \, \text{T}$ einen p-artigen-Charakter und sollte im Anschluss an das Kreuzen bei $B_{\perp} \approx 15 \, \text{T}$ zu einer ringförmigen Gestalt wechseln. In der Tat tritt dies ein, jedoch wird bei mittleren Feldern keine Mischform aus den beiden extremen Formen beobachtet. Bei den Messungen in einem exakt senkrechten Feld (d.h. die tangential Komponente ist Null) beobachtet man einen Scheitelpunkt bei der Auftragung der Energie gegen das Magnetfeld, welcher ein Indiz für ein Kreuzen der Niveaus ist. Das gleiche gilt auch für den sechsten Kapazitätspeak. Hierbei ist jedoch die Verbreiterung der Wellenfunktion im Impulsraum die einzige Änderung bei zunehmendem $B_{\perp}$.

Diese Erkenntnisse sind gänzlich unerwartet, da sie nicht durch die einfache Theorie, in welcher der Quantenpunkt als zweidimensionaler harmonischer Oszillator behandelt wird, erklärt werden. Sie können die Frage aufwerfen, ob diese Resultate den tatsächlichen Lochwellenfunktions-Betragsquadraten in InAs-Quantenpunkten mit magnetischen Ladungsträger einschluss entsprechen. Im Bestreben, diese Frage zu beantworten, wurden die Transmissionskoefizienten der Tunnelbarriere für verschiedene Systemenergien berechnet und eine Änderung kleiner als 25 %, für das entsprechende interessierende Impulsraumintervall, erhalten. Gemäß dem verwendeten Modell für die $k$-Raum Wellenfunktionen sollte der Transmissionskoeffizient nicht vom Magnetfeld abhängen, oder wenigstens nur langsam variieren. Aufgrund der monotonen Variation des Transmissionskoeffizienten mit dem angelegten parallelen Magnetfeld sollte man mit der oben dargelegten experimentellen Methode zumindest ein qualitatives Bild erhalten, sodass die Messergebnisse der Niveaukreuzungen im Prinzip als richtig einzustufen sind.

In Zukunft kann man erwarten, dass theoretische Berechnungen, welche auf realistischeren Modellen beruhen, mehr Licht auf diese experimentellen Ergebnisse werfen werden.

Dauerhafte Änderungen des Einschlusspotentials der Quantenpunkte erhält man durch Modifizierung ihrer strukturellen Eigenschaften, entweder durch Herstellungsprozesse während oder nach dem Wachstum. Die sich einstellenden Änderungen in Größe, Form und Komposition der Quantenpunkte bewirken eine Verschiebung in ihren Emissions-energien. Hierdurch kann nicht nur eine Manipulation der optischen Eigenschaften der Quantenpunkte erhalten.
erreicht werden, sondern auch die Wechselwirkungsstärke der Ladungsträger in Quan-
tenpunkten untereinander, durch Verändern ihrer Struktur, kontrolliert werden. Dies
kann insbesondere wichtig für die Realisierung von neuen optoelektronischen Bauele-
menten werden, welche auf selbst-organisierten Quantenpunkten beruhen, wie z.B.
Einzelphotonomitter.

Aufgrund ihrer technischen Bedeutung wurde die Coulomb-Blockade-Energie der
Grundzustandselektronen an Quantenpunkt-Ensembles, welche durch eine Indium Spül-
technik während des Wachstumsprozesses oder nach dem Wachsen mittels schnel-
lem thermischen Ausheizen erhalten wurden, untersucht. Es wurde herausgefunden,
dass trotz der Tatsache, dass die Quantenpunkt-Ensembles unabhängig von der Ma-
nipulationsmethode die gleiche Tendenz (Blauverschiebung) aufweisen, sich je nach
verwendeter Methode die Coulomb-Energien unterschiedlich verhalten. Für den Fall
von In-gespülten Quantenpunkten ändert sich die Coulomb-Blockade im Elektronen-
grundzustand nur um 15 % gegenüber dem entsprechenden Wert gemessen an ei-
inem herkömmlich gewachsenen Quantenpunkt-Ensemble und steigt sogar nach ei-
inem anfänglichen Abfall leicht an. Im Gegensatz hierzu nehmen die Elektron-Elektron-
Wechselwirkungen für Quantenpunktproben, welche einem schnellen thermischen Aus-
heilschritt unterworfen wurden, stark ab und machen für die höchste Ausheiltempera-
tur bis zu 50 % des Wertes für die unbehandelten Referenzquantenpunktproben aus.

Fasst man diese Ergebnisse zusammen, ergibt sich unter Berücksichtigung der gut be-
kannten Blauverschiebung des Emissionsspektrums ein erweitertes Bild über das Aus-
maß der Möglichkeiten zur Manipulation von Quantenpunkt-Eigenschaften mit Hilfe
von In-Spülung und RTA. Dies kann insbesondere für die Entscheidung von Bedeutung
sein, welche der beiden Methoden angewandt werden sollte, um die Eigenschaften der
Quantenpunkte für einen speziellen Verwendungszweck zu optimieren.

Die vorliegende Arbeit kann mit der Untersuchung des Einflusses von Indium-Spülung
und RTA auf Löcher-Löcher-Wechselwirkungsenergien fortgesetzt und ergänzt werden.
Interessant wäre es auch, zu überprüfen, ob die Coulomb-Blockade Energie nach einem
Überwachsen der Quantenpunkte mit AlAs ansteigt.

Das Wellenfunktions-Betragsquadrat-Mapping betreffend, sollten ergänzende Un-
tersuchungen unternommen werden, um die Natur der beobachteten Effekte zu ergrün-
den. Als erstes Schritt können die Wellenfunktions-Betragsquadrate der Elektronen im
Rückkontaktreservoir durch Verwendung eines zwei-dimensionalen Elektronen- (Lö-
cher) Gases (anstatt des 3D Kontakts) bei der Magneto- Kapazitätsspannungsspektros-
kopie gezielt beeinflusst werden. Auch der mögliche Einfluss des Magnetowiderstands
des Rückkontakts auf die Tunneldynamik sollte überprüft werden.

Zusammenfassend deckt diese Arbeit interessante und verblüffende Eigenschaften
von selbst-organisierten InAs/GaAs Quantenpunkten auf, welche sowohl grundlegende
as auch praktische Relevanz haben.
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Note: the numbers appearing at the end of each entry in the list indicate the page numbers where the item was cited.
Appendices
Appendix A

MBE growth recipes of the samples

The MBE growth-sheets corresponding to the samples used to acquire the results presented in this thesis are given in the following pages. They contain important parameters for the growth process like substrate temperature, growth pressure, layer sequence and layer thickness, etc.

Note: The $p$-type samples have been grown in two stages with an over-night pause to assure no traces of Carbon ($p$-type dopant) remain in the MBE chamber after the deposition of the back contact layer. Accordingly, two growth-sheets will correspond for such kind of samples.
<table>
<thead>
<tr>
<th>Sample</th>
<th>11599a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material:</td>
<td>GaAs</td>
</tr>
<tr>
<td>Orientation:</td>
<td>(100)</td>
</tr>
<tr>
<td>Wafer:</td>
<td>S3654</td>
</tr>
<tr>
<td>Rotation:</td>
<td>5</td>
</tr>
<tr>
<td>Pressure (Torr):</td>
<td>$3.0 \times 10^{-7}$</td>
</tr>
<tr>
<td>Date:</td>
<td>11.08.2003</td>
</tr>
<tr>
<td>File:</td>
<td>11599.ascii</td>
</tr>
</tbody>
</table>

### Ga-LF:
- $978.0 \, ^\circ\text{C}$

### Ga-UF:
- $1008.0 \, ^\circ\text{C}$

### Al:
- $1163.0 \, ^\circ\text{C}$

### C:
- Active

### Layer Information:

<table>
<thead>
<tr>
<th>Layer</th>
<th>Loop</th>
<th>$T , [\circ\text{C}]$</th>
<th>Dur. $[\text{s}]$</th>
<th>Thickn. $[\text{nm}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>660.0</td>
<td>257.7</td>
<td>50.0</td>
<td></td>
</tr>
<tr>
<td>AlAs</td>
<td>start: 20x</td>
<td>660.0</td>
<td>19.0</td>
<td>2.0</td>
</tr>
<tr>
<td>GaAs</td>
<td>end</td>
<td>660.0</td>
<td>10.3</td>
<td>2.0</td>
</tr>
<tr>
<td>GaAs</td>
<td>660.0</td>
<td>1030.9</td>
<td>200.0</td>
<td></td>
</tr>
<tr>
<td>GaAs:C</td>
<td>660.0</td>
<td>1546.4</td>
<td>300.0</td>
<td></td>
</tr>
</tbody>
</table>

**Cells ($^\circ\text{C}$):**
- Ga-LF: 978.0 °C
- Ga-UF: 1008.0 °C
- Al: 1163.0 °C
- C: Active

**Comment:**
- Unknown
- Standardhalter
- T(pyro) = 595°C
- As: 110mil/410/700°C
- C-Zelle: 1500V; 450mA

---

Angewandte Festkörperphysik, Ruhr-Universität Bochum, Germany
## Sample: 11599b

**Material:** GaAs  
**Orientation:** (100)  
**Wafer:** S3654  
**Rotation:** 5  
**Pressure (Torr):** $2.8 \times 10^{-7}$  
**Date:** 12.08.2003  
**File:** 11599b.ascii

### Layer Loop T [°C] Dur. [s] Thickn. [nm] Cells (°C)

<table>
<thead>
<tr>
<th>Layer</th>
<th>Loop</th>
<th>T [°C]</th>
<th>Dur. [s]</th>
<th>Thickn. [nm]</th>
<th>Cells (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td></td>
<td>660.0</td>
<td>26.2</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>GaAs</td>
<td></td>
<td>660.0</td>
<td>62.8</td>
<td>12.0</td>
<td></td>
</tr>
<tr>
<td>InAs</td>
<td>Do: 15x</td>
<td>570.0</td>
<td>4.0</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>GaAs</td>
<td></td>
<td>560.0</td>
<td>41.9</td>
<td>8.0</td>
<td></td>
</tr>
<tr>
<td>GaAs</td>
<td></td>
<td>660.0</td>
<td>115.2</td>
<td>22.0</td>
<td></td>
</tr>
<tr>
<td>AlAs</td>
<td>start: 27x</td>
<td>660.0</td>
<td>28.6</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>GaAs</td>
<td>end</td>
<td>660.0</td>
<td>5.2</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

### Comment

- Quantum Dots  
- Standardhalter  
- C(V)-Probe  
- $T(\text{pyro}) = 570°C$  
- As: 110mil/410/700°C  
- $T_{s-QD} = 570°C$
Sample: 11618a
Material: GaAs
Orientation: (100)
Wafer: S3654
Rotation: 5
Pressure (Torr): $4.6 \times 10^{-7}$
Date: 20.08.2003
File: 11618a.ascii

<table>
<thead>
<tr>
<th>Layer</th>
<th>Loop</th>
<th>$T \ [°C]$</th>
<th>Dur. [s]</th>
<th>Thickn. [nm]</th>
<th>Cells (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td></td>
<td>660.0</td>
<td>253.8</td>
<td>50.0</td>
<td>Ga-LF:</td>
</tr>
<tr>
<td>AlAs</td>
<td>start: 20x</td>
<td>660.0</td>
<td>6.8</td>
<td>2.0</td>
<td>1013.0 °C</td>
</tr>
<tr>
<td>GaAs</td>
<td>end</td>
<td>660.0</td>
<td>10.2</td>
<td>2.0</td>
<td>Al:</td>
</tr>
<tr>
<td>GaAs</td>
<td></td>
<td>660.0</td>
<td>1015.2</td>
<td>200.0</td>
<td>1224.0 °C</td>
</tr>
<tr>
<td>GaAs:C</td>
<td></td>
<td>660.0</td>
<td>1522.8</td>
<td>300.0</td>
<td>C: Active</td>
</tr>
</tbody>
</table>

Comment
Unknown
Standardhalter
T(pyro) = 590°C
As: 110mil/410/700°C
C-Zelle: 1500V; 400mA

Layer Loop $T \ [°C]$ Dur. [s] Thickn. [nm] Cells (°C)
GaAs | | | |
AlAs | start: 20x | | |
GaAs | end | | |
GaAs | | | |
GaAs:C | | | |
#### APPENDIX A. GROWTH RECIPES

<table>
<thead>
<tr>
<th>Layer</th>
<th>Loop</th>
<th>T [°C]</th>
<th>Dur. [s]</th>
<th>Thickn. [nm]</th>
<th>Cells (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td></td>
<td>630.0</td>
<td>25.8</td>
<td>5.0</td>
<td>As-LF: 700.0 °C</td>
</tr>
<tr>
<td>GaAs</td>
<td></td>
<td>660.0</td>
<td>72.2</td>
<td>14.0</td>
<td>As-UW: 410.0 °C</td>
</tr>
<tr>
<td>InAs</td>
<td>Do: 15x</td>
<td>565.0</td>
<td>4.0</td>
<td>0.2</td>
<td>Ga-LF: 983.0 °C</td>
</tr>
<tr>
<td>GaAs</td>
<td></td>
<td>565.0</td>
<td>41.2</td>
<td>8.0</td>
<td>Ga-UW: 1013.0 °C</td>
</tr>
<tr>
<td>GaAs</td>
<td></td>
<td>660.0</td>
<td>113.4</td>
<td>22.0</td>
<td>Al: 1163.0 °C</td>
</tr>
<tr>
<td>AlAs</td>
<td>start: 32x</td>
<td>660.0</td>
<td>28.6</td>
<td>3.0</td>
<td>In-LF: 700.0 °C</td>
</tr>
<tr>
<td>GaAs</td>
<td>end</td>
<td>660.0</td>
<td>5.2</td>
<td>1.0</td>
<td>In-UW: 730.0 °C</td>
</tr>
<tr>
<td>GaAs</td>
<td></td>
<td>660.0</td>
<td>51.5</td>
<td>10.0</td>
<td></td>
</tr>
</tbody>
</table>

**Sample:** 11618b  
**Material:** GaAs  
**Orientation:** (100)  
**Wafer:** S3654  
**Rotation:** 5  
**Pressure (Torr):** $3.1 \times 10^{-7}$  
**Date:** 21.08.2003  
**File:** 11618b.ascii  
**As-LF:** 700.0 °C  
**As-UW:** 410.0 °C  
**Ga-LF:** 983.0 °C  
**Ga-UW:** 1013.0 °C  
**Al:** 1163.0 °C  
**In-LF:** 700.0 °C  
**In-UW:** 730.0 °C  

**Comment**  
Quantum Dots  
Standardhalter  
C(V)-Probe  
$T$(pyro) = 567°C  
As: 110mil/410/700°C  
Ts-QD = 575°C
### Sample: 11638
- **Material:** GaAs
- **Orientation:** (100)
- **Wafer:** S3654
- **Rotation:** 5
- **Pressure (Torr):** $2.6 \times 10^{-7}$
- **Date:** 01.09.2003
- **File:** 11638.ascii

#### Quantum Dots
- **Standardhalter C(V)-Probe**
- **T(pyro) = 586°C**
- **As: 115mil/410/700°C**
- **Ts-QD = 585°C**
- **Tp(inner QD) = 515 - 521°C**
- **Tp(top QD) = 508 - 515°C**

<table>
<thead>
<tr>
<th>Layer</th>
<th>Loop</th>
<th>$T$ [°C]</th>
<th>Dur. [s]</th>
<th>Thickn. [nm]</th>
<th>Cells (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>start: 30x</td>
<td>660.0</td>
<td>19.4</td>
<td>2.0</td>
<td>As-LF: 700.0 °C</td>
</tr>
<tr>
<td>GaAs</td>
<td>end</td>
<td>660.0</td>
<td>10.3</td>
<td>2.0</td>
<td>As-UF: 410.0 °C</td>
</tr>
<tr>
<td>GaAs:Si</td>
<td>start: 15x</td>
<td>585.0</td>
<td>4.0</td>
<td>0.2</td>
<td>Ga-LF: 987.0 °C</td>
</tr>
<tr>
<td>GaAs</td>
<td>Do: 15x</td>
<td>575.0</td>
<td>41.0</td>
<td>8.0</td>
<td>Ga-UF: 1017.0 °C</td>
</tr>
<tr>
<td>GaAs</td>
<td>end</td>
<td>660.0</td>
<td>112.8</td>
<td>22.0</td>
<td>Al: 1163.0 °C</td>
</tr>
<tr>
<td>InAs</td>
<td>start: 34x</td>
<td>660.0</td>
<td>29.1</td>
<td>3.0</td>
<td>In-LF: 700.0 °C</td>
</tr>
<tr>
<td>GaAs</td>
<td>end</td>
<td>660.0</td>
<td>5.1</td>
<td>1.0</td>
<td>In-UF: 730.0 °C</td>
</tr>
<tr>
<td>AlAs</td>
<td>start: 30x</td>
<td>660.0</td>
<td>19.4</td>
<td>2.0</td>
<td>Si(max): 1310.0 °C</td>
</tr>
</tbody>
</table>

**Comment**
- Quantum Dots Standardhalter
- C(V)-Probe

#### Dark Illumination

<table>
<thead>
<tr>
<th>Layer</th>
<th>$u$ [cm$^2$/Vs]</th>
<th>$n$ [cm$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>300K</td>
<td>660.0</td>
<td>256.5</td>
</tr>
<tr>
<td>77K</td>
<td>660.0</td>
<td>19.4</td>
</tr>
<tr>
<td>4.2K</td>
<td>660.0</td>
<td>10.3</td>
</tr>
<tr>
<td>1K</td>
<td>660.0</td>
<td>1538.5</td>
</tr>
</tbody>
</table>

**Material**

<table>
<thead>
<tr>
<th>Layer</th>
<th>$u$ [cm$^2$/Vs]</th>
<th>$n$ [cm$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>300K</td>
<td>660.0</td>
<td>256.5</td>
</tr>
<tr>
<td>77K</td>
<td>660.0</td>
<td>19.4</td>
</tr>
<tr>
<td>4.2K</td>
<td>660.0</td>
<td>10.3</td>
</tr>
<tr>
<td>1K</td>
<td>660.0</td>
<td>1538.5</td>
</tr>
</tbody>
</table>
**Sample:** 12948  
**Material:** GaAs  
**Orientation:** (100)  
**Wafer:** WV/16570/Un67  
**Rotation:** 4  
**Pressure (Torr):** $3.9 \times 10^{-7}$  
**Date:** 08.03.2007  
**File:** 12948.csv  

### Quantum Dots  
**Standardhalter**  
**T(pyro)** = 597°C  
**As-LF:** 400.0°C  
**As-UF:** 700.0°C  
**Ga-LF:** 996.0°C  
**Ga-Uf:** 1026.0°C  
**Al:** 1152.0°C  
**In-LF:** 704.0°C  
**In-Uf:** 734.0°C  
**Si(max):** 1310.0°C  

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
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<td>635.0</td>
<td>270.3</td>
<td>50.0</td>
<td></td>
</tr>
<tr>
<td>AlAs</td>
<td>start: 30x</td>
<td>635.0</td>
<td>20.0</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>GaAs</td>
<td>end</td>
<td>635.0</td>
<td>10.8</td>
<td>2.0</td>
<td></td>
</tr>
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<td>635.0</td>
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<tr>
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<td>27.0</td>
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<td>635.0</td>
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<td></td>
</tr>
<tr>
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</tr>
<tr>
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<td></td>
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<td>118.9</td>
<td>22.0</td>
<td></td>
</tr>
<tr>
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<td>start: 34x</td>
<td>635.0</td>
<td>30.0</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>GaAs</td>
<td>end</td>
<td>635.0</td>
<td>5.4</td>
<td>1.0</td>
<td></td>
</tr>
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**Comment**  
Quantum Dots  
Standardhalter  
T(pyro) = 597°C  
As: 75%/400/700°C

**Ts-QD = 555°C**  
**Tp(inner QD) = 520°C**  
**Tp(top QD) = 513°C**

---

Angewandte Festkörperphysik, Ruhr-Universität Bochum, Germany
<table>
<thead>
<tr>
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<th>Thickn. [nm]</th>
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**Comment**
- Quantum Dots
- Standardhalter

T(pyro) = 600°C
As: 71%/400/700°C
T50% = 566°C
Tf(Inner QD) = 520-521°C
Tf(Top QD) = 512°C
Sample: **12987**

Material: GaAs

Orientation: (100)

Wafer: WV/18753/Un20

Rotation: 4

Pressure (Torr): $2.0 \times 10^{-7}$

Date: 13.04.2007

File: 12987.csv

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<td>0.0</td>
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Quantum Dots

Standardhalter

$T_{\text{pyro}} = 600^\circ\text{C}$

As: 75%/400/700°C

$T_{\text{SQD}} = 563^\circ\text{C}$

$T_{\text{inner QD}} = 520-521^\circ\text{C}$

$T_{\text{top QD}} = 511^\circ\text{C}$
Sample: **12988**

Material: GaAs

Orientation: (100)

Wafer: WV/18753/Un32

Rotation: 4

Pressure (Torr): $2.3 \times 10^{-7}$

Date: 13.04.2007

File: 12988.csv

**Comment**

Quantum Dots

**Standardhalter**

$T$(pyro) = 600°C

As: 75%/400/700°C

Ts-QD = 560°C

Tp(inner QD) = 520-521°C

Tp(top QD) = 510°C

---

### Table: Dark and Illuminated Carrier Concentration and Mobility

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</table>

### Cells (°C)

- As-LF: 420.0 °C
- As-UH: 700.0 °C
- Ga-LF: 1003.0 °C
- Ga-UH: 1033.0 °C
- Al: 1149.0 °C
- In-LF: 704.0 °C
- In-UH: 734.0 °C
- Si(max): 1310.0 °C

---

Angewandte Festkörperphysik, Ruhr-Universität Bochum, Germany
Sample: 12989
Material: GaAs
Orientation: (100)
Wafer: WV/18753/Un32
Rotation: 4
Pressure (Torr): $2.1 \times 10^{-7}$
Date: 13.04.2007
File: 12989.csv

Layer Loop T [°C] Dur. [s] Thickn. [nm] Cells (°C)
--- --- --- --- ---
GaAs start: 30x 650.0 264.6 50.0 As-LF: 420.0 °C
GaAs end 650.0 21.5 2.0 As-UF: 700.0 °C
GaAs 650.0 10.6 2.0 Ga-LF: 1003.0 °C
GaAs 650.0 264.6 50.0 Ga-UF: 1033.0 °C
GaAs:Si 650.0 1587.3 300.0 Al: 1149.0 °C
GaAs 620.0 26.5 5.0 In-LF: 704.0 °C
GaAs 650.0 105.8 20.0 In-UF: 734.0 °C
InAs Do: 11x 560.0 4.0 0.0 Si(max): 1310.0 °C
GaAs 535.0 21.7 4.1
GaAs 650.0 137.0 25.9
AlAs start: 34x 650.0 32.3 3.0
GaAs end 650.0 5.3 1.0
GaAs 650.0 52.9 10.0
InAs Do: 11x 560.0 4.0 0.0

Quantum Dots
Standardhalter
T(pyro) = 603°C
As: 75%/400/700°C
Ts-QD = 650°C
Tp(inner QD) = 520-521°C
Tp(top QD) = 509°C
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### Layer Information:

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<td>10.0</td>
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</table>

### Temperature Details:

- As-LF: 99.0 °C
- As-UF: 99.0 °C
- Ga-LF: 1002.0 °C
- Ga-UF: 1032.0 °C
- Al: 1147.0 °C
- C: Active

### Comment:
- Quantum Dots
- $T$(pyro) = 535°C
- $T$(As) = 185°C
Appendix B

Crystal direction

In general, the orientation of the crystallographic axes for our samples, having a rectangular shape, was made by keeping a reference with the flats of the 2" GaAs (100) wafers from which they have been cut-off. However, to rule out any doubt, the crystal directions were double-checked. This was necessary mainly for two different reasons: (a) existence of older samples with a squarely shape whose orientations could not be tracked in the sample growth-sheet; (b) a great demand for samples cut from the same wafer, as is the case of our best wafers, which would result in small stripes separated from the ones containing the wafer flats, making impossible to have a proper reference.

The identification of the correct orientation of the sample with respect to the crystal axes is relevant to establish if there is a difference in the asymmetry of electron and hole wavefunctions, as it was previously reported [113]. Moreover, given the fact the quantum dots are slightly elongated instead of having a perfect circular symmetry in the growth plane, one can relate the anisotropy of the wave functions with the shape of InAs islands.

To be sure no errors have been made for the assignment of the crystal directions when comparing the asymmetry of the electron and hole wavefunctions, those directions were determined by employing an anisotropic etching in a \( \text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O} \) (1:8:1) solution [145, 146]. The etching was performed for 60 s at room-temperature while steering the solution with the sample lying horizontally. Only fresh solutions were used, otherwise the anisotropic etching was subjected to failure.

Rectangular pieces with a high aspect ratio, shown in green in Figure B.1 (a), were cut parallel to the flats of the wafers and subjected to a photolithographic process as described in Section 4.1.2. in order to obtain a T-shaped feature with orthogonal lines \( \approx 100\mu\text{m} \) wide, aligned with the cleaved edges. In this way, there is an unambiguous correspondence between the T-shaped figure and the wafer flats with a known orientation. In Figure B.1 (b), SEM shows the resulted situation after the etching. It can be easily seen there are differences for the two crystal directions, as it was expected for the anisotropic etching: the bright region along [0-11] shows the tilted walls of the etched channel while for the [011] a different wall seems to appear.

To be more rigorous, profiles of the etched grooves for the two directions were investigated. To present the results in Figure B.2, the etched sample was cleaved again through the T-shaped zone and \( \text{SEM} \) was performed on the edges. It can be seen that the bright region along [0-11] is due to the presence of a trench-like wall on the etched groove (Figure B.2 (a)). On the contrary, there is an undercut when etching
along [011] (Figure B.2 (b)) related with an increased speed of reaction due to weaker bounds in GaAs planes.

Figure B.1: The method applied to double-check the sample orientation in relation with the orthogonal directions [011] and [0-11]: (a) The sample was cleaved paying attention to the orientation of its edges concerning the flats of the wafer for which orientation was known; this method is reliable for samples with a rectangular shape. (b) A T-shaped figure was etched in a $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ solution, which is known to produce different results for [011] and [0-11] directions in GaAs. This method is suitable for square-shaped samples or for wafers from where the flats are no longer able to be recognized.

Concluding, the orientation of the samples edges with respect to orthogonal directions [011] and [0-11] was established in two different ways: by comparing with the alignment to the wafer flats and with the results reported earlier in the literature for anisotropic etching of GaAs.

Based on these results, it had been shown [117] the anisotropy in the ground state quasi-particle probability densities is the same for electrons and holes and not orthogonal, as previously reported. This points to a predominantly structural reason for the anisotropy in the confinement potential, most probably due to an elongated quantum
dot shape, and not to a strong piezoelectric contribution [147] as proposed in the original publication.

Figure B.2: Profiles of the etched grooves after anisotropic etching: (a) undercut along [0-11] direction; (b) normal cut, with trench-like walls which would show bright when seen from above, as in the figure on the previous page.
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Appendix C

Labtalk programming for Origin®

The following code and instructions were developed for the automatic processing of huge amount of data by using Origin software package from OriginLab Corp. It is strongly recommended to use the last available updates. The script in here is made in LabTalk language for OriginPro 7.5 Service Release 6. It has been also successfully tested for the newly released version (OriginPro 8).

Because of a 8 character limitation in Origin window names, it is important to prepare the file names prior to their import in Origin. For this, "multiple rename" option in TotalCommander can be used. These file-names should contain information about the magnetic field strength and the rotation angle. Their names will be imported as worksheet (wks.) names into the Origin project and will be subsequently transferred to the column names as a result of data processing. They constitute tracking labels for the datasets and will be used eventually after completing all the tasks.

For the ease of use of this code, as well as for having the possibility of controlling the results in some critical steps, the program was developed in several modules. In some cases, user interaction is needed for loading and exporting the processed data. Moreover, full control of the data processing is possible with minimum input from the user.

In this section, guidelines for using the program are provided.

Extract background and prepare the datasets

With so many datasets to be processed (for a complete wavefunction mapping they can reach easily 500 $C(V)$ traces, each of them with at least 6 Gaussian peaks), it is more convenient to have a program to realize this task automatically. This can save huge amount of time and gives the possibility to focus on other tasks. However, interaction with the program is needed in several critical points and the intermediary results should be briefly evaluated at some stages. Therefore the script is divided in modules, some of them being designed to work also separately, whenever the corresponding task is needed.

The following script takes care of conditioning the datasets in order to make them ready to be processed for extraction of $C(V)$ peaks information.

The first step is to extract a linear background from all the $C(V)$ data (see section 4.2.2) and then to reduce the size of the project by creating a single worksheet containing all the $C(V)$ traces. In order to combine all the datasets into one single file some
care should be taken:

- all measurements should be performed over the same bias range with the same scan-step;

- all files should be properly named for a facile identification in the subsequent processing steps (e.g., \textit{xykHz}abcdnmpqrdeg.dat) where \textit{xy} is the frequency at which measurement was performed, \textit{abcd} is the applied magnetic field strength in mT and \textit{mnpqr} is the rotation angle in the magnetic field, in degrees, including the two digits corresponding to 0.01 degrees precision;

- all datasets should contain the same set of measured parameters (the same number of columns with the same designation).

It should be noted that the information about measurement conditions, which is stored in the filename and then imported by Origin as window name (no more than 8 characters), will be transferred to the column label when reducing the file-size of the Origin project (OPJ). This information will be provided as an output several times and they should be manually processed with a text editor (for example Notepad) to separate \textit{xykHz}, \textit{abcd}T and \textit{mnpqr}deg in three columns for a further usage.

\textbf{Step 1 - arranging the output}

It deals with the output of the script, redirecting the saved data to Notepad window:

\begin{verbatim}
win -n n fitparam; //create a note window for fit parameters
type.redirection=2; //redirect the output from the script window
type.notes$=fitparam; //it goes with the line above
type"LINEAR FIT PARAM"; //print
%type "______"; //print
%type ; //print
\end{verbatim}

\textbf{Step 2 - the linear fit}

Performs the linear fit for the \textit{C(V)} spectra:

\begin{verbatim}
doc -e W | //run script on all wks
lr %H_Capacitance -b 1 -e 61;
\end{verbatim}

\begin{verbatim}
type slope is $(lr.b); //dataset and range for fitting//USER INPUT HERE
\end{verbatim}

\begin{verbatim}
type intercept is $(lr.a);
\end{verbatim}

\begin{verbatim}
type "**********";
\end{verbatim}

\begin{verbatim}
aa=lr.a;
bb=lr.b;
\end{verbatim}

\begin{verbatim}
win -a %H;
\end{verbatim}

\begin{verbatim}
wo -c linear;
\end{verbatim}

\begin{verbatim}
col(5)=aa + bb*col(1);
\end{verbatim}

\begin{verbatim}
wo -c substracted;
\end{verbatim}

\begin{verbatim}
col(6)=col(2)-col(5); }
\end{verbatim}

\begin{verbatim}
//create a new column for the line
//calculate the points on the line
//create a new column for the substracted spectrum
//make subraction and close the loop
\end{verbatim}
APPENDIX C. PROGRAMMING FOR ORIGIN®

Step 3 - tracking the data

This section was developed for tracking the data because a transpose of the worksheet will be made; one has just to copy the values from the output of this section in the transposed worksheet.

```plaintext
type "You’ll need data from this section;"
// print message
type ""
// give some space
doc -e W {
    type %H;}
// extract the file names
```

Step 4 - combine datasets

It is intended for reducing the size of the project; it will copy the only interesting column of every worksheet into a new one, deleting the original data afterwards (the original dataset stores other values like conductance, phase, etc., which are not necessary for our further processing):

```plaintext
cc=6;
win -t D;
%W=%H;
del col(2);
nn=1;
doc -e W {
    if("%H"!="%W") {
        nn++;
        %W!wks.addCol();
        %W!wks.col$(nn).label$=%H;
copy %(%H,cc) %(%W,nn);
copy %(%H,1) %(%W,1);
    };
}
win -cd %H;
win -a %W;
wks.labels();
type $(@D,D10);
```

Data conditioning

Smoothing of the measured data is needed in order to minimize the errors in the fitting process. Three points adjacent averaging has been used for the handling of all datasets. This implies that the new data points are obtained from original data by performing an average on the values of the actual point and 3 points to its left and to its right. In principle, this will smoothen the data without losing precision but reduce the kinks when making derivatives.

```plaintext
doc -ef W
{ for (ii = 2; ii <= 123; ii++)
    {%B=%(%H,ii);
     ave -n 3 %B;};
}
```

//apply to all wks in the current folder
//loop from 2nd col on//USER INPUT HERE
//get the name of the column
//average on (2$cdot3+1) values//USER INPUT

//USER INPUT HERE
The position and height of the capacitance peaks are altered when performing \( C(V) \) measurements in a perpendicular (see 4.2.2) or parallel (see 4.2.2) magnetic field. Usually, the spectra are taken with sweeping the magnetic field such that there are small differences from one \( C(V) \) spectrum to the next one. Provided that the data-files are imported in the order they have been measured, there will be a monotonic variation of the position, respectively height, of each individual peak. This will be exploited by the following Labtalk script.

As mentioned above, due to a huge amount of data to be processed, care should be taken with when attempting to extract the information needed. In the case of \( C(V) \) spectroscopy, each spectrum contains a number of Gaussian peaks superimposed on a linear curve which has already been extracted by the previously presented script. For the remaining of the spectrum, the charging of the wetting layer which resembles an exponential rise should receive special attention because it can mask or strongly influence the peaks corresponding to the charging of quantum dots. To account for the charging of the wetting layer, the exponential rise in the spectrum was simulated by another Gaussian (or a combination of two Gaussian peaks) and the corresponding parameters have been kept constant over the whole iteration process. This was the simplest approach and it has been proven as an effective one. At this point, all the datasets should consist only of Gaussian functions and the task of processing them can be greatly reduced by using a module developed for this. Fortunately, OriginLab software is enhanced by hundreds of specialized applications developed by different users which can be integrated into Origin. Such an application is MultiFit which can realize sequential or simultaneous fits for multiple datasets.

In the following the script used to process the measured data will be presented together with some details and hints related with the script. All the modules are designed to work independently and to take advantage of the MultiFit add-on module for Origin.

First of all, after the module is downloaded, it should be un-packed into the Origin (by drag-and-drop when a project is open) and re-compiled (for further details about installation see the instruction enclosed with the package). When the add-on is ready to be used, it can be addressed by the Labtalk scripts as described in the following. It should be noted that the script will do its job automatically, but there are some parameters which should be updated manually (for example the desired number of peaks to be fitted). The interaction from the user is indicated by a red text in the comments of the code, reminding that the input from the console is expected to fine-tune the fitting procedure.

**Module 1 - preparation**

The program starts by clearing the internal memory of parameters which might be stored from the previous runs. Then, the fit function type and its multiplicity (i.e., number of its replicas) are loaded. A new worksheet is to be created from a template and its name is kept for the next steps. This new worksheet stores the values needed for the parameter initialization during the fitting procedure.
Module 2 - initialization

This step cannot be automated and requires input from the user. The initialization values for the all peaks parameters are to be typed from the keyboard in the second column of the worksheet. The names of the parameters are in the form \( y_0_i, x_{c_i}, w_i \) and \( A_i \), for baseline, peak center, FWHM and area, respectively, the index \( i \) corresponding to the rank of the peak in the spectrum. The third column of the worksheet makes the program aware that the corresponding parameter in the second column is to be fixed (value 0) or it should be varied (value 1). One might chose to fix the values for the peak(s) corresponding to the charging of the wetting layer. More than this, in the case the measurements were made in parallel magnetic field, where a shift of the peak’s position is not expected, all the center positions of the Gaussians \( x_{c_i} \) should be fixed.

The initialization values for the Gaussian fitting can be obtained by a careful "manual" fitting of the \( C(V) \) spectrum taken at 0 Tesla. This can be easily accomplished using the Peak Fit Module inside Origin.

Once the initialization is completed, before proceeding to the next step, a manual activation of the worksheet storing the measured data is needed.

Module 3 - the fit

This is the module which does the actual fitting. It processes the datasets one by one, producing a new worksheet which holds the peaks parameters resulted from the fit. A quick inspection of this worksheet will show if the fit was successful or not (if the values for the peaks areas are positive and different than zero), or if the parameters are not all equal with the ones from the initialization worksheet. There are two possibilities to fit the data, choosing one of them being depending on the user’s preference or how the effective is the procedure for the given dataset.

The first fit mode loads the initialization parameters before starting to process each dataset, while the second fit mode loads these parameters only for the first dataset and uses the fitted parameters as initialization parameters for the second dataset and so on.

Full control of the fitting procedure can be achieved by the use of the constraints, option which is activated by \( \text{nlsf.constraints}=1 \). Most of the times, it will be necessary to
declare the peaks areas and the widths to take only positive values. Further conditions can be imposed also, for example both s-like peaks to have the same FWHM.

**Module 4 - track the datasets**

This part will print in the script window the labels containing information of measurement conditions, in the order they were processed by the fit. This resulted text should be processed separately (manually) in a Notepad document to split and arrange the text into columns for a further usage.

```plaintext
// select the wks ...  // where measured data are stored
ee=wks.nCols;  // register the number of columns
for (gg=2; gg <= ee; gg++)  // scan from 2nd column to the end
{%(L=%(gg, @L);  // save the wks labels
 type %L;)
}  // print @ the script window the wks labels
```

**Module 5 - publish the results**

After a successful completion of the fit procedure, a new module is to be executed in order to automatically track and gather the peak heights (or some other parameters if the script is reconfigured). By performing this, the needed data are prepared so that they are ready for export to other worksheets for further operations or to be plotted. In this example, the height of each Gaussian peak is outputted into a new worksheet with the name "HEIGHTS". Activate the results worksheet by a mouse click and run:

```plaintext
%W=%H;  // save name of results (active) wks
win -t D;  // create new wks to store the values
win -r %H HEIGHTS;  // rename created (active) wks as HEIGHTS
npeaks=6;  // declare peaks you fitted
work -a npeaks;  // add necessary columns
for (mm=2; mm<=npeaks+1; mm++)  // rename the columns in the output wks ...  
{work -n $(mm) peak$(mm-1);  // ...to facilitate tracking of the peaks
copy %(%W,1) %(%H,1);  
loop(ii,0,npeaks-1)
{ jj=2*(3*ii+1);  
col($(ii+2))=gauss(%(%W,jj+2),%(%W,2),%(%W,jj+2),%(%W,jj+4),%(%W,jj+6)); }
}
```

**Module 6 - verify the fit (optional)**

The final step is important as an ultimate proof for the fitting procedure. One has the opportunity to verify the fit parameters by evaluating briefly the results worksheet and can spot easily if major failures have occurred but, beside this, all other approaches are time consuming and not so effective. The following module collects all the parameters resulted from the fit, generates the individual Gaussians and calculate their superposition. Afterwards, the original dataset is plotted together with the simulated spectrum such that the problematic regions can be spotted. By doing this, the user can take appropriate countermeasures to improve the fitting (usually imposing supplementary constraints). Nevertheless, because there are too many datasets to be verified in
this way, one might prefer to focus on a small number of different, randomly choosen, datasets for which to apply this script.

```plaintext
//activate by mouse click//
rowNum=1;
%A=cell(rowNum,1);
y0=cell(rowNum,2);
win -t D;
win -r %H GAUSSIANS;
npeaks=6;
work -a npeaks;
for (pp = 2; pp <= npeaks+1; pp++)
{ work -n $(pp) peak$(pp-1);
  if (pp==$npeaks+1)
    work -n $(pp+1) CVsimulated;
}
col(1)=xof(%A);
col(2)=%A;
wcol($(npeaks)+2)=0*col(1);
loop(ii,0,npeaks-1) {
  jj=2*(3*ii+1);
  win -o %W {
    xc=cell(rowNum,jj+2);
    w=cell(rowNum,jj+4);
    A=cell(rowNum,jj+6);
    wcol(ii+2)=gauss(col(1),y0,xc,w,A);
    wcol($(npeaks)+2)=wcol($(npeaks) +2)+wcol(ii+2);
  };
  work -s 0;
  work -p 200;
legend;
label -s -q 2 Gaussian fit for %Ajj
}
```

//the results worksheet//USER INPUT HERE
// save name of results wks
// the data to verify//USER INPUT HERE
// dataset name
// y0 is same for all replicas
// create new wks to store the values
// rename the active window GAUSSIANS
// total nr. of peaks//USER INPUT HERE
// add columns for them//USER INPUT HERE
// following FOR instruction is renaming
  the columns in the output worksheet
  to facilitate tracking of the peaks
// rename the columns including word "peak"
// stores gaussians superposition
// rename the last column
//
// fill 1st column with X data
// fill 2nd column with Y data
// fill column with 0
// make a loop over the peak numbers
// accounts for y_err columns
// run script only for the selected wks
// track the xc value
// track the widths
// track the peak areas
// terminate the iteration on jj
//
// create peak ii+1
// calculate the gaussian superposition
//
// terminate the iteration on peaks number
// plot entire wks
// update the legend for the plot
// include the name of the simulated dataset
// for the test in the 2nd quadrant
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Acknowledgements

In the end, I would like to express my gratitude to all the people who have helped me in one way or another to accomplish this work.

First of all, I want to thank Prof. Dr. Andreas D. Wieck who accepted me as a PhD candidate under his supervision and gave me the opportunity to work in his group. I appreciate his continuous support and encouraging, his kindness and understanding.

This work would not have been possible without the support and directions of PD Dr. Dirk Reuter. I am indebted to Dr. Reuter for his invaluable tuition and guidance, for helping me advance with new ideas and his enormous expertise.

This work was financially supported by the German Science Foundation through GRK 384: "Nanoelectronics, Micromechanics and Microoptics: Analysis and Synthesis by Ions, Electrons and Photons". Support from Ruhr-University Research School is also gratefully acknowledged.

I would like to thank all the AFP colleagues for the great atmosphere they have created, for the time spent together as well as for their kind support. Special thanks to Rolf Wernhardt for his advices and recommendations, both technical and administrative. Many thanks also to Georg Kortenbruck for preparing and reconfiguring the sample holders, and in general for all the small but essential things he took care of so that I could continue my experiments.

I am grateful to Fang-Yuh Lo for his help in the cryogenic business and, in general, for being such a reliable person. I acknowledge Peter Kailuweit as being the one who introduced me the details of $C(V)$ and $PL$ measurements.

I enjoyed so much sharing the same office with Aleksander Melnikov and Paul Mazarov. For their friendly attitude and many discussions, a great "Спасибо".

I consider myself lucky to have met such extraordinary people as Arne Ludwig and Ashish Rai. Respect!

I value their friendship and appreciate the time spent together over these years with Sinan Ünlübayir, Sébastien Pezzagna, Leonard Stoica and Aleksandar Miltenovic. I still need their support in the search for an acceptable answer on two important questions: "What should we do?" and "What is life?".

I am thankful to Minisha Mehta and Mirja Richter for the effort and the time spent growing almost all the samples I have used in these years, as well as to Nadine Viteritti for preparing the best electrical contacts of my $C(V)$ samples.
The success of the measurements at the High Field Magnet Laboratory in Nijmegen, the Netherlands, would have not been possible without the support of Dr. Ulrich Zeitler who made everything to work like a Formula 1 engine. Also, my stay in the Netherlands was much easier to bear due to the company of my friend Lucian Jdira. Salut ali!

It is the case to express my gratitude to Mihai Drăghici, Sorin Poenariu and Victorina Stavarache-Poenariu who helped me all the time they were in Bochum and even when they were away. The three of them, together with Ioana Pera and Irina Dumitriu were also the ones encouraging me to start a PhD in Germany.

This work contains extensive reference to papers published in different scientific journals, some of them not readily available. I appreciate the effort of Victor Diculescu, Diana Beşliu-Ionescu, Irina Dumitriu, Andreia Popa and Cristian Simion in providing access to literature whenever I was in need. The German translation of the Summary section has been done by Sinan Ünlübeyir and double-checked by Arne Ludwig. Additional contributions of Nadine Viteritti and Oxana Berezhna are also acknowledged.

For the corrections and proof reading this thesis, I would like to thank to Mihai Drăghici, Sébastien Pezzagna, Minisha Mehta and Irina Dumitriu, as well as to Diana Alupej whose help has been priceless. For the help in completing the programming tasks needed to simultaneously process hundreds of data-sets, I acknowledge the guidance of Mike Buess from Origin WebRing as well as the support provided by the Chinese and U.S. OriginLab® Support teams.

I appreciate a lot the fruitful discussions I had with Marian Niţă and Răzvan Coca before and after leaving Bucharest. I am also thankful to my colleagues from the National Institute for Materials Physics (INCDFM) in Bucharest-Măgurele for their support in the years before coming to Bochum. I will mention here Dr. Ştefan Frunză, Dr. Magdalena-Lidia Ciurea, Prof. Dr. Alexandru Aldea, Prof. Dr. George Filoti and Dr. Adelina Tomescu.

Special thanks to Răzvan Coca for his effort of driving thousands of kilometers to bring Alfa to her new home.

I cannot end this section without expressing my gratitude for the continuous support I received from my mother and my sister. I am thankful for their understanding and patience, especially the one my mother had for keeping "pampanţoanca" in such a great shape. Săru'măna, mama!
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2005 – 2009   Assistant Researcher / PhD candidate at Lehrstuhl für Angewandte Fest-
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List of publications


Conference contributions


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Bochum, 12 Oktober 2008

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