Contacting single quantum dots with nano-electrodes

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Abstract

In this thesis semiconductor quantum dots were contacted with nano-electrodes to yield single-electron devices. For this purpose different approaches for quantum dot preparation and nano-electrode fabrication were investigated. The resulting devices were electrically characterized and their behavior was compared to theoretical models.

For quantum dot preparation two approaches were taken. On the one hand, silicon quantum dots were prepared from a SOI substrate by means of a self-assembled colloidal etch mask and reactive ion etching. On the other hand, CdSe/ZnS core/shell quantum dots were employed and deposited onto the electrodes with special linker molecules.

To contact the quantum dots electrode pairs with a separation of only a few nanometers were necessary, which were obtained in three different ways. All methods were based on electron beam lithography yielding electrode separations down to about 10 nm. Electrode pairs with even smaller distance were fabricated with a controlled electromigration process. Additionally, electrochemical deposition was employed as further method, which also was capable to realize electrode separations of only a few nanometers.

By combining the above methods single-electron devices with a quantum dot attached to two electrodes via tunneling barriers were fabricated. These devices were characterized by transport measurements.

The single-electron transistors based on silicon quantum dots showed the characteristic phenomenon of the Coulomb blockade for lower source-drain voltages. For higher bias voltages a step-like increase in the current was observed, which is referred to as Coulomb staircase. By applying a gate voltage, the single-electron transistors could be switched from a non-conducting to a conducting state.

In the transport measurements on the significantly smaller CdSe/ZnS quantum dots also a step-like increase was observed in the current. This time the steps were not equidistant and their positions could be correlated with the energy spectrum of the quantum dot’s electron states.

For both cases model calculations based on the orthodox theory were performed. The behavior of the silicon quantum dot devices was well described by the simple model. In case of the CdSe/ZnS based devices first the energy spectrum of the quantum dot’s electron states was calculated from its geometry. The spectrum was included into the
model calculation and then also a very good agreement with the measurement was achieved.
Kurzfassung


Durch Kombination der oben beschriebenen Methoden wurden Einzelelektronenbauelemente produziert, bei denen ein Quantenpunkt über Tunnelbarrieren mit zwei Elektroden verbunden ist. Diese Bauelemente wurden mittels Transportmessungen charakterisiert.


Bei den Transportmessungen an den deutlich kleineren CdSe/ZnS Quantenpunkten wurde ebenfalls ein stufenartiger Anstieg des Stroms mit steigender Vorspannung beobachtet. Hier waren die Stufen allerdings nicht äquidistant und ihre Positionen konnten mit dem Energiespektrum der Elektronenzustände im Quantenpunkt
in Verbindung gebracht werden.

Für beide Fälle wurden Modellrechnungen basierend auf der Orthodox Theory angestellt. Im Fall der Siliziumquantenpunkte konnte das Verhalten der Bauelemente gut mit dem einfachen Modell beschrieben werden. Bei den CdSe/ZnS Quantenpunkten wurden zuerst die Energieniveaus der Elektronenzustände aus der Geometrie der Quantenpunkte berechnet und diese in das Modell einbezogen. Auch hier wurde dann eine erstaunlich gute Übereinstimmung erzielt.
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1. Introduction

The evolution of integrated circuit performance, in particular of computer processors and memory cells, is well described by Moore’s law first formulated by Gordon Moore in 1965 [80]. The law claims that the complexity and the integration density is doubled approximately every two years. This ongoing development is obviously accompanied by a reduction in the device size, the current necessary to operate it and the charge used to store information. Despite the enormous efforts necessary to fabricate the ever-shrinking structures to follow Moore’s law (at the time of writing the 45 nm technology node was state of the art), also physical problems associated with the operability of the nano-devices themselves are foreseeable. In a few years, for example, the number of charges used to store one bit of information in a memory cell will approach the single electron limit. Considering the statistical fluctuations of the actual carrier number, a variation by one electron might switch the bit from 1 to 0 and thus lead to the loss of data. Also quantization and tunneling effects become increasingly important when the lines are further narrowed and the gate oxide thickness is reduced.

On the other hand, the effects described above do not only prevent classical electronic devices from proper operation, but also offer the possibility to develop novel types of devices. With the discovery of the single-electron tunneling effect [84, 45, 76], which states that an electron cannot tunnel into a small island if charging its capacitance with only one electron exceeds thermal energy, the development of the so-called single-electron transistor [41] was possible. This device is based on a nanometer sized metallic island coupled to source and drain electrodes via tunneling barriers and an additional gate electrode. Quantum dots and single molecules are also promising building blocks for future nano-electronic devices. The energy spectrum of a quantum dot can be adjusted via its shape and material whereas molecules can readily be synthesized with tailored properties by means of organic chemistry.

The key to get access to these nano-objects in order to built such devices is the ability to fabricate nano-electrodes to make electronic contact. When it is possible to contact quantum dots and single molecules, a whole range of novel, interesting devices gets within reach [66, 89, 90, 74, 62, 60, 122, 58]. An even wider variety of applications becomes available if these nano-structures are combined with ferromagnetic electrodes [50]. Due to their spin-dependent density of states they are capable
1. Introduction

of injecting spin-polarized carriers and open the door to spintronic devices such as the quantum dot spin valve [25]. Nano-electrodes also provide the facility to characterize nano-objects via tunneling spectroscopy. In comparison to scanning tunneling spectroscopy the ability to add a gate electrode yields additional insight into the object under investigation.

The scope of this thesis was the development of techniques to contact nano-objects, and in particular semiconductor quantum dots, and thereby fabricate nano-electronic devices. This included the establishment of different preparation techniques for semiconductor quantum dots serving as the nano-object in our devices. The main focus of the work was put on the investigation of several fabrication processes for nano-electrodes. By combining these methods different types of single-electron devices were fabricated. The devices were then characterized with a variety of electronic measurements. Therefore the manuscript is structured as follows.

To be able to describe the electronic properties of such novel nano-electronic devices, the standard formalism of the Boltzmann transport equation is not appropriate anymore. Instead new concepts like the Launder formula for ballistic transport, the transfer Hamiltonian method for tunneling and the orthodox theory for single-electron effects are necessary. An overview of important theoretical tools for nano-electronic devices is given in chapter 2. In addition the energy spectrum of semiconductor quantum dots and its impact on their transport properties are discussed. The chapter is completed by a section on spin-dependent transport.

For the quantum dot preparation, which is the topic of chapter 3, two approaches were taken. One method was based on colloidal CdSe/ZnS core/shell quantum dots, which were deposited onto gold nano-electrodes by thiol linker molecules. The other technique was a top down approach starting from a silicon-on-insulator substrate. The substrate was covered with self-assembled gold colloids, which served as an etch mask in an anisotropic reactive ion etch. After removing the etch mask silicon quantum dots remained on the insulating buried oxide layer of the SOI substrate.

Nano-electrodes were fabricate in three different ways, which are discussed in chapter 4. The easiest approach was the utilization of electron beam lithography to expose an appropriate resist followed by a lift-off technique to obtain metallic nano-electrodes. This standard method was optimized to reduce the electrode separation. As alternative approach a controlled electromigration process was developed to gradually break a previously defined metallic wire to yield two separated nano-electrodes. As third method a controlled electrochemical deposition process was implemented where metal was plated onto two well separated electrode templates while monitoring the conductance between them. Thereby the electrodes were gradually grown together until the monitor conductance reached a preset value.
Devices were fabricated by either preparing a sample with SOI quantum dots and patterning nano-electrodes on top or by using an insulating substrate, defining the nano-electrodes and chemically attaching the CdSe/ZnS QDs. On both types of samples lateral gate electrodes were included and the silicon substrate was used as a back gate. The devices obtained by these methods were then electrically characterized, which is the topic of chapter 5. The measurements were typically performed at cryogenic temperatures and an electronic measurement setup had to be assembled to measure in the picoampere range and to record differential conductance traces. The I-V characteristic of samples based on SOI quantum dots was measured and compared to orthodox theory calculations. Also gate-dependent measurements were performed to show the devices’ single-electron transistor properties. CdSe/ZnS-QD based devices were measured by similar means, but with the aim to reveal information about the electronic structure of the quantum dots.
2. Transport in nanostructures

As outlined in the previous chapter, future electronic devices will be based on nano-objects. Therefore it is important to understand the electronic transport in such nanostructures. In this chapter the theories necessary to understand and discuss the results of the following experiments is compiled and reviewed.

In macroscopic systems the transport is said to be diffusive and is well described by the Boltzmann transport equation (BTE), which will be treated in the first section of this chapter. In these systems the geometric dimensions are much larger than the mean free path of electrons between scattering events such that one averages over single scatterers. In this regime it is possible to define the conductance of a structure \( G = I/V \), which states how much current is passed through the whole device at a given voltage. One can also define a quantity referred to as conductivity \( \sigma = J/E \), which relates the current density to the applied field at a specific point in the structure.

If the system size is smaller than the mean free path, the transport is called ballistic as electrons may pass through the system without being scattered on impurities. In this ballistic regime only the conductance \( G \) is of importance as a conductivity can not be defined. As it is no longer possible to average over scattering events, a new treatment of the transport properties is needed, which is introduced in section 2.2.

In ballistic junctions the two reservoirs are connected by only a narrow conducting region. If this connection is now removed and the reservoirs are separated by a more or less thin barrier, no classical transport is possible. In this regime quantum mechanical tunneling is responsible for the electron transport, which is caused by the non-vanishing wave functions within the barrier and on the other side. This is discussed in section 2.3.

If tunneling occurs from a reservoir to a very small conducting island, the capacitance of the island may be so small that charging it with just one electron exceeds thermal energy. In this case a voltage corresponding to this Coulomb charging energy has to be applied to charge the island. This is called the single-electron tunneling effect and will be explained in section 2.4. It gives rise to a whole new class of single-electron devices.

Quantum dots are important building blocks for future nano-electronic devices. Therefore their transport properties are also discussed. Due to the spacial confinement, electrons and holes may only occupy discrete energy levels. If a quantum dot is now coupled to two reservoirs via tunneling barriers, these energy levels together with
2. Transport in nanostructures

the Coulomb charging energy determine the transport through the structure, as we
will see in section 2.5.

In the case of magnetic electrodes the story becomes even more complicated. Due to
the Zeeman splitting one carrier type (spin up or spin down) is energetically preferred
depending on the magnetization. As shown in section 2.6 the transmission through a
ferromagnetic nanostructure also depends on the orientation of its magnetization.

2.1. Diffusive transport regime

In the diffusive transport regime electrons are scattered by impurities when moving
through the structure. In the very simple approach of the Drude model this scattering
is accounted for by a friction term in the equation of motion, which is proportional
to the inverse scattering time \( \frac{1}{\tau} \). A more sophisticated model is provided by the
Boltzmann transport equation, which describes the evolution of a distribution function
and includes the scattering via a specific integral. As an approximation, this integral
can again be expressed in terms of the scattering or relaxation time.

2.1.1. Drude model

The Drude model was developed by Paul Drude in the 1900s and treats electrons as a
non-interacting electron gas of density \( n \). If an electric field \( E \) is applied, the electrons
are accelerated in the field direction and their motion is damped by a frictional force
due to collisions with impurities. This is accounted for by a momentum relaxation
time \( \tau \). For the average velocity one can write down the following kinetic equation
\[ m \frac{d}{dt} \langle v \rangle = -eE - \frac{m}{\tau} \langle v \rangle. \]

For the steady state the time derivative is zero and the average velocity \( \langle v \rangle \) becomes

\[ \langle v \rangle = -\frac{e\tau}{m} E = -\mu E \]

with \( \mu \) being the mobility of the carriers. With the charge carrier density \( n \) the
current density \( J \) can be calculated to

\[ J = -en\langle v \rangle = \frac{ne^2\tau}{m} E = \sigma E \]

which is the continuum form of Ohm’s law. From this we see that the conductivity \( \sigma \)
is proportional to the relaxation time \( \tau \). It is important to note that not all electrons
in a material may contribute to this conductivity. Due to Pauli’s exclusion principle
2.1. Diffusive transport regime

Electrons require unoccupied states nearby to gain energy from the field, and consequently only those electrons with energies close to the Fermi level \( E_F \) participate in transport. This is captured by the Einstein relation

\[
\sigma = e^2 g(E_F) D = e^2 g(E_F) \frac{\mu k_B T}{e} = g(E_F) k_B T \frac{e^2 \tau}{m}
\]

where \( g(E_F) \) denotes the density of states (DOS) at the Fermi energy and \( D \) the diffusion constant. Comparison with equation 2.1 shows that \( g(E_F) k_B T \) corresponds to an effective carrier density.

Of course the Drude model is only a very simple picture and does not capture all effects present in a real conductor. In particular, \( \tau \) is generally a function of the velocity.

2.1.2. Boltzmann transport equation

A more appropriate transport theory is the semi-classical Boltzmann equation, which describes the time evolution of a distribution function characterizing the carriers of the system [57]. It is based on the assumption that even under non-equilibrium conditions a local equilibrium can be defined for areas large compared to the atomic scale and the Fermi wavelength. This implies that the structures which can be treated by this theory must have potentials which vary smoothly on the atomic scale.

In a material the charge carriers may be described by a distribution function \( f \), which among \( k \) may in general also depend on the position \( r \) and the time \( t \). In equilibrium this function is the well-know Fermi-Dirac distribution:

\[
f(k) = \frac{1}{e^{(E(k)-\mu)/kT} + 1}
\]

Under non-equilibrium conditions the distribution function will deviate from the Fermi distribution and it will change with time due to applied fields and scattering processes. Observing how electrons in some test volume evolve from the time \( t - dt \) to \( t \), we see that carriers in this volume will move from \( r - v(k) dt \) to \( r \) and their wave vector will change from \( k - \frac{F}{\hbar} dt \) to \( k \). Here \( F \) is the force acting on the carriers. Therefore we can write for the distribution function

\[
f(r, k, t) = f \left( r - v(k) dt, k - \frac{F}{\hbar} dt, t - dt \right) + \left( \frac{\partial f}{\partial t} \right)_{\text{scatt}} dt
\]

where the last term was added to account for scattering processes.

As \( \left[ f(r, k, t) - f(r - v(k) dt, k - \frac{F}{\hbar} dt, t - dt) \right] / dt \) is the time derivative of \( f \), one can rewrite the above equation as
2. Transport in nanostructures

\[
\frac{\partial f}{\partial t}_{\text{scatt}} = \frac{df}{dt}_{\text{diff}} + \frac{\partial f}{\partial t}_{\text{force}} + \frac{\partial f}{\partial t}_{\text{scatt}}.
\]

Solving for \(\partial f/\partial t\) and substituting \(\frac{\partial \mathbf{r}}{\partial t} = \mathbf{v}\) and \(\frac{\partial \mathbf{k}}{\partial t} = \frac{e}{\hbar} \mathbf{E} + \mathbf{v} \times \mathbf{B}\) we obtain the Boltzmann transport equation (BTE):

\[
\frac{\partial f}{\partial t} = \left( \frac{\partial f}{\partial t} \right)_{\text{diff}} + \left( \frac{\partial f}{\partial t} \right)_{\text{force}} + \left( \frac{\partial f}{\partial t} \right)_{\text{scatt}}
\]

\[
= -\mathbf{v} \cdot \nabla \mathbf{r} f - \frac{e}{\hbar} \mathbf{E} \cdot \nabla \mathbf{k} f + \left( \frac{\partial f}{\partial t} \right)_{\text{scatt}}
\]

The first term on the right side describes the drift of carriers due a spacial gradient in their distribution, the second terms accounts for forces due applied fields and the last term is caused by scattering. For the steady state \(\partial f/\partial t = 0\) and the contribution due to diffusion, force and scattering have to compensate each other. In general, the scattering term is given by an integral over all final states \(\mathbf{k}_f\)

\[
\left( \frac{\partial f}{\partial t} \right)_{\text{scatt}} \propto \int d\mathbf{k}_f \left[ w_{\mathbf{k}_f \mathbf{k}_i} (1 - f(\mathbf{k}_i)) f(\mathbf{k}_f) - w_{\mathbf{k}_f \mathbf{k}_i} f(\mathbf{k}_i) (1 - f(\mathbf{k}_f)) \right]
\]

with the matrix elements \(w_{\mathbf{k}_f \mathbf{k}_i} \propto |\langle \mathbf{k}_f | H_{\text{scatt}} | \mathbf{k}_i \rangle|^2\), which results in an integro-differential equation. As this equation is mathematically quite complicate to handle, one very often uses the relaxation time approximation for the Boltzmann equation dealt with in the following section.

2.1.3. Relaxation time approximation

For the relaxation time approximation it is assumed that the rate at which the distribution function \(f\) is driven back to the equilibrium distribution \(f_0\) is proportional to its deviation from it. The proportionality constant is the inverse of the relaxation time \(\tau\).

\[
\left( \frac{\partial f}{\partial t} \right)_{\text{scatt}} = -\frac{f(\mathbf{k}) - f_0(\mathbf{k})}{\tau(\mathbf{k})}
\]

Here \(\tau\) can also depend on the position. If an external perturbation is switched off, the system exponentially relaxes into the equilibrium state with \(\tau\) being the corresponding time constant. By substituting this into the Boltzmann equation one obtains

\[
-\frac{e}{\hbar} \mathbf{E} \cdot \nabla \mathbf{k} f(\mathbf{k}) = -\frac{f(\mathbf{k}) - f_0(\mathbf{k})}{\tau(\mathbf{k})}
\]
\[ f(\mathbf{k}) = f_0(\mathbf{k}) + \frac{e}{\hbar} \tau(\mathbf{k}) \mathbf{E} \cdot \nabla_k f(\mathbf{k}) \]

for the steady state \( \frac{\partial f}{\partial t} = 0 \) in a homogeneous \( (\nabla f = 0) \) case without magnetic field. A first order approximation linear in \( \mathbf{E} \) for the solution of this differential equation can be found by inserting \( f_0 \) for \( f(\mathbf{k}) \) on the right hand side. The result can then be considered as an expansion of \( f_0(\mathbf{k}) \) around \( \mathbf{k} \).

\[ f(\mathbf{k}) \simeq f_0[\mathbf{k} + \frac{e}{\hbar} \tau(\mathbf{k}) \mathbf{E}] \]

The interpretation of this expression is that the Fermi distribution is shifted by \( \frac{e}{\hbar} \tau(\mathbf{k}) \mathbf{E} \) due to the applied electrical field. When the field is switched off, the shifted Fermi sphere relaxes back to its equilibrium position. The asymmetry in the distribution function induced by the electric field results in an electrical current. The corresponding conductivity can then be written as a tensor \( \hat{\sigma} \) of the following form

\[ \hat{\sigma} = \frac{e^2}{8\pi^3\hbar} \int_{E=E_F} \frac{\mathbf{v}(\mathbf{k}) \mathbf{v}(\mathbf{k})}{v(\mathbf{k})} \tau(\mathbf{k}) dS_F. \]

Even though the Boltzmann transport equation is a powerful tool to describe bulk systems, it is no longer valid if the dimensions of the structure under investigation become of the same order as the mean free path between scattering events. If this is the case, one can no longer average over individual scattering events and the boundaries of the system become increasingly important, as outlined in the next section.

### 2.2. Ballistic transport regime

As already mentioned, systems with sizes smaller than the mean free path are called ballistic as electrons pass through them without being scattered on impurities. In these structures electrons are primarily scattered at the system boundaries.

Mesoscopic systems may be categorized into different regimes by comparison with two characteristic length scales [4]. One is the mean free path of the electrons which corresponds to their scattering time \( (\Lambda = v_F \tau) \), the other is the Fermi wavelength \( \lambda_F = \frac{2\pi}{k_F} \).

- Systems with dimensions smaller than the mean free path, but still large compared to the Fermi wavelength. In this regime electrons can be regarded as moving on classical trajectories according to Newton’s laws of mechanics without being scattered. Hence, the systems can be considered classical ballistic.

- Systems with sizes comparable to the Fermi wavelength, which in metals is on
2. Transport in nanostructures

the order of a few angstroms. In this regime the wave properties of electrons are dominant and quantization effects may be observed. Therefore it could be called quantum ballistic.

Due to the fact that one can no longer average over scattering events and that the geometry essentially determines the transport properties, the Boltzmann equation is not adequate anymore to describe such systems. One formalism to treat mesoscopic systems was developed by Landauer \[70, 71\] and is discussed in the following section. Afterwards its application to quantum point contacts, which are systems in the quantum ballistic regime, is shown.

2.2.1. Landauer formula

The Landauer formula describes a scattering region which is attached to two reservoirs via ideal conducting leads where no scattering takes place (see figure 2.1). The reservoirs are characterized by their chemical potentials $\mu_1$ and $\mu_2$ corresponding to the electron densities and they randomize the phase and absorb the energy of injected carriers.

Following the derivation of Ferry and Goodnick \[39\], first the single-channel case, where only one subband is available, is examined. Afterwards the theory is extended to the multi-channel case.

![Figure 2.1: Sketch of a scattering structure with one conducting channel coupled to two reservoirs via ideal leads (following 39). At the top the respective chemical potentials are shown.](image)
2.2. Ballistic transport regime

Single-channel case

To calculate the number of electrons injected into the junction from the left and from the right side per unit time one has to multiply the density of states, their probability of being occupied $f$, the corresponding velocity $v$ and their transmission probability $T$ and integrate over all $k$. With the charge $e$ one obtains the following current for the 1D case:

$$I = \frac{2e}{2\pi} \left[ \int_{0}^{\infty} dk \ v(k) \ f_1(k) \ T(E) - \int_{0}^{\infty} dk' \ v(k') \ f_2(k') \ T(E') \right]$$

At low temperatures the Fermi distribution is very sharp and only electrons up to energy $\mu_1$ and $\mu_2$ are injected from the left and right respectively. If we now convert the $k$ integrals to energy integrals, we can combine the two terms.

$$I = \frac{2e}{2\pi} \left[ \int_{\mu_1}^{\mu_2} dE \left( \frac{dk}{dE} \right) v(k) f_1(k) T(E) - \int_{0}^{\mu_2} dE \left( \frac{dk'}{dE} \right) v(k') f_2(k') T(E') \right]$$

$$= \frac{2e}{2\pi \hbar} \int_{\mu_1}^{\mu_2} dE \ T(E)$$

As the velocity is $v = \frac{1}{\hbar} \frac{dE}{dk}$, it cancels out with the factor arising from the substitution of variables to the constant $1/\hbar$. If the applied bias and thus the difference in the chemical potentials $\mu_1 - \mu_2$ is small, the transmission coefficient $T$ can be assumed to be independent of energy. This allows us to evaluate the now trivial integral and the current becomes

$$I = \left( \frac{2e}{\hbar} \right) T (\mu_1 - \mu_2). \quad (2.2)$$

For the derivation we have used equilibrium distribution functions for the contacts, even though an applied bias voltage leads to non-equilibrium conditions. As a consequence there is a reduction in carrier concentration on the left side of the scattering region while there is a pile-up on right side due to transmission through the structure. As long as we are still in a linear response regime, we can account for the charge rearrangement by introducing average charge densities for the ideal leads to either side of the scatterer, which correspond to the Fermi levels $\mu_A$ and $\mu_B$ \[39\]. The potential drop $V$ across the scattering structure is then given by

$$eV = \mu_A - \mu_B < \mu_1 - \mu_2$$

By comparing the carrier densities in the ideal leads obtained from the near-equilibrium distributions $f_A$ and $f_B$ to the fluxes from the left and right reservoirs \[39\], the potential
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drop across the scattering structure can be deduced to \( \mu_A - \mu_B = (1 - T) (\mu_1 - \mu_2) \). Substituting this into equation 2.2, the expression for the current becomes

\[
I = \left( \frac{2e}{h} \right) \frac{T}{1 - T} (\mu_A - \mu_B) = \left( \frac{2e^2}{h} \right) \frac{T}{R} V
\]

which is known as the single-channel Landauer formula. It can also be expressed in terms of the conductance of the structure

\[
G = \frac{I}{V} = \left( \frac{2e^2}{h} \right) \frac{T}{1 - T} = \left( \frac{2e^2}{h} \right) \frac{T}{R}
\]

The above expression is valid for a 4-terminal measurement as it relates the current through the scattering structure with the voltage drop at the structure itself. If the voltage is measured through the same leads as the current is applied (2-terminal setup), the factor \((1 - T)\) is missing as the voltmeter shows not only the potential drop at the structure itself, but also the contact potential in the leads. This gives rise the following form of Landauer’s formula:

\[
G = \left( \frac{2e^2}{h} \right) T
\]

The conductance of a mesoscopic structure where only one channel is available is thus given by the transmission of this channel at the Fermi energy times the fundamental conductance \(2e^2/h\), which corresponds to a resistance of 12.9 kΩ.

**Multi-channel case**

Let us now consider the more complex case where several channels contribute to the conductance. In this case the wave functions on both sides of the scattering region are connected by a scattering matrix.

\[
S = \begin{pmatrix} r & t' \\ t & r' \end{pmatrix}
\]

Here \( r, r', t \) and \( t' \) represent submatrices of size \( N \times N \), where \( N \) is the number of modes. An incoming wave in mode \( j \) from the left side has probability \( T_{ij} = |t_{ij}|^2 \) to be transmitted into mode \( i \) on right side and the probability \( R_{ij} = |r_{ij}|^2 \) to be reflected back into mode \( i \) on the left side. Following the derivation for the single-channel case, carriers injected from mode \( j \) on the left side into mode \( i \) on the right side give rise to a current

\[
I_{ij} = \frac{2e}{h} T_{ij} (\mu_1 - \mu_2).
\]
Here \((\mu_1 - \mu_2)\) is again the potential drop between the two reservoirs. Such a pair of modes \(i\) and \(j\) can be interpreted as a single channel. To get the overall current through the structure one has to sum over all possible channels, thus over all combinations \(i, j\).

\[
I = \sum_{i,j} I_{ij} = \frac{2e}{h} (\mu_1 - \mu_2) \sum_{i,j} T_{ji} = \frac{2e}{h} (\mu_1 - \mu_2) \sum_{i=1}^{N} T_{i} = \frac{2e}{h} (\mu_1 - \mu_2) \text{Tr}(tt^\dagger)
\]

This is Landauer’s formula for the multi-channel case. As in the last section, we can express it in terms of the conductance measured with a two-terminal setup. Therefore the current has to be divided by the voltage drop \(V = (\mu_1 - \mu_2)/e\) across the two reservoirs.

\[
G = \frac{2e^2}{h} \sum_{i,j} T_{ji} = \frac{2e^2}{h} \sum_{i=1}^{N} T_{i} = \frac{2e^2}{h} \text{Tr}(tt^\dagger)
\]

This formula will be applied to describe the transport properties of quantum point contacts in the following section.

### 2.2.2. Quantum point contacts

Quantum point contacts (QPCs) are one of the most prominent examples where the model developed by Landauer and Büttiker can be applied. They were first discovered experimentally in 1988 by two independent groups from Britain [126] and the Netherlands [124] using a split-gate setup on top of GaAs/AlGaAs 2D electron gas (2DEG). The split-gates separate two reservoirs and leave a void of just a few hundred nanometers. When a negative voltage is applied, the 2DEG is depleted below the gates where the region of influence depends on the applied voltage. Thereby the quantum channel that the carriers have to pass can be adjusted very accurately by tuning the gate voltage. In the experiments the low temperature conductance versus gate voltage showed plateaus at integer multiples of the conductance quantum \(G_0 = 2e^2/h\).

The interpretation of these results was that the electron waves are laterally confined at the constriction of the 2DEG as schematically shown in figure 2.2. As a consequence only waves matching the boundary conditions are allowed. These so-called lateral subbands or modes only contribute to the conductance if their confinement energy is located below the Fermi level. This gives rise to a distinct number of conduction channels depending on the width of the constriction, and thus on the applied gate voltage.

Let us now calculate the conductance of such a QPC. Therefore we assume that
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scattering between different modes is weak ($T_{ij} \simeq 0$ for $i \neq j$) and the transmission within one mode is close to unity ($T_{ij} \simeq 1$ for $i = j$). With these assumptions the double sum in Landauer’s formula can be evaluated and the conductance of the QPC becomes

$$G = \frac{2e^2}{h} \sum_{i,j} T_{ji} = \frac{2e^2}{h} \sum_i T_{ii} = \frac{2e^2}{h} N$$

where $N$ is the number of contributing modes. One can see that the total conductance of a QPC is just the conductance quantum multiplied by the number of modes lying below the Fermi energy. As the gate voltage is made more negative, the confinement of the electrons is increased and less modes fall below the Fermi level. This phenomenon is called conductance quantization.

Later, conductance quantization was also shown in metallic QPCs fabricated using mechanically controllable break junctions [1]. It is important to note that not only the mean free path and the phase coherence length have to be larger than the system dimensions, but also the Fermi wavelength has to be comparable to the constriction width for confinement to be effective. In semiconductors the Fermi wavelength is on the order of a few tenth of nanometers whereas in metals it is only a few angstroms. This means that in a metallic QPC only a few atoms are connecting the two reservoirs.

2.3. Tunneling regime

Now we take a look at a system where the narrow channel connecting the two reservoirs is completely closed so that they are separated by a potential barrier. In the classical picture a particle can not penetrate a barrier with a higher potential than its total
energy. In such a case a classical particle is always reflected. A quantum mechanical wave function, however, does not completely vanish inside a barrier unless the barrier is infinitely high, but decays exponentially into it. If the barrier is thin enough, some of the amplitude of the wave function is still present at the other side of the barrier. As the absolute square of the wave function corresponds to the probability to find the particle in the corresponding position, there is a non-vanishing probability for it to reach the other side of the barrier. This process is referred to as quantum mechanical tunneling.

The above situation is well described by Schrödinger’s equation, which has to be solved for either side of the barrier and the barrier itself and the solutions have to be matched at the boundaries (done for a rectangular barrier in section 2.3.1). In section 2.3.2 this is extended to arbitrarily shaped barrier using a Wentzel-Kramers-Brillouin (WKB) approximation resulting in the so-called Simmons formula. Finally, an alternative many-particle approach is introduced in section 2.3.3 which will allow us later to express tunneling rates from one mode on the initial side to another mode on the final side in terms of Fermi’s golden rule.

### 2.3.1. Tunneling through a rectangular barrier

Let us first consider a planar symmetric rectangular barrier as sketched in figure 2.3. Taking an independent electron approach we can describe the electron by the 1D Schrödinger equation

\[
\left( -\frac{\hbar^2}{2m^*} \frac{1}{m^*(z)} \frac{\partial}{\partial z} + V_{\text{eff}}(z) \right) \varphi(z) = E \varphi(z).
\]

The effective mass \( m^* \) may be different for the barrier region and the potential is \( V_0 \) for the barrier and 0 elsewhere.

\[
V_{\text{eff}} = \begin{cases} 
0 & z < -a \\
V_0 & -a \leq z \leq a \\
0 & z > a 
\end{cases}
\]

The Schrödinger equation can be solved piecewise and results in a wave function

\[
\varphi(z) = \begin{cases} 
Ae^{ikz} + Be^{-ikz} & z < -a \\
Ce^{\gamma z} + De^{-\gamma z} & -a < z < a \\
Ee^{ikz} + Fe^{-ikz} & z > a 
\end{cases}
\]
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Figure 2.3.: Model for a symmetrical rectangular tunneling barrier.

with \( k = \sqrt{\frac{2m^*E}{\hbar}} \) and \( \gamma = \sqrt{\frac{2m^*(V_0-E)}{\hbar}} \). For the solution on either side of the barrier we obtain plane waves, whereas the wave function within the barrier has an exponentially decaying form. The coefficients \( A \) and \( B \) correspond to the amplitude of incident and outgoing waves from the left, while \( E \) and \( F \) to respective waves from the right.

At the boundaries \(-a\) and \(a\) the wave function \( \varphi \) and its derivative have to be continuous, which gives rise to the following set of boundary conditions.

\[
\varphi_L(\pm a) = \varphi_R(\pm a)
\]

\[
\frac{1}{m_L^*} \partial \varphi_L \bigg|_{\pm a} = \frac{1}{m_R^*} \partial \varphi_R \bigg|_{\pm a}
\]

Matching the coefficients \( A \) to \( D \) at boundary \(-a\) results in a set of two equations

\[
A e^{-ika} + Be^{ika} = Ce^{-\gamma a} + De^{\gamma a}
\]

\[
 ik \left( A e^{-ika} + B e^{ika} \right) = \gamma \left( C e^{-\gamma a} + D e^{\gamma a} \right)
\]

which can be written in a matrix formulation.

\[
\begin{pmatrix}
A \\
B
\end{pmatrix}
= 
\begin{pmatrix}
\left( \frac{ik+\gamma}{2\gamma} \right) e^{(ik-\gamma)a} & \left( \frac{ik-\gamma}{2ik} \right) e^{-(ik+\gamma)a} \\
\left( \frac{ik-\gamma}{2ik} \right) e^{-\left(ik+\gamma\right)a} & \left( \frac{ik+\gamma}{2\gamma} \right) e^{-(ik-\gamma)a}
\end{pmatrix}
\begin{pmatrix}
C \\
D
\end{pmatrix} \tag{2.3}
\]

Analog, a matrix equation relating \( \begin{pmatrix} C \\ D \end{pmatrix} \) to \( \begin{pmatrix} E \\ F \end{pmatrix} \) can be derived.

\[
\begin{pmatrix}
C \\
D
\end{pmatrix}
= 
\begin{pmatrix}
\left( \frac{ik+\gamma}{2\gamma} \right) e^{(ik-\gamma)a} & -\left( \frac{ik-\gamma}{2ik} \right) e^{-(ik+\gamma)a} \\
-\left( \frac{ik-\gamma}{2ik} \right) e^{\left(ik+\gamma\right)a} & \left( \frac{ik+\gamma}{2\gamma} \right) e^{-(ik-\gamma)a}
\end{pmatrix}
\begin{pmatrix}
E \\
F
\end{pmatrix} \tag{2.4}
\]
2.3. Tunneling regime

Substituting the right side of equation (2.4) into (2.3) we obtain an overall matrix equation relating the wave amplitudes from the left to those from right side of the barrier.

\[
\begin{pmatrix}
A \\
B
\end{pmatrix} = \begin{pmatrix}
M_{11} & M_{12} \\
M_{21} & M_{22}
\end{pmatrix} \begin{pmatrix}
E \\
F
\end{pmatrix}
\]

(2.5)

\[
M_{11} = \left( \cosh(2\gamma a) - \frac{i}{2} \left( \frac{k^2 - \gamma^2}{k\gamma} \right) \sinh(2\gamma a) \right) e^{2ika}
\]

\[
M_{21} = -\frac{i}{2} \left( \frac{k^2 + \gamma^2}{k\gamma} \right) \sinh(2\gamma a)
\]

\[
M_{22} = M_{11}^* \quad M_{12} = M_{21}^*
\]

The transmission coefficient \( T \) is now defined as ratio of absolute squares of the outgoing amplitude on the right \( E \) and the incoming amplitude from the left \( A \). Expressing \( A \) and \( E \) by the above equations one obtains an energy dependent transmission coefficient of the form

\[
T(E) = \frac{|E|^2}{|A|^2} = \frac{1}{|M_{11}|^2} = \frac{1}{1 + \left( \frac{k^2 + \gamma^2}{2k\gamma} \right)^2 \sinh^2(2\gamma a)}.
\]

Figure 2.4 shows the transmission coefficient plotted over energy normalized to the barrier height. For energies far below the barrier height, the transmission is basically zero. At energies close to but still below the barrier height, the transmission sets in. This is referred to as quantum mechanical tunneling as it would classically not be allowed. For energies above \( V_0 \), the transmission oscillates and approaches one. This oscillation also has no classical analogon.

For sufficiently thick barriers the transmission coefficient simplifies to

\[
T(E) \rightarrow \left( \frac{4k\gamma}{k^2 + \gamma^2} \right)^2 e^{-4\gamma a} \propto e^{-2w\sqrt{2m^*(V_0-E)/\hbar}}
\]

(2.6)

where \( w \) is the width of the barrier. We can see that the transmission decreases exponentially with barrier width and with the square root of the barrier height. This simplified expression is later used to derive the transmission coefficient for an arbitrarily shaped barrier.

Furthermore, equation 2.5 can be converted into a scattering matrix form, where a
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matrix relates the incoming waves to the outgoing waves.

\[
\begin{pmatrix}
B \\
E
\end{pmatrix} = 
\begin{pmatrix}
S_{11} & S_{12} \\
S_{21} & S_{22}
\end{pmatrix} 
\begin{pmatrix}
A \\
F
\end{pmatrix} = 
\begin{pmatrix}
r & t' \\
t & r'
\end{pmatrix} 
\begin{pmatrix}
A \\
F
\end{pmatrix} = S 
\begin{pmatrix}
A \\
F
\end{pmatrix}
\]

(2.7)

Again A and F correspond to the incident waves on the barrier and B and E to the scattered, outgoing waves. This formulation is compatible with the Landauer formula from section 2.2.1 and S is again called scattering matrix.

2.3.2. Tunneling through an arbitrary barrier - Simmons formula

In the last section we have analyzed tunneling through a symmetrical, rectangular barrier. In reality this condition is rarely met as the system becomes asymmetric as soon as a voltage is applied and the shape of the barrier is no longer rectangular. For this reason we want to extend the above considerations to tunneling through arbitrary barriers, e.g. a triangular shaped one [107].

For this purpose we first apply the Wentzel-Kramers-Brillouin (WKB) approximation. Therefore the arbitrary barrier is divided into N slices, which are then substituted by rectangular barriers as sketched in figure 2.5. The transmission through one of these slabs is approximately given by equation 2.6 and the overall transmission is obtained by summing over all slices in the exponent. Letting N go to infinity this sum becomes
2.3. Tunneling regime

Figure 2.5.: Schematic illustration of an arbitrary barrier and its WKB approximation.

an integral over the barrier width and the tunneling probability takes the form

\[ T(E_x) = \exp \left( -\frac{4\pi}{\hbar} \int_{s_1}^{s_2} \sqrt{2m (V(x) - E_x)} dx \right) \]  (2.8)

with \( E_x = \frac{1}{2}mv_x^2 \) being the energy component in \( x \) direction. The number of electrons tunneling from electrode 1 to 2 can be written as

\[ N_1 = \int_0^{v_m} v_x n(v_x) T(E_x) dv_x = \ldots = \frac{4\pi m^2}{h^3} \int_0^{E_m} T(E_x)dE_x \int_0^\infty f(E)dE_r \]

where \( n(v_x) dv_x \) is the number of electrons per unit volume with a velocity between \( v_x \) and \( v_x + dv_x \). The carrier density \( n \) can be extracted from Fermi-Dirac statistics.

Next, polar coordinates were introduced to separate \( E_x \) from \( E_r = \frac{1}{2} m (v_y^2 + v_z^2) \). The number of electrons \( N_2 \) tunneling the other way round can be deduced in the same manner and the net number of electrons passing the barrier is

\[ N = N_1 - N_2 = \int_0^{E_m} T(E_x)dE_x \left[ \frac{4\pi m^2}{h^3} \int_0^\infty (f(E) - f(E + eV)) dE_r \right] . \]

Multiplying by the electron charge \( e \) we get the corresponding current density

\[ J = \int_0^{E_m} T(E_x)\xi dE_x = J_0 \left[ \overline{\varphi} \exp \left( -A \sqrt{\varphi} \right) - (\overline{\varphi} + eV) \exp \left( -A \sqrt{\varphi + eV} \right) \right] \]  (2.9)

with \( J_0 = e/2\pi \hbar (\beta \Delta s)^2 \), \( A = \frac{4\pi \beta \Delta s}{\hbar} \sqrt{2m} \) and \( \overline{\varphi} = \frac{1}{\Delta s} \int_{s_1}^{s_2} \varphi(x)dx \) being the mean barrier height above the Fermi level. To obtain the right hand side of equation 2.9 first the integral in equation 2.8 has to be evaluated and then the left expression of eq. 2.9 can be integrated (for details see [107]). The formula is known as Simmons formula for
the current density through an arbitrarily shaped barrier.

In eq. 2.9 the term \( J_0 \phi \exp(-A\sqrt{\phi}) \) corresponds to the current density flowing from electrode 1 to 2, while \( J_0 (\phi + eV) \exp(-A\sqrt{\phi} + eV) \) is the current density in the opposite direction. At \( V = 0 \) a state of dynamic equilibrium is reached where the two currents compensate each other. The model basically substitutes an arbitrarily shaped barrier with an effective rectangular barrier with the same transport properties as sketched in figure 2.6. For very low voltages the junction can be described like an Ohmic resistance.

\[
J = \frac{\sqrt{2m\phi} e^2}{\Delta s h^2} e^{-A\sqrt{\phi}} V
\]

A very important case where equation 2.9 can be applied is the triangular barrier. Here the barrier width at the Fermi level is the absolute width \( \Delta s = s \), the average barrier height above \( E_F \) is \( \phi = (\phi - eV/2) \) and \( \beta \approx 1 \). This yields a symmetric expression for the current density through such a tunnel junction.

\[
J = \frac{e}{2\pi h s^2} \left[ \left( \phi - \frac{eV}{2} \right) \exp \left( -\frac{4\pi s}{h} \sqrt{2m \left( \phi - \frac{eV}{2} \right)} \right) \right. \\
\left. - \left( \phi + \frac{eV}{2} \right) \exp \left( -\frac{4\pi s}{h} \sqrt{2m \left( \phi + \frac{eV}{2} \right)} \right) \right]
\]

This is Simmons formula for a triangular barrier at intermediate bias voltages. It is plotted in figure 2.7 for different values of \( \phi \) and \( s \). The two diagrams show that both parameters influence the shape of the curve in a similar way.

The formula is used to fit measured I-V curves and characterize tunnel junctions.

![Figure 2.6: Schematic illustration of real and effective tunneling barrier for an arbitrary shape and for a triangular barrier.](image-url)
Figure 2.7.: Simmons formula plotted for different values of the barrier width (left) and the barrier height (right). The current is normalized for the curves to be illustrated in one plot.

later on in this work. The disadvantages of this model are that it is strictly valid only for a 1D configuration and that it does not account for an energy dependent density of states, which is e.g. present in semiconductor quantum dots.

2.3.3. Transfer Hamiltonian method

The approach discussed in the previous sections is based on a single Schrödinger equation for a single wave function defined on either side of the tunneling barrier. An alternative approach was taken by Bardeen [14], where the two electrodes are treated as quasi separated systems with their own Hamiltonians $H_L$ and $H_R$ and the corresponding eigenstates $\psi_L$ and $\psi_R$, as depicted in figure 2.8.

Figure 2.8.: Illustration of the separated eigenstates in the left and right reservoir and their interaction within the tunneling barrier.
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The two systems are then coupled by introducing a weak perturbation with a corresponding Hamiltonian $H_T$, which is called transfer-Hamiltonian. With this the overall system can be described by the following Hamiltonian:

$$H = H_L + H_R + H_T$$

$H_L$ and $H_R$ can be written in second quantization [35, 39]

$$H_{LR} = \sum_{k_{LR}} E_{k_{LR}} c_{k_{LR}}^{\dagger} c_{k_{LR}}$$

where $c_{k_{LR}}^{\dagger} c_{k_{LR}}$ represents the number operator and $E_{k_{LR}}$ the corresponding energy eigenvalue. The tunneling Hamiltonian $H_T$ can be expressed as

$$H_T = \sum_{k_{LR},k_{LR}} T_{k_{LR},k_{LR}} c_{k_{LR}}^{\dagger} c_{k_{LR}} + \sum_{k_{LR},k_{LR}} T_{k_{LR},k_{LR}} c_{k_{LR}}^{\dagger} c_{k_{LR}}.$$

In the first term an electron is annihilated on the right side while one is created on the left side and in the second term vice versa. $T_{k_{LR},k_{LR}} = \langle k_{LR} | H_T | k_{LR} \rangle$ is the matrix element connecting a state $k_{LR}$ on the left to a state $k_{LR}$ on the right side. The tunneling rate from a state $k_{LR}$ on the left into a state $k_{LR}$ on the right is calculated using Fermi’s golden rule

$$\Gamma_{k_{LR} \rightarrow k_{LR}}^+ = \frac{2\pi}{\hbar} |T_{k_{LR},k_{LR}}|^2 f(E_L) [1 - f(E_R)] \delta(E_L - E_R)$$

where $f(E)$ is the Fermi function and the $\delta$-function takes care of energy conservation. Summing over all states and going from wave vectors to energies by introducing the density of states $D(E)$, the total tunneling rate from left to right becomes

$$\Gamma^+ = \frac{2\pi}{\hbar} |T|^2 \int_{E_{CL}}^\infty dE_L \int_{E_{CR}}^\infty dE_R D_L(E_L) D_R(E_R) f(E_L) [1 - f(E_R)] \delta(E_L - E_R).$$

The tunneling rate from right to left $\Gamma^-$ is obtained analogously. To get the total current through the tunnel junction one has to balance $\Gamma^+$ and $\Gamma^-$ and multiply with the elementary charge $e$.

$$I = e (\Gamma^+ - \Gamma^-)$$

This model yields similar results as the coherent, independent electron model, especially for thick and high barriers [35]. Beyond that, it will be very useful in the following sections to calculate the current through single-electron devices. Further-
2.4. Single-electron tunneling

The quantum mechanical tunneling effect discussed in the last section causes another effect called single-electron tunneling. The reason for this effect is that tunneling can be regarded as a “Boolean” process compared to normal conduction, where an arbitrary charge can flow through an imaginary section of a conductor. If we take a look at a tunnel junction, one electron has either tunneled through it or not. As a consequence, current is passed through a tunneling barrier like drops coming from a water tap. This was first theoretically considered by Likharev \[76\] in 1988, while the experimental verification of single-electron tunneling through a single barrier is extremely difficult to achieve, as the junction is always shunted by stray capacitances which smooth out small current fluctuations.

Technically more relevant is single-electron tunneling through a double barrier configuration, which can be realized by coupling a conducting island to two electrodes via tunneling barriers (see figure 2.9). If the size of the island and with it its capacitance is small enough, the energy needed to charge it with just one single electron exceed thermal energy. As electrons can tunnel onto the island only as a whole and thus charge the island, tunneling is blocked. This is called the Coulomb blockade.

In section 2.4.1 this phenomenon will be discussed qualitatively by an electrostatical analysis of the corresponding equivalent circuit. This will tell us under which conditions current can pass through such a single-electron device. To quantitatively describe the amount of current the so-called orthodox theory is employed in section 2.4.2. Finally, the co-tunneling process will be discussed in section 2.4.3, which is a higher order transport mechanism that allows current flow even within the Coulomb blockade regime.

2.4.1. The single-electron transistor

As we have already heard, transport through a small island tunneling coupled to a source and a drain electrode is suppressed at low temperatures due to Coulomb blockade. By attaching a third gate electrode, which is only capacitively coupled to the island, one can shift the island potential and thus switch the device from a non-conducting to a conducting state. Such a device is referred to as single-electron transistor and is sketched in figure 2.9.

To analyze the transport properties of a single-electron transistor it is useful to derive
its equivalent circuit shown in figure 2.9. The two symbols on the top represent the
two tunnel junctions with their corresponding capacitances \( C_{1,2} \) and their tunneling
resistances \( R_{T1,2} \). The black circle symbolizes the conductive island.

From the equivalent circuit we obtain the charges stored in the capacitors of the
tunnel junctions \( Q_1 = C_1V_1 \), \( Q_2 = C_2V_2 \) and the charge on the gate capacitance
\( Q_G = C_G(V_G - V_2) \). Following the notation of \([39]\) we can write the total charge on
the island as

\[
Q = Q_2 - Q_1 - Q_G = -ne + Q_P
\]

where \( n \) is the number of excess electrons on the island and \( Q_P \) is the so-called
background polarization charge. By combining these expressions and solving for \( V_1 \)
and \( V_2 \), respectively, one obtains the voltage drop across tunnel junction 1 and 2.

\[
V_1 = \frac{1}{C_{\Sigma}} \left[ (C_G + C_2)V - C_GV_G + ne - Q_P \right]
\]

\[
V_2 = \frac{1}{C_{\Sigma}} \left[ C_1V + C_GV_G - ne + Q_P \right]
\]

Here \( C_{\Sigma} = C_1 + C_2 + C_G \) is the overall capacitance of the island. Now we can calculate
the total electrostatic energy stored in the three capacitors of the equivalent circuit by
multiplying each capacitance \( \frac{C_i}{2} \) with the square of the corresponding voltage and sum
them up.

\[
E_S = \frac{1}{2C_{\Sigma}} \left[ C_GC_1(V - V_G)^2 + C_1C_2V^2 + C_GC_2V_G^2 + Q^2 \right]
\]
2.4. Single-electron tunneling

To draw an energy balance we also have to consider the work performed by the voltage sources in moving charges to and from the island. This can be done by evaluating the time integral over the delivered power.

\[ W_S = \int VI(t) \, dt = V \Delta Q \]

The total work needed to transfer \( n_2 \) electrons through tunnel junction 2 is

\[ W_S(n_2) = -n_2 \left[ \frac{C_1}{C_\Sigma} eV + \frac{C_G}{C_\Sigma} eV_G \right]. \]

It is important to note that here also the work performed by the gate voltage source and the charges loaded onto the gate capacitor are included. Similarly the work needed to pass \( n_1 \) electrons through junction 1 can be derived.

\[ W_S(n_1) = -n_1 \left[ \frac{C_2}{C_\Sigma} eV + \frac{C_G}{C_\Sigma} e(V - V_G) \right]. \]

The total energy of the system is obtained from the electrostatic energy minus the work done by the sources \( E = E_S - W_S \). The change in total energy caused by a tunneling event through either junction can now be determined to

\[ \Delta E_{\pm 1} = E(n_1, n_2) - E(n_1 \pm 1, n_2) \]
\[ = \frac{e}{C_\Sigma} \left( -\frac{e}{2} \mp [en - Q_P + (C_G + C_2) V - C_G V_G] \right). \]
\[ \Delta E_{\pm 2} = E(n_1, n_2) - E(n_1, n_2 \pm 1) \]
\[ = \frac{e}{C_\Sigma} \left( -\frac{e}{2} \pm [en - Q_P - C_1 V - C_G V_G] \right). \]  \hspace{1cm} (2.11)

At 0 K temperature it is required that \( \Delta E_{\pm i} > 0 \) for the corresponding tunneling event to take place. If no gate voltage is applied and \( Q_P \) is zero, this leads to a current suppression until the bias voltage exceeds the threshold value \( |V| > \frac{e}{C_\Sigma} \). This threshold voltage corresponds to the Coulomb energy needed to charge the island with one electron and the effect is referred to as Coulomb blockade. When the bias voltage is increased over this threshold, the current rises in a step-like fashion as more and more electrons can be simultaneously loaded onto the island. This corresponds to an opening of new independent transport channels and results in a step-like I-V curve known as Coulomb staircase. A schematic I-V trace is depicted in figure 2.10.

In a band diagram illustration (figure 2.11) the Coulomb charging energy can be seen as a gap in the available states on the island. At 0 V bias the Fermi levels of the leads lie both within this gap and only when the applied voltage is large enough that the
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Figure 2.10.: Schematic illustration of the I-V curve of an asymmetric double barrier system showing Coulomb blockade around 0 V bias and a Coulomb staircase at higher voltages.

two Fermi levels enclose the next available state, current can flow through the device.

Figure 2.11.: Band diagram illustration of a double barrier system without bias voltage (left) where Coulomb blockade is present and with a bias larger than the Coulomb voltage (right).

When the bias voltage is kept constant at a value below $V_T$ or at 0 V and the gate voltage is varied, the potential in the island is electrostatically shifted. As soon as a state in the island aligns with the Fermi levels of source and drain, tunneling sets in and the conductance shows a maximum as depicted in figure 2.12. The distance between two neighboring peaks is $e/C_G$ and therefore inverse to the coupling of the gate electrode.
The gate voltage labeled with $A$ in figure 2.12 corresponds to the left band diagram illustration in figure 2.13, where the Fermi levels of source and drain lie between two states of the island within the gap caused by the Coulomb blockade effect. Gate voltage $B$ is sketched by the right band diagram and here one state in the island is aligned to the levels of the electrodes such that tunneling is permitted.

Figure 2.12.: Schematic illustration of the SET conductance as a function of gate voltage showing Coulomb oscillations.

Figure 2.13.: Band diagram illustration showing the gate voltage dependence of the SET conductance. On the left both Fermi levels are situated between two island levels and tunneling is prohibited due to the Coulomb blockade, while on the right one island level is aligned to the Fermi levels and electrons may tunnel resonantly.

When I-V curves for different gate voltages are collected and their derivatives plotted
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in a 2D color plot, one obtains the so-called stability diagram, which is sketched in figure 2.14. The dark areas are referred to as Coulomb diamonds and correspond to a stable configuration of the device where the number of electrons on the island is constant and no current can flow.

![Stability Diagram](image)

Figure 2.14.: Schematic illustration of the stability diagram for a SET. The dark areas correspond to a suppressed conduction due to Coulomb blockade and are called Coulomb diamonds.

The above considerations were only qualitative in a sense that this model only allows us to determine at which voltages current flow should set in, but it is not capable to calculate realistic I-V curves. For a more quantitative analysis of the current flowing through a single electron device, the so-called orthodox theory is introduced in the next section. During its derivation we will rely on the expressions for energy differences corresponding to single tunnel events (equations 2.11) we have deduced in this section.

2.4.2. Orthodox theory

The orthodox theory of single-electron tunneling was developed by Averin and Likharev [7, 76] and its aim is to derive a kinetic equation for the distribution function describing the charge state of the system. With knowledge of the distribution function it is possible to calculate e.g. the current through the system. Following the derivation of [39], the transfer Hamiltonian method is used to describe tunneling through the barriers, which was already introduced in section 2.3.3. Using equation 2.10 for the case of a double barrier system, the tunneling rate through junction $j$ is given by

$$\Gamma_j^\pm = \frac{2\pi}{\hbar} \sum_{k_i,k_f} |T_{ij}|^2 f(E_i) \left[ 1 - f(E_f) \right] \delta \left( E_i - E_f + \Delta E_j^\pm \right) .$$
2.4. Single-electron tunneling

Here \( k_i \) stands for the initial and \( k_f \) for the final state, respectively. The \( \delta \)-function accounts for the change in total energy \( \Delta E_j^\pm \) due to the tunneling event, which was discussed in section 2.4. By summing over all combinations of initial and final states the overall rate through the junction is obtained.

The sums over \( k_i \) and \( k_f \) can be converted into integrals over \( E \) by introducing the density of states \( D(E) \) for the corresponding sides of the junction. If we assume a weak energy dependence of the tunneling matrix element \( T \) and the density of states \( D \), we can take them both outside of the integrals. Furthermore the delta function reduces the two integrals to one and the tunneling rate through junction \( j \) becomes

\[
\Gamma_j^\pm(V) = \frac{2\pi e}{\hbar} |T|^2 D_{jL} D_{jR} \int_{E_{Cm}}^{\infty} dE f(E) \left[ 1 - f(E + \Delta E_j^\pm) \right].
\]

By inserting the Fermi function the integration can be performed analytically.

\[
\Gamma_j^\pm(V) = \frac{1}{e^{2R_{ij}}} \frac{\Delta E_j^\pm}{1 - e^{-\Delta E_j^\pm/k_BT}}
\]

It is important to note that \( \Delta E_j^\pm \) is of course depending on the number of charges on the island as can be seen from equation \[2.11\]. On the other hand, the tunneling rate \( \Gamma \) in turn influences the charge distribution on the island.

To analyze this situation a distribution function \( \rho(n,t) \) for the charge state of the island is introduced. It represents the probability to find the system in a state with \( n \) charges at a given time \( t \). The change of one charge state of the island depends on the tunneling rates bringing the system from a different state into that particular state and on the rates bringing it out-of the state. Thus the time derivative of the distribution function \( \partial \rho/\partial t \) can be written as a function of the corresponding tunneling rates times the distribution itself.

\[
\frac{\partial \rho(n,t)}{\partial t} = \sum_{j=1,2} \left[ \Gamma_j^+(n-1)\rho(n-1,t) + \Gamma_j^-(n+1)\rho(n+1,t) \right] - \left[ (\Gamma_j^+(n) + \Gamma_j^-(n)) \rho(n,t) \right]
\]

This kinetic equation for the distribution function is often referred to as master equation. For the steady state the time derivative becomes zero. Furthermore the exchange rates between 2 different states have to cancel, which leads to a first order difference equation \[3\]

\[
[\Gamma_1^+(n) + \Gamma_2^+(n)] \rho(n) = [\Gamma_1^-(n + 1) + \Gamma_2^-(n + 1)] \rho(n + 1) = 0
\]
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with the following solution:

\[
\rho(n) = \frac{(\prod_{i=-\infty}^{n-1} \Gamma_1^+(i) + \Gamma_2^+(i)) (\prod_{i=n+1}^{\infty} \Gamma_1^-(i) + \Gamma_2^-(i))}{\sum_{j=-\infty}^{\infty} (\prod_{i=-\infty}^{j-1} \Gamma_1^+(i) + \Gamma_2^+(i)) (\prod_{i=j+1}^{\infty} \Gamma_1^-(i) + \Gamma_2^-(i))} \quad (2.12)
\]

The tunneling rates and therefore also \(\rho\) depend on the bias voltage \(V\). To numerically calculate \(\rho(n,V)\) one can either solve the infinite matrix equation \(\Gamma \rho = 0\) or evaluate expression 2.12. In either case one has to determine or guess which states are relevant, as it is not possible to numerically calculate infinite sums and products. This can be a non-trivial task for complex systems but is relatively easy for the double barrier case. Details on the numerical implementation of the orthodox theory calculations performed in this work can be found in appendix A.1.

With the knowledge of \(\rho(n,V)\) the current is given by

\[
I(V) = e \sum_n \left[ \Gamma_j^-(n,V) - \Gamma_j^+(n,V) \right] \rho(n,V).
\]

Here one can either use the first or the second junction for \(j\). With this theory an I-V curve can be calculated for a set of given device parameters. Figure 2.15 shows five curves calculated for different background polarization charges \(Q_P\), which is equivalent to applying different gate voltages to the device. As parameters for the calculation tunneling resistances of 0.9 GΩ and 0.1 GΩ and capacitances of 2.5 aF and 0.28 aF were used for junction 1 and 2, respectively.

From the plot one can see that the device is in a non-conducting state around 0 V bias if \(Q_P = 0\). The flat plateau around 0 V is due to the Coulomb blockade. If the bias voltage is increased, the current shows a Coulomb staircase behavior. When a background polarization charge of \(e/2\) is present, the device exhibits conductance even at 0 V bias. The calculation was performed for a temperature of 4 K. For higher temperatures the Coulomb blockade and Coulomb staircase features start to smear out and at high enough temperatures one obtains ohmic behavior with a resistance of the two tunneling resistances in series.

2.4.3. Co-tunneling

Up to now we have only considered first order perturbation, which corresponds to one electron tunneling through one junction at a given point in time. As electrons tunnel one after another, this is called sequential tunneling and normally dominates transport. However, in the regime of the Coulomb blockade higher order processes may become important, especially for low tunneling resistances. In this regime “classically” no electron may tunnel through either junction, because this would charge the island
Figure 2.15.: I-V curves for different background polarization charges calculated with the orthodox theory.

and increase the electrostatic energy of the system. Considering higher order processes, one electron may tunnel into or out of the island occupying a so-called virtual state of higher energy, temporarily breaking energy conservation. If the same or a different electron leaves or enters the island within a very short period of time, such that the system goes back to a state of lower energy again, the overall process conserves energy.

This phenomenon was explained with the jail-top-ocean-model by Averin [46] and it is possible due to quantum fluctuations of the macroscopic variable $Q$ being the charge on the island. An electron is allowed to spend some time ($\Delta t \simeq \hbar / \Delta E$) in the forbidden state due to Heisenberg’s uncertainty principle [46]. During this period of time either the same electron or a different electron may tunnel out of or into the island such that the combined charge transfer process conserves energy. The rate for this second order process is thus something like the rate or probability for an electron to tunnel into the island times the probability for the same or another electron to tunnel out of it again within an appropriate period of time $\frac{\hbar}{\Delta E}$.

\[ \Gamma^{(2)} \simeq \Gamma^{(1)} \frac{\hbar}{\Delta E} \Gamma^{(1)} \simeq \Gamma^{(1)} \frac{R_K}{R_t} \]

Here $\Delta E$ is the Coulomb charging energy that has to be borrowed to occupy the virtual state, which can be estimated to be $e^2/2C_S$ and is exactly calculated with equations 2.11. In the limit under consideration the tunneling resistance $R_t$ is much
larger than the fundamental resistance $R_K = h/2e^2$ and therefore the co-tunneling rate is much smaller than the sequential tunneling rate. The whole process may be elastic if the same electron enters and leaves the island (2.16 left) or inelastic if a second electron with a different energy is involved (2.16 right). The term co-tunneling refers to the inelastic process, which typically dominates except for very low voltages and temperatures [39, 46], whereas the elastic process is often called macroscopic quantum tunneling of charge (q-mqt). Because of its higher relevance, only the co-tunneling process is discussed in more detail below.

Let us look at a situation where one electron tunnels into the island occupying a state above the Fermi level $E_F$ and another electron with an energy below $E_F$ tunnels out of it leaving an “electron-hole-pair”. Note that the order of the tunneling events may also be reverse. The rate for a process leading from an initial state $i$ to a final state $f$ can be calculated using a Fermi’s golden rule treatment for higher order transitions [46]

$$\Gamma = \frac{2\pi}{\hbar} |<i|M|f>|^2 \delta (E_i - E_f) \quad (2.13)$$

with the matrix element

$$<i|M|f> = T^{(1)}T^{(2)} \left( \frac{1}{E_2 - E_1 + \Delta E_1} + \frac{1}{E_4 - E_3 + \Delta E_2} \right).$$

Here $T^{(j)}$ is the tunneling matrix element for junction $j$, $\Delta E_j$ is the energy difference associated with the corresponding tunneling event and $E_j$ are the participating energy
levels in the leads and on the island. The two energy denominators reflect the fact that the process becomes less likely as more energy has to be borrowed.

For the total rate one has to sum the “partial” rates \(2.13\) over all possible states \(E_j\) with their probabilities \(f(E_1)\) and \([1 - f(E_2)]\) of being occupied and unoccupied, respectively. By further expressing the absolute value of the tunneling matrix element and the densities of states \(D\) in terms of the junction resistance \(R_{ij}\)

\[
R_{ij}^{-1} = \frac{4\pi e^2}{\hbar} |T^{(j)}|^2 D_0 D_j,
\]

the total rate at \(T = 0\) becomes \(46\)

\[
\Gamma = \frac{\hbar}{2\pi e^3 R_{t1} R_{t2}} \left[ \left( 1 + \frac{2}{eV \Delta E_1 + \Delta E_2 + eV} \right) \left( \sum_{i=1,2} \ln \left( 1 + eV/\Delta E_i \right) \right) - 2 \right] V.
\]

By balancing the forward and backward tunneling rates \(I(V) = e [\Gamma(V) - \Gamma(-V)]\), the total current due to inelastic co-tunneling can be calculated even for non-vanishing temperatures.

\[
I_{in} = \frac{\hbar}{12\pi e^2 R_{t1} R_{t2}} \left( \frac{1}{|\Delta E_1^\pm|} + \frac{1}{|\Delta E_2^\pm|} \right)^2 \left[ (eV)^2 + (2\pi k_B T)^2 \right] V
\]

Here \(\Delta E_j^\pm\) are again the changes in electrostatic energy due to tunneling of an electron through junction \(j\) in either direction (see equations \(2.11\)). At low temperatures the term \((2\pi k_B T)^2\) vanishes and the current has a power-law dependence \(V^3\) in voltage. This dependence has been experimentally observed by Geerligs et al. \(42\) in metallic tunnel junctions.

Inelastic co-tunneling discussed in this section is an incoherent process, whereas elastic macroscopic quantum tunneling of charge (q-mqt) is coherent and electron motion within the island becomes important \(46\). Therefore the shape of the island plays a prominent role and interference of the wave functions has to be taken into account. The quantitative treatment of this goes beyond the scope of this work and can be found in reference \(46\).

To conclude this section it might be worth mentioning that co-tunneling is a limiting factor for the usability of the single-electron tunneling effect and therefore considered undesirable.
2. Transport in nanostructures

2.5. Quantum dots

The orthodox theory of single-electron tunneling, which was derived in section 2.4.2 to describe the transport properties of SETs, is based on the assumption of a constant density of states (DOS) in the energy range of interest. For SETs with metallic islands this assumption is met quite well, but if semiconductors are used as island material, a non-constant DOS might have to be considered. Due to a much larger Bohr radius in semiconductors ($a_B \simeq 100\,\text{Å}$ for GaAs), the discreteness of the kinetic energy $\epsilon$ becomes comparable to the Coulomb charging energies $E_C$.

The discrete energy levels and the corresponding density of states of such quantum dots (QDs) is discussed in section 2.5.1. If a QD is used as conducting island in a SET device, this discrete DOS will also manifest itself in the transport properties of the device. This effect will be analyzed in section 2.5.2. Furthermore, this manifestation implies the opportunity to characterize a QD (and also a molecule) by performing transport measurements, which will be considered in section 2.5.3.

2.5.1. Discrete energy levels and density of states

Basic quantum mechanics tells us that an electron confined to a 1D box leads to discrete states with quantized energies. For a box with length $L$ and infinitely high potential barriers, the solution to Schrödinger’s equation for the single-particle wave functions $\psi_n$ is

$$\psi_n = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi x}{L} \right)$$

with the corresponding energy eigenvalues

$$\epsilon_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2.$$ 

This can be extended to a three-dimensional box with the dimensions $L_x$, $L_y$ and $L_z$ in a straightforward manner.

$$\epsilon_{n_x,n_y,n_z} = \frac{\hbar^2 \pi^2}{2m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

Here $n_x$, $n_y$ and $n_z$ are independent quantum numbers. This result tells us that the confinement energy of a quantum dot will roughly scale with one over its size squared. However, for a more accurate calculation of the energy levels of the QDs used in this work, two further aspects have to be taken into account. First, the dots are rather spherical than a rectangular box, and second, they don’t have infinitely high barriers.
For a spherical potential well the problem can be separated into an angle-dependent \( Y \) and a radial \( R \) part [86].

\[
\psi (\vec{r}) = R_{nl} (r) Y_{lm} (\vartheta, \varphi)
\]

The solutions to the angular equation are the spherical harmonics well known from the hydrogen eigenvalue problem

\[
\left| L \right|^2 Y_{lm} (\vartheta, \varphi) = \hbar^2 l (l + 1) Y_{lm} (\vartheta, \varphi) \quad l = 0, 1, 2, ...
\]

\[
L_z Y_{lm} (\vartheta, \varphi) = \hbar m Y_{lm} (\vartheta, \varphi) \quad m = -l, -(l - 1), ..., 0, 1, ..., +l.
\]

The orbital angular momentum quantum number \( l \) is a positive integer and the magnetic quantum number \( m \) is an integer between \(-l\) and \( l\). The remaining radial Schrödinger equation is then

\[
\left[ -\frac{\hbar^2}{2m^*} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} \right) + V(r) \right] R(r) = \epsilon R(r).
\] (2.14)

For infinitely high potential barriers the equation can again be analytically solved and the solutions are

\[
R_{nl}(r) = \sqrt{\frac{2}{a^3}} \frac{j_l (k_{nl}a)}{j_{l+1} (k_{nl}a)}
\]

with \( k_{nl} \) being the \( n \)th null of the Bessel function \( j_l \) and \( a \) the radius of the QD. The corresponding energy eigenvalues are

\[
\epsilon_{nl} = \frac{\hbar^2}{2m^*} \frac{k_{nl}^2}{a^2}.
\]

For a finite potential well

\[
V(r) = \begin{cases} -V_0 & r \leq a \\ 0 & a > a \end{cases}
\]

the Schrödinger equation has to be solved in the corresponding regions. For \( r < a \), inside the potential well, the solution

\[
R_l(r) = a_l j_l (k_0r)
\]

has the form of a spherical Bessel function \( j_l \), as already seen in the infinite barrier case. For \( r > a \), within the barrier region, the solution is give by Hankel functions \( h_l^{(+)} \)
2. Transport in nanostructures

\[ R_l(r) = \alpha_l^{(+)} h_l^{(+)}(ikr). \]

Next, the boundary conditions (the wave function must be continuous, and continuously differentiable) have to be applied at the discontinuity of the potential \( r = a \), as already done in section 2.3.1 to calculate the transmission through a rectangular barrier. For problems with finite potential walls this typically leads to a transcendental equation where no analytical solutions are available. In our case this wave matching leads to a distinct secular equation for each value of \( l \). For \( l = 0 \) the energy levels satisfy

\[ k_0 \cot(k_0a) = -\kappa \]

while for \( l = 1 \) the states are determined by

\[ \frac{k^2}{\kappa^2}(\kappa a + 1) = k a \cot(k a) - 1. \]

Both secular equations can either be solved numerically or by graphical methods. By applying a numerical solution the first 6 energy levels for a CdSe quantum dot embedded in an infinite ZnS matrix were calculated and are plotted as a function of dot radius in figure 2.17.

From the diagram it can be seen that for large dots the electron energy is about -1.55 eV, which is the conduction band offset between CdSe and ZnS and corresponds to the depth of the potential well. For decreasing dot radii the energy levels rise similar to a \( 1/r^2 \) dependence and eventually reach 0 eV. Above 0 eV, obviously no more bound states may exist.

Alternatively, the energy levels and also the wave functions of a spherical QD can be calculated by directly solving the radial equation, extending the matrix method in [120] to the radial equation. The details for this numerical method are given in appendix A.2. In figure 2.17 the results obtained with this matrix method are plotted as solid lines for comparison with the data from the secular equation method.

The plot shows that both methods virtually yield the same results. This comparison is important to validate the correctness and performance of the matrix method. Compared to the conventional secular equation method, the matrix method is much more flexible and allows for an arbitrary radial potential. This will later be utilized in chapter 5.3.1 to calculate the energy states of a core/shell quantum dot.

In semiconductor QDs not only electrons but also holes are confined and exhibit corresponding energy levels, which can be calculated analogously. To distinguish electron and hole levels, the upper indices \( e \) and \( h \) are introduced. Often the energy scale is
chosen such that the hole levels start from 0 in negative direction while the electron levels are positive and set off by the band gap $E_g$. The electron and hole states together with their wave functions are sketched in figure 2.18.

For the transport properties of a QD its density of states (DOS), meaning the number of states within an energy interval $dE$, is of interest. The above considerations about the discrete QD level spectrum would result in a DOS consisting of a comb of delta functions

$$ D(E) \propto \frac{dN}{dE} = \sum_{n,l} \delta(E - \epsilon_{nl}). $$

However, these delta functions are broadened due to the uncertainty principle and a limited lifetime of the corresponding states. Assuming an exponential decay of the excited states, the energy level broadening might be described by Lorentz functions, which are the Fourier transform of the exponential decay.

$$ D(E) \propto \sum_{n,l} \frac{1}{\pi} \frac{\Delta_{nl}}{(E - \epsilon_{nl})^2 + \left(\frac{\Delta_{nl}}{2}\right)^2} $$

Here $\Delta_{nl}$ is the width of the peak in the DOS associated with the state with the quantum numbers $n$ and $l$. Besides this intrinsic broadening also other mechanisms may influence the lineshape. A broadened density of states corresponding to the energy levels in the sketched QD is also shown in figure 2.18.
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Figure 2.18.: Sketch of a semiconductor QD with its discrete energy levels (left) and the corresponding density of states (right).

2.5.2. Quantum dots as conducting island

Now that we know the levelspectrum of the quantum dot and the corresponding density of states, we are in the position to analyze its transport properties if used as island in a SET device. The total energy of such a QD coupled to two electrodes and charged with \( n \) electrons and \( p \) holes is

\[
E(n_e, n_h) = \sum_i n_i \epsilon^e_i - \sum_i p_i \epsilon^h_i + \frac{C_1}{C_S} eV (p - n) + \frac{e^2}{2C_S} (p - n)^2.
\]

Here \( \epsilon^e_i \) and \( \epsilon^h_i \) are the single-particle energy levels for electrons and holes as calculated in the previous section. The change in total energy of the system caused by a tunneling event into or out of electron state \( i \) through either junction is

\[
\Delta E^\pm_1 (n, \epsilon_i) = \mp \epsilon_i^e + \frac{e}{C_S} \left( -\frac{e}{2} \mp [en + C_2 V] \right)
\]

\[
\Delta E^\pm_2 (n, \epsilon_i) = \mp \epsilon_i^e + \frac{e}{C_S} \left( -\frac{e}{2} \pm [en - C_1 V] \right).
\]

If the tunneling event involves a hole state, the change in energy can be calculated analogously using the corresponding hole energy level. Assuming that relaxation rates are much faster than the tunneling rates, electrons and holes remain in equilibrium and the occupation of their energy levels \( \epsilon^{e,h} \) can be described by the following distribution function \([6]\)
2.5. Quantum dots

\[ g_n (\epsilon_k) = \sum_{k_1,\ldots,k_{n-1}} F (\epsilon_k, \epsilon_{k_1}, \ldots, \epsilon_{k_{n-1}}) \]  

(2.15)

with \( F (\epsilon_{k_1}, \ldots, \epsilon_{k_n}) \) being the equilibrium Gibbs distribution for a configuration \( k_1, \ldots, k_n \).

\[ F (\epsilon_{k_1}, \ldots, \epsilon_{k_n}) = \frac{\exp \left( -\frac{1}{k_B T} \sum_{i=1}^n \epsilon_{k_i} \right)}{\sum_{k_1,\ldots,k_n} \exp \left( -\frac{1}{k_B T} \sum_{i=1}^n \epsilon_{k_i} \right)} \]

When \( k_B T \) is much smaller or larger than the average interval between the eigenenergies \( \epsilon_k \), \( g_n (\epsilon) \) coincides with the Fermi distribution function \( f (\epsilon) \). Another way of dealing with the distribution on the dot is to directly set it to the target parameter later on in the master equation. This allows one to even calculate situations governed by a non-equilibrium distribution, but is beyond the scope of this work.

The tunneling rate for an incident lead electron in state \( k \) through junction \( j \) into a QD state \( \epsilon_i \) is again given by Fermi’s golden rule

\[ \Gamma_{j \rightarrow i} = \frac{2\pi}{\hbar} |T_{ik}|^2 f (E_k) [1 - g_n (\epsilon_i)] \delta (E_k - \Delta E^+_j (n, \epsilon_i)) \]

Here, the probabilities \( f \) for the lead state being occupied and \([1 - g]\) for the dot state being unoccupied, are already taken into account. To obtain the overall tunneling rates one has to sum over all discrete quantum dot states \( i \) and integrate over all quasi-continuous lead states \( k \) (again using the density of states \( D \)). By evaluating the integral via the delta function, the rates for tunneling into \((\Gamma^+)\) and out of \((\Gamma^-)\) the island become

\[ \Gamma^+_j (n) = \frac{2\pi}{\hbar} D_k \sum_i |T_{ik}|^2 f (E^+_j (n, \epsilon_i)) [1 - g_n (\epsilon_i)] \]

\[ \Gamma^-_j (n) = \frac{2\pi}{\hbar} D_k \sum_i |T_{ik}|^2 [1 - f (E^+_j (n, \epsilon_i))] g_n (\epsilon_i) \]

\[ \Gamma^\pm (n) = \Gamma^+_1 (n) + \Gamma^-_2 (n). \]

Again, as for the metallic islands, these transition rates determine the time evolution of a distribution function \( \rho (n, t) \) describing the charge state of the system. The master equation for \( \rho \) is formally identical to the one in the metallic case:

\[ \frac{\partial \rho (n, t)}{\partial t} = \Gamma^+ (n - 1) \rho (n - 1, t) + \Gamma^- (n + 1) \rho (n + 1, t) - (\Gamma^+ (n) + \Gamma^- (n)) \rho (n, t) \]
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As already discussed in section 2.4.2 for the steady state the equation simplifies to

\[ \Gamma^+(n)\rho(n) - \Gamma^-(n+1)\rho(n+1) = 0. \]

When \( \rho(n) \) is known, the current may again be calculated with

\[ I(V) = e \sum_n [\Gamma_j^-(n,V) - \Gamma_j^+(n,V)] \rho(n,V). \]

Figure 2.19 shows a set of exemplary I-V curves calculated with this approach. As spectrum for the simulations the electron and hole states of a 6 nm CdSe quantum dot, obtained by the matrix method introduced in the previous section, were assumed. The capacitances \( C_1 \) and \( C_2 \) were chosen to be 0.33 aF and 0.0033 aF, respectively. The overall tunneling resistance of the system was 1 G\( \Omega \) and distributed over the junctions in three different ways giving rise to the three different I-V curves shown in the plot. A ratio \( R_1/R_2 \) of 99 leads to a completely filled quantum dot, the inverse configuration leads to an empty dot and a symmetric arrangement of \( R_1 = R_2 \) to an intermediate, rather complex situation.

![I-V curves for a 6 nm CdSe quantum dot calculated for different tunneling resistance ratios. A ratio \( R_1/R_2 \) of 99 leads to a full QD (red), 1/99 leads to an empty dot (green) and 1 to an intermediate situation (blue).](image)

The steps on the left side of the current gap correspond to transport through the hole states of the dot while the steps on the right are connected to the electron states. As we will see in the next section, the I-V curve of the empty dot is dominated by steps occurring each time the Fermi level of electrode 2, which is scanned with respect to the dot, passes an energy level making it available for transport. For the full QD,
the curve is characterized by steps which coincide with the energy needed to charge
the dot with an additional carrier. If a degenerate state is only partially occupied, the
energy to add another electron is given by the Coulomb energy, otherwise the energy
needed to reach the next state in the spectrum has to be additionally spent. In the
symmetric case both types of steps are more or less pronounced giving rise to a rather
complex curve.

Because of the many parameters which enter into the simulation, it is not feasible
to fit an experimentally measured curve with this model. Instead, the measured data
needs to be analyzed manually to make an educated guess on at least some of the
parameters. If the most important parameters are extracted, I-V curves may be calcu-
lated numerically. By comparing the results to the measurements, the manual analysis
can be verified. The following section gives a rough guideline on how to systematically
analyze I-V curves and their derivatives, respectively.

2.5.3. Tunneling spectroscopy on QDs

As we have seen in the previous section, the density of states of the island has a
prominent influence on electrical transport in SET systems. This not only allows one
to tailor a QD’s electronic properties to suit the demands of a desired SET device, but
it also provides the opportunity to obtain information about the DOS of the object
used as island. This object is not necessarily a QD, but it may also be a single molecule,
as long as it provides states for the transport.

If a scanning tunneling microscope (STM) is used to realize such a characterization,
this technique is referred to as scanning tunneling spectroscopy (STS). In principle it
is also possible to use static nano-electrodes instead of a STM to perform the measure-
ments. The advantage would be that the setup is mechanically more stable and that a
gate electrode may be attached at the price of being not as flexible. While in optical
spectroscopy only transitions from the valence band (VB) to the conduction band (CB)
are observed, tunneling spectroscopy can probe VB and CB states separately.

To obtain information about the DOS of an object of interest, I-V curves are mea-
sured and numerically differentiated or their derivative is measured directly with a
lock-in technique. The interpretation of such tunneling spectra is a non-trivial task as
not only the DOS but also the capacitances and tunneling resistances as well as the
background polarization charge influence the shape of the I-V curves. Also the inter-
play between single-electron charging and resonant tunneling through the states of the
QD is important, because it can provide information about degeneracy and symmetry
of energy levels [13].

In the following paragraphs some rules on how to interpret I-V traces are collected:
2. Transport in nanostructures

Tunneling spectra of islands with quasi constant DOS

If no discrete energy levels are present and the density of states is more or less constant in the energy range of interest (like in larger metallic islands), the I-V traces show equidistant steps corresponding to the Coulomb charging energy $E_C$ as already discussed in section 2.4.

Influence of the capacitance distribution

In case of an asymmetric arrangement of the junction capacitances (e.g. $C_1 << C_2$), the applied bias voltage basically drops at the tunneling barrier associated with the smaller capacitance. The position of the Fermi level of the electrode with the larger capacitance is fixed with respect to the states in the island while the Fermi level of the other electrode is scanned. Therefore, the spacings between peaks in the spectrum directly represent the separation of energy levels in the system.

However, if $C_1$ and $C_2$ are of the same order, the voltage division $V_1/V_2 = C_2/C_1$ affects the positions at which steps occur in the I-V curves. As a consequence, the distance between peaks in the tunneling spectra does not coincide with the real level spacing in such a case. The measured peak separation is larger than the real spacing by a factor of

$$V_B/V_1 = (1 + C_1/C_2)$$

for $C_1 < C_2$, which reaches a maximum of 2 if $C_1 = C_2$.

The Fermi level position with respect to the gap

Another parameter influencing the shape of a tunneling spectrum and in particular the width of the current gap is the position of the Fermi level at 0 V bias with respect to the level structure of the QD. It can be situated midgap or somewhere closer to either the conduction or the valence band states. Its position is for example affected by the background polarization charge and may also be adjusted by means of a gate electrode. It determines the energetic distance to the first accessible level and hence the voltage of current onset.

Interpretation of the current gap

Different combinations of the two factors above give rise to current gaps $\Delta V$ ranging from 0 to theoretically more than twice the quasiparticle gap, which is given by

$$E_{G}^{QP} = \epsilon_1^e - \epsilon_1^h + 2E_C.$$
2.5. Quantum dots

Here $\epsilon_1^{(e)}$ denotes the electron (hole) ground states \[85\] and $E_C$ is the Coulomb charging energy. In the following, four extreme cases will be discussed.

- When the Fermi level is situated midway between the electron and hole ground state and the capacitances are distributed very asymmetrically, the current gap $\Delta V$ around 0 V bias is proportional and close to the quasiparticle gap $E_{QP}^G$ with $\eta = C_1/(C_1 + C_2)$ being a measure for the asymmetry \[85\].

$$e\Delta V = \frac{E_{QP}^G}{\eta}$$

This situation is depicted in figure 2.20 (A I).

- If $E_F$ is located midgap and the capacitances $C_1$ and $C_2$ are comparable, $\Delta V$ can become as large as twice the QD band gap plus charging energies as illustrated in figure 2.20 (A II). In addition, the spectra will be relatively symmetric, as at negative biases the Fermi level in one electrode scans through the electron states of the island while the other scans through the hole states and at positive voltages vice versa.

- When the Fermi level is located in the vicinity of one of the band edges, we can again distinguish two cases. If the setup is asymmetric with respect to the voltage drop, the current gap will again be approximately the quasiparticle gap $\epsilon_1^e - \epsilon_1^h + 2E_C$, but this time very asymmetric with respect to 0 V bias (see figure 2.20 (B I)).

- On the other hand, if the setup is now symmetric in the capacitances, $\Delta V$ can be much smaller than the QD band gap, as for small positive as well as negative voltages the Fermi level of one of the electrodes will reach the near band edge. Again one would expect a rather symmetrical spectrum for the reasons mentioned above. The situation is sketched in figure 2.20 (B II).

**Influence of the tunneling resistances**

Two more parameters which influence transport are the tunneling resistances $R_1$ and $R_2$. Their distribution over the two junctions determines the degree of charging in the dot \[13\].

- If $R_1 \gg R_2$ and assuming that $C_1 << C_2$, electrons tunneling through junction $J_1$ leave the QD through $J_2$ before the next electron tunnels through $J_1$ and therefore no charging takes place. As a consequence, a peak will occur in the tunneling spectra every time the Fermi energy of electrode 1 aligns with an
2. Transport in nanostructures

Figure 2.20.: Influence of the Fermi level position with respect to the island states, (A) midgap and (B) band edge, as well as the effect of an asymmetric (I) and a symmetric (II) capacitance distribution.

excited CB level, which then becomes accessible for electron transport. These so-called excitation peaks dominate the spectra for this configuration [85]. For the first peak in the spectrum appearing at a voltage $V_1$ always the energy for both charging and accessing the first state has to be provided. In case of an empty dot the second peak occurs at a voltage $V_B$ when the energy separation $\Delta_{CB}$ to the next CB level is additionally spent (figure 2.21, top).

$$eV_B = eV_1 + \Delta_{CB}$$

- On the other hand, if $R_2 \gg R_1$, charge may accumulate on the island and prohibit multiple occupation of a degenerate state due to Coulomb interaction. In this case a new transport channel is opened every time the Coulomb charging energy $E_C$ is additionally provided and a peak in the spectrum appears. In this configuration the most visible peaks correspond to opening of new charge states and are referred to as addition peaks [85]. The second peak in the spectrum will appear at a voltage $V_B$ with a spacing to the first peak ($V_1$) corresponding to the Coulomb energy $E_C$ (figure 2.21, bottom).

$$eV_B = eV_1 + E_C$$

In a very asymmetric capacitance configuration one side of the tunneling spectrum corresponds to transport through electron the other side through hole states. Depend-
2.5. Quantum dots

Figure 2.21.: Influence of the tunneling resistance distribution on transport \[13\]. Top: A configuration where the tunneling resistance associated with the junction, where most of the applied bias voltage drops, is limiting transport, leading to an empty dot. Bottom: Opposite configuration resulting in a filled QD.

Interpretation of conductance peaks

The electron ground state of a quantum dot is s-like and often reported to be twofold degenerate \[13\]. Therefore a tunneling spectrum will show two peaks separated by the Coulomb energy \( E_C \) if the configuration of tunneling resistances does favor charging, while only one peak is pronounced if no charging is present.

The first excited state is assumed to be p-like and fourfold degenerate. This corresponds to four peaks with \( E_C \) spacing if charging is present. The separation between the second (ground state) and third (excited state) peak in the spectrum is given by the charging energy \( E_C \) plus the interlevel spacing \( \Delta_{CB} \) modified by the voltage division ratio \( \eta \). If charging is suppressed, again only the first of the four peaks is
2. Transport in nanostructures

pronounced [13].

In all of the above considerations it was assumed that additional charges neither substantially change the single particle levels nor the tunneling barriers and capacities. This is of course not always completely fulfilled and one can see that due to the complex situation it will not always be possible to unambiguously determine the islands energy levels.

2.6. Spin-dependent transport

Despite the degeneracy of quantum dot levels we have so far neglected the spin property of electrons in our consideration. As we will see in section 2.6.1 the spin also affects electronic transport. These magnetoresistive effects can be utilized to implement a new class of devices, often referred to as spintronics. One example for such a device based on the spin property is the quantum dot spin valve discussed in section 2.6.2. To experimentally realize this type of devices one needs to be able to inject spin-polarized electrons into a quantum dot and control this spin-polarization. A way to achieve this is by using shape anisotropy as detailed in 2.6.3.

2.6.1. Tunneling magnetoresistance - Julliere model

The influence of the electron spin on transport manifests itself in a multitude of so-called magnetoresistive effects. Therefore it is reasonable to first clarify what is understood by magnetoresistance. It is defined as the change in resistance \( R \) when a magnetic field \( B \) is applied with respect to the resistance without field and normalized to it.

\[
MR(B) = \frac{R(B) - R(0)}{R(0)} = \frac{\Delta R}{R}
\]

As already mentioned, there is a whole range of magnetoresistive effects such as the anisotropic magnetoresistance (AMR), the giant magnetoresistance (GMR), the colossal magnetoresistance (CMR), the ballistic magnetoresistance (BMR) and the tunneling magnetoresistance (TMR). For this work mainly the tunneling magnetoresistance is of relevance and that is why this effect is now discussed in more detail.

To tackle the TMR it is necessary to introduce the spin polarization

\[
P = \frac{N_+(E_F) - N_-(E_F)}{N_+(E_F) + N_-(E_F)}
\]

Here \( N_{\pm}(E_F) \) denotes the electron concentration of the corresponding spin type at the Fermi level. In a band ferromagnet like nickel spin polarization is caused by
the exchange interaction of electrons, which energetically favors electrons with parallel spins. This is well described by the Stoner-Wohlfarth model \cite{57, 47}. Assuming for the beginning an equal band structure for spin up and spin down electrons with a common Fermi energy (figure 2.22 (a)), electrons below the Fermi level of one spin type will spontaneously populate free states above the Fermi energy of the other spin type as shown in figure 2.22 (b). This rearrangement is energetically possible as long as the gain in kinetic energy is compensated by reduced exchange energy. In turn, states of this now majority spin type are energetically preferred and hence the corresponding band is shifted to lower energies. Figure 2.22 (c) illustrates such a d-band splitting. It can be seen from the sketch that the density of states at the Fermi energy now differs for the two spin orientations, which corresponds to a non-vanishing spin polarization. For nickel this spin polarization is about 20 \% \cite{18}. The type of spins constituting the majority can be adjusted by an external magnetic field.

![Figure 2.22](image_url)

Figure 2.22.: Schematic of d-band splitting in transition metals due to exchange interaction: initial situation with equal spin distribution (a), spontaneous rearrangement of spins (b) and resulting band splitting (c).

If two ferromagnetic electrodes are separated by a tunneling barrier, the tunneling rate depends on the spin polarization of the electrons. This can be explained in the so-called two spin-channel current model \cite{48}. If the magnetization of the electrodes is parallel, the tunneling rate for majority spins is very large, while the rate for minority carriers is very small. For the antiparallel case, spin up electrons are majority carriers in one electrode but minority ones in the other electrode and vice versa. The corresponding tunneling rates are both larger than that of the minority carriers in the parallel case, but still much smaller than the majority ones. Hence the sum of the rates is less than in the parallel case, which leads to a higher resistance in the antiparallel than in the parallel configuration.

The tunneling magnetoresistance can be defined as
2. Transport in nanostructures

\[ TMR = \frac{R_{AP} - R_P}{R_P} \]

where \( R_P \) and \( R_{AP} \) are the tunneling resistances for parallel and antiparallel spin alignment of the electrodes, respectively.

To refer the TMR to the spin polarization of the electrodes, the Julliere model \[61\] is employed. It is based on the assumptions that the spin of electrons is conserved during the tunneling process and that the tunneling conductance is proportional to the spin-dependent DOS in both electrodes. With these assumptions the conductance for parallel magnetization of the electrodes can be written as

\[ G_P \propto a_1 a_2 + (1 - a_1) (1 - a_2) = \frac{1}{2} (1 + P_1 P_2). \]

For the conductance of an antiparallel configuration one correspondingly obtains

\[ G_{AP} \propto a_1 (1 - a_2) + (1 - a_1) a_2 = \frac{1}{2} (1 - P_1 P_2). \]

In both expressions \( a_1 \) and \( a_2 \) are the fractions of tunneling electrons in electrode 1 and 2 with magnetic moments parallel to the electrode magnetization. They can also be expressed in terms of the respective spin polarization \( P \).

\[ a_i = \frac{N_{i\uparrow}}{N_{i\uparrow} + N_{i\downarrow}} = \frac{1 + P_i}{2} \]

With this the tunneling magnetoresistance takes the following form:

\[ TMR = \frac{R_{AP} - R_P}{R_P} = \frac{G_P - G_{AP}}{G_{AP}} = \frac{2 P_1 P_2}{1 - P_1 P_2}. \]

In the parallel case a voltage \( V \) results in a high number of occupied majority carriers on one electrode with a corresponding high number of free states on the opposite electrode with the same spin, as depicted in figure 2.23 (a). In the antiparallel case on the other hand, the high number of occupied majority carriers in one electrode see a small number of free states on the other electrode and the small number of minority carriers see a large number of free states, which results in a reduced conductance (figure 2.23 (b)).

In this model a spin polarization of 100 % would even lead to zero conductance and an infinite tunneling resistance. For transition metals and alloys TMR values up to 50 % were experimentally obtained. Calculating the TMR for two nickel electrodes with a spin polarizations of 20 % results in a value of about 8 %.

Furthermore, the Julliere model predicts an always positive TMR, which is in contradiction to experiments that also show a negative tunneling magnetoresistance \[130\].
2.6. Spin-dependent transport

Figure 2.23.: The two spin-channel model: schematic of majority and minority carrier densities for parallel (a) and antiparallel (b) spin polarization in the leads and the resulting TMR effect [48].

This discrepancy can be explained by a spin-dependent tunneling matrix element as the assumption that it is independent of the spin only holds for very thick and high barriers. An enhancement of the Julliere model taking this into account was given by Slonczewski [108]. For electrodes with intermediate angles of relative magnetization directions this enhanced model also predicts that the conductance should follow a square cosine function of the enclosed angle.

$$\frac{G(\theta) - G_{AP}}{G_{AP}} = \frac{2P_1P_2}{1 - P_1P_2} \cos^2\left(\frac{\theta}{2}\right)$$

2.6.2. Quantum dot spin valve

As we have seen in the previous section, tunneling rates depend on the spin of the electron if the electrodes are ferromagnetic. This effect can be utilized to extend a single-electron transistor to become a spintronic device called quantum dot spin valve. Therefore the nonmagnetic conducting island has to be coupled to two ferromagnetic electrodes. In such an arrangement the electron transport depends on the relative magnetization angle between the two electrodes.
If a bias voltage is applied to the device, electrons are injected from one electrode into the quantum dot. As the electrons coming from that electrode are spin polarized in a direction $\mathbf{n}_1$, more electrons of spin direction $\mathbf{n}_1$ than of $-\mathbf{n}_1$ will tunnel into the island. To leave the island through junction 2, electrons are favored if their spin is aligned parallel to the magnetization direction $\mathbf{n}_2$ of lead 2. As a consequence, the charge current leads to a spin accumulation with direction $\mathbf{n}_1 - \mathbf{n}_2$ on the island. The spin, in turn, acts back on the current via the TMR and inhibits transport. This effect is referred to as spin blockade [25].

Furthermore, an exchange interaction arises from the coupling between the electrons on the QD and the spin polarized leads. This exchange field can be interpreted as an effective magnetic field, which leads to a precession of the accumulated spin. This precession reduces the TMR and hence the spin blockade effect.

The overall transport is determined by a complex interplay between charge and spin. The spin dynamics may be studied by means of electrical transport measurements, while an external magnetic field or a gate voltage can be used to manipulate the system. For a theoretical description the orthodox theory is no longer sufficient. To treat the system either a generalized master equation approach including a spin-dependent term [25, 23] or a non-equilibrium Green’s function method [78] is used. These theories are beyond the scope of this work, but their results are briefly reviewed in the paragraphs below.

First the influence of the relative magnetization angle between the two leads on the device’s conductance in the linear-response regime is analyzed (see figure 2.24). As one would expect, the conductance has a maximum for parallel magnetization of the two electrodes and a minimum for the antiparallel case. The $\phi$-dependence follows from the exchange interaction between the island electrons and the spin polarized electrodes and directly reflects the accumulated spin [24]. The shape of the curve and the width of the minimum depends on the position of the QD energy level used for transport with respect to the Fermi level, and can therefore be manipulated by a gate voltage.

Next, the current-voltage characteristic of a QD spin valve is discussed. As one can see in figure 2.25 (a), the general shape of the I-V curve for an antiparallel configuration does not deviate from that of a conventional single-electron transistor. However, the height of the steps and thus the absolute current through the device depends on the magnitude of the polarization. A higher spin polarization causes increased spin accumulation on the dot and hence a stronger spin blockade. For 99 % spin polarization the current is almost completely blocked.

For relative magnetization angles between 0° and 180° and in particular for 90°, which is plotted in figure 2.25 (b), also the shape deviates from that of a conventional SET. Here a negative differential conductance in the I-V traces is predicted, who’s amplitude
again depends on the degree of spin polarization. The dip in the I-V curve is caused by two competing effects. On the one hand, the charge current causes spin accumulation on the dot and hence spin blockade leading to a reduction in current. On the other hand, the exchange field, which is a function of the applied bias voltage, causes spin precession. This, however, leads to a reduction of the spin blockade and therefore an increase of the conductance. At the current minimum this exchange field completely vanishes [24].

This distinct feature in the I-V curve would provide a good signature to experimentally test the theory. But, as one can see from the plot, a very high degree of spin polarization seems to be necessary to clearly identify this effect.

One further knob to turn is an external magnetic field. Like the exchange field, this would also introduce a spin precession. By the precession the spin blockade is lifted, which results in an increased conductance at higher fields, as depicted in figure 2.26. The curve can be analytically described by a Lorentzian and its width is directly related to the decoherence time \( \tau_s \) of the spin on the island [24].

Despite the sophisticated theoretical description, experimental realizations of this type of devices are still rare. Some experimental results on or related to quantum dot spin valves were demonstrated in references [18, 87, 99, 91]. One key ingredient for an experimental implementation is the ability to adjust the magnetization and therefore the spin polarization of the two electrodes individually. One approach to this challenge is the use of shape anisotropy, which will be explained in the next section.
2. Transport in nanostructures

Figure 2.25.: QD spin valve: calculated I-V curves for different spin polarizations and relative polarization angles (illustration by M. Braun [24], reprinted with permission).

Figure 2.26.: QD spin valve: influence of an external magnetic field on the linear conductance of the device. From the line width the spin decoherence time $\tau_s$ is obtained (illustration by M. Braun [24], reprinted with permission).
2.6.3. **Shape anisotropy**

As outlined in the previous section, spintronic devices such as a QD spin valve demand electrodes where the relative magnetization can be adjusted individually, e.g. by an external magnetic field. This can, for example, be achieved by using two electrodes of different ferromagnetic materials with different coercive fields. At high external magnetic fields the electrodes will have a parallel magnetization, but when the field is swept to the opposite sign, the magnetization of the two electrodes will switch at a different threshold field strengths. Thus the electrodes change from a parallel to an antiparallel and back to a parallel configuration, as shown in figure 2.27.

![Figure 2.27: Schematic magnetization curves for two electrodes with different coercive fields illustrating the switching between a parallel and an antiparallel configuration.](image)

Unfortunately, it is technically very difficult to realize electrodes of two different materials with a separation of only a few nanometers. One alternative approach to obtain leads with different switching fields is to fabricate electrodes of the same material but with different geometries. The effect utilized in this approach is called magnetic shape anisotropy.

Magnetic anisotropy refers to the part of the free energy of a ferromagnet, which depends on the direction of its magnetization. It has two major contributions, the magnetocrystalline anisotropy and the already mentioned shape anisotropy. Expanding the anisotropic part of the free energy into a power series of the direction cosine (e.g. up to second order) it can be written as \[111\]
2. Transport in nanostructures

\[ E_{\text{aniso}} = K_1 \cos^2(\theta) + K_2 \cos^4(\theta) + K_3 \cos^6(\theta) + \ldots \approx \left( K_{\text{shape}} + K_v + \frac{2 K_s}{d} \right) \cos^2(\theta) + \ldots \]

\( K_i \) denote the phenomenological anisotropy coefficients with \( K_1 \) being the integral and \( K_{\text{shape}} \), \( K_v \) and \( K_s \) being the shape, volume and surface magnetocrystalline anisotropy constants. The volume magnetocrystalline anisotropy is caused by spin-orbit interaction while the surface anisotropy is due to a broken symmetry at the interface. The origin of shape anisotropy is the magnetic dipole-dipole interaction and it corresponds to the stray field energy which is a function of the shape of the magnet. The corresponding anisotropy constant can be written as \([44, 111]\)

\[ K_{\text{shape}} = -\frac{1}{2} \mu_0 M^2 \]

with the saturation magnetization \( M \).

For thin ferromagnetic films a magnetization in-plane is typically more favorable than a magnetization perpendicular to the film and for long wires the easy-axis typically coincides with the axis of the wire. It is obvious that shape anisotropy also influences the coercive field of a magnet. Thus, two ferromagnetic electrodes of the same material and with different shape may have a different switching field. This results in a set of equivalent magnetization curves to the ones depicted in figure \([2.27]\) and makes the electrodes usable for spintronic applications. An experiment employing shape anisotropy for a magnetic tunnel junction was already demonstrated by Pasupathy et al. \([92]\). However, for arbitrarily shaped electrodes no analytic solutions are available and numeric micromagnetic simulations are needed to predict their magnetic behavior.
3. Quantum dot preparation

As we have seen in the previous chapter, one essential ingredient to fabricate SET devices is an island with a very small capacitance and hence nanometer size. Despite the small size the island has to provide electronic states which are necessary to store charges on it. In the first single-electron experiments small metallic grains [28, 102] or metallic electron-beam lithography structures [41, 67] were employed for this purpose. However, it is also possible to use semiconductor quantum dots [66] or single molecules [74, 68] to satisfy these requirements. This work was focused on semiconductor QDs, whose discreteness of states offers one additional device parameter.

Two different methods to fabricate and assemble semiconductor QDs have been investigated. On the one hand, silicon QDs were prepared by etching into a silicon-on-insulator (SOI) substrate utilizing a self-assembled colloidal etch mask, as described in section 3.1. On the other hand, colloidal CdSe QDs with a ZnS shell were attached to gold electrodes by linker molecules (section 3.2). Both methods were established with the aim to built SET devices, but they can also be used for other purposes.

3.1. SOI-based silicon QDs

Silicon QDs were fabricated starting from a silicon-on-insulator (SOI) substrate. Therefore the substrate was covered with a self-assembled gold colloidal etch mask and the top silicon layer was etched with a reactive ion etching (RIE) process. Finally the gold etch mask was removed with a wet chemical etch. An overview of the fabrication process is given in figure 3.1.

![Figure 3.1.: Schematic overview of the fabrication process for SOI-based silicon QDs: SOI substrate (a), self-assembly of gold colloids (b), RIE process (c), and gold etch (d).](image)

Figure 3.1.: Schematic overview of the fabrication process for SOI-based silicon QDs: SOI substrate (a), self-assembly of gold colloids (b), RIE process (c), and gold etch (d).
3. Quantum dot preparation

3.1.1. SOI substrates

Silicon-on-insulator (SOI) substrates are available in two different types. One type is fabricated with the so-called separation by implantation of oxygen (SIMOX) technology, where oxygen is implanted into a silicon wafer at a defined depth and converted into silicon oxide by annealing. This buried oxide (BOX) layer insulates the top silicon layer from the rest of the wafer.

The other type is prepared with a wafer bonding technique (UNIBOND\textsuperscript{TM}). Therefore one wafer is oxidized until the desired BOX thickness is reached. Then hydrogen is implanted into the silicon under the oxide layer at a depth corresponding to the desired top silicon thickness. Next, the oxidized side of wafer is bonded onto a second handle wafer. Finally, the implanted hydrogen forms a layer of bubbles at which the surplus silicon of the oxidized wafer is cleaved off (SmartCut) leaving behind a thin SOI layer.

For this work SIMOX wafers with SOI thicknesses of 50 and 83 nm as well as a UNIBOND\textsuperscript{TM} wafer with an initial SOI thickness of 70 nm were used. The buried oxide (BOX) had thicknesses of 375, 145 and 145 nm, respectively. It was found that the quality, homogeneity and uniformity of the SIMOX wafers was insufficient and therefore the UNIBOND\textsuperscript{TM} wafer was used for all later experiments.

As the thickness of the top silicon layer of 70 nm was too large, it had to be thinned to an appropriate value. For this purpose an isotropic CF\textsubscript{4} plasma etcher (Plasma Lab \( \mu \text{Etch} \)) was employed. Typical process parameters are given in table 3.1 and resulted in a reflected RF power during the process of typically 3 W. Before and after the process a 1 min \( \text{O}_2 \) plasma was applied to clean the sample surface before the etch and form a thin oxide layer on the thinned silicon afterwards.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF\textsubscript{4} flux</td>
<td>40 sccm (20 %)</td>
</tr>
<tr>
<td>RF power</td>
<td>15 W (5 %)</td>
</tr>
<tr>
<td>Process pressure</td>
<td>100 mTorr</td>
</tr>
</tbody>
</table>

The etch rates for the process were determined by using partially masked reference samples and measuring the etch depth by AFM (DI NanoScope Dimension 3100) as well as with a profilometer (Tencor AlphaStep 200). Figure 3.2 shows etch depths measured for different samples and with different methods. It can be seen from the diagram that depending on the sample and the characterization method, there is a big variation in the measured etch depth. For this reason a linear regression was applied to the most relevant data points and with it the etch time for a desired SOI thickness
was determined. Starting from the 70 nm thick SOI substrate, etch times of 4:14, 6:00 and 7:09 minutes were used to obtain SOI thicknesses of 50, 32 and 20 nm. With etch time the color of the substrate changed from purple to reddish gold to dark blue when all top silicon was removed.

Figure 3.2.: Etch depth as a function of the etch time for the CF$_4$ plasma with 20 % flux and 5 % RF power at a chamber pressure of 100 mTorr. Data points for different samples and analysis methods together with a linear fit to the most relevant samples are shown.

It was found that the subsequent self-assembly of gold colloids described in the next section would not work properly if directly performed after the thinning procedure. For this reason the samples were kept under ambient conditions for at least 24 hours to recover a native oxide layer before being further processed.

### 3.1.2. Self-assembly of colloidal etch mask

To fabricate quantum dots from the thinned SOI substrates, an appropriate etch mask was needed. One possible approach to obtain mask structures of the desired size was electron beam lithography (EBL), but this is a very expensive and time consuming technique. Instead self-assembly of commercial gold colloids was used for this work, as this is a very cost-efficient method and the colloids are available in various sizes. Furthermore, these sizes extend into regions not accessible with EBL at the moment.

For self-assembly of the colloids a method introduced by Sato et al. [102] based on the aminosilane molecule [3-(2-aminoethylamino)propyltrimethoxysilane] (APTS) was used. Therefore the SOI substrates were immersed into APTS diluted in deionized water (1:2000) for 5 min and subsequently baked at 120 °C on the hot plate for 30 min. During this procedure the silane groups of the APTS molecules replace the hydroxyl
3. Quantum dot preparation

(−OH) previously adsorbed on the native SiO₂, forming a siloxane bond. The amino group is thereby extended away from the SOI surface as sketched in figure 3.3 (a).

![Figure 3.3.: Schematic illustration of the APTS-based self-assembly process of gold colloids according to Sato et al. (a) and an AFM scan of the colloidal etch mask after self-assembly (b).](image)

Thereafter the samples were immersed into a solution of gold colloids of desired size for 24 hours. Depending on the SOI layer thickness particles with diameters of 100, 50 or 20 nm have been used in the experiments. The commercial gold colloids from British Biocell International came in an aqueous solution and were stabilized by a citrate ligand shell.

When the gold colloids in the solution approach the sample surface, some of their stabilizing citrate ligands are substituted by the extended amino group of the APTS molecules bound to the substrate and thereby immobilized. The coverage of the gold particles on the surface increases with the immersion time, but saturates at some density as the negatively charged particles repel each other. After rinsing and drying the gold particles had arranged in a sub-monolayer, which then served as an etch mask in the following reactive ion etching (RIE) process. An AFM scan of a sample covered with a sub-monolayer of 50 nm gold colloids is shown in figure 3.3 (b).

3.1.3. Reactive ion etching of QDs

To obtain separated silicon quantum dots the SOI layer had to be etched away selectively everywhere except below the gold particles. For this purpose reactive ion etching (RIE) with CF₄ gas as etchant was employed for its anisotropic behavior. The reactor used for the process was a Plasma Lab μP and a typical range of process parameters applied for the QD fabrication is given in table 3.2.
3.1. SOI-based silicon QDs

Table 3.2.: Process parameters for the anisotropic CF$_4$ reactive ion etch used to form the QDs.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value / range</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_4$ flux</td>
<td>20 sccm (20 % of mass flow controller)</td>
</tr>
<tr>
<td>RF power</td>
<td>37.5 ... 75 W (10 ... 20 %)</td>
</tr>
<tr>
<td>Process pressure</td>
<td>ca. 38 mTorr</td>
</tr>
<tr>
<td>DC bias voltage</td>
<td>40 ... 130 V</td>
</tr>
</tbody>
</table>

For the RF power two settings with 37.5 W (10 %) and 75 W (20 %) were tested. Thereby it was found that the process was very unstable if the RF power source was set to only 10 % of its maximum power and therefore all later samples were etched with 20 %. The chamber pressure was kept as low as possible during the process to achieve a maximum anisotropic etching behavior and typically settled to about 38 mTorr. Under the above conditions the DC bias voltage, which is responsible for the reactive ions to be accelerated onto the sample surface, adjusted to 40-70 V for 10 % RF power and to 120-130 V for 20 % RF power. The reflected RF power typically lay between 5 and 15 W.

The etch rate of the process was again determined with partially masked reference samples measured with AFM or a profilometer. In figure 3.4 the etch depths measured for different samples is plotted as a function of etch time. To the data of a preliminary test series a linear fit was applied and with it the required etch times were calculated. For the 20 % RF power setting an etch rate of approximately 13 nm/min was obtained.

![Figure 3.4: Etch depth as a function of the etch time for the CF$_4$ RIE process with 20 % flux and 20 % RF power. Data points for different samples together with a linear fit to the data of a preliminary test series are shown.](image)

Since the reactor was driven at the lower end of its RF power capabilities, the
3. Quantum dot preparation

The matching network responsible for coupling the RF into the plasma did not always couple with the same efficiency, which resulted in a relatively high variability in the bias voltage and the etch rate. As a consequence, partially masked reference samples were usually processed in parallel to confirm that the SOI layer was really etched down to the buried oxide and an additional etch step was performed if necessary. For samples with a 50 nm thick SOI layer and 50 nm gold colloids an etch time of 5:15 minutes yielded good results.

After the RIE process the samples were investigated with a scanning electron microscope (SEM). The SEM micrograph in figure 3.5(a) shows a 50 nm SOI sample with 50 nm gold colloids after the RIE process where the etch mask is still on top of the silicon dots.

After the RIE process the gold mask was removed with a wet chemical etch in an aqueous I$_2$KI solution. The final result was a sample with individual silicon QDs on an insulating SiO$_2$ layer as shown in the SEM micrograph in figure 3.5(b). With this method quantum dots with dimensions of 50 nm height and diameter as well as 20 nm height and diameter were fabricated. Additionally quantum discs with a diameter of nominally 100 nm and a thickness of about 30 nm were prepared.

3.1.4. Characterization of QDs by TEM

To check whether we have actually obtained crystalline silicon quantum dots, some samples were investigated with transmission electron microscopy (TEM) after etch mask removal. In order to image single quantum dots with the TEM, a preparation method called small angle cleavage technique (SACT) [79] was applied.

First the [100] oriented samples had to be polished from the backside to reduce the substrate thickness to about 100 µm. Then a precision diamond knife was used to
cut the samples into stripes along the \{120\} plane of the silicon crystal. Next, these
stripes were cut into 18.43° wedges by cleaving the crystal along the \{110\} plane. For
energetic reasons this procedure forms a sharp tip bounded by the cleaved \{120\} plane,
a \{111\} plane and the \{100\} sample surface with the QDs \cite{79}. The wedges were then
attached to a TEM grid with a special glue such that one looks at a cross section of
the sample. At the tip of the wedges the sample is so thin that single quantum dots
can be investigated. The preparation and the TEM investigation have been carried
out at the Electron Microscopy Group of Materials Science of the University of Ulm
by Christian Zaubitzer and Sören Selve.

In figure 3.6 TEM micrographs taken from a sample with nominally 50 nm quantum
dots are shown. The overview TEM image shows several silicon QDs on top of the
buried oxide layer. In the two magnified images below the crystalline structure of
the silicon core of the dots can clearly be seen. This is an important information as
thinning the SOI substrate and performing the reactive ion etch could potentially have
destroyed the crystalline structure. The quantum dots have a cylindric shape with a
height of roughly 40 nm and diameter of also 40 nm. Furthermore, the bottom right
image shows the interface to the buried oxide layer. Here one can see that the top
silicon layer was really etched down to the BOX.

![TEM images](image)

Figure 3.6.: TEM images of 50 nm SOI-based silicon quantum dots. An overview showing several dots (top), one single QD (bottom left) and the top silicon - buried oxide interface (bottom right).

The silicon quantum dots are supposed to be covered by a native oxide layer, which
is typically a few nanometers thick. From the TEM images the oxide layer seems to be
3. Quantum dot preparation

on the order of 5 nm. Some of the oxide could also be due to sputtering effects during the RIE process rather than grown by natural oxidation. There could also be residual glue from the sample preparation which could not be clearly distinguished from the amorphous silicon. Therefore the information on the tunneling oxide obtained from this TEM investigation is limited.

Figure 3.7 shows the TEM results for 20 nm QDs. On the left side the bright field image of a 20 nm QD is given whereas on the right a 2D Fourier transform of the indicated area is shown. In the FFT image one can see four distinct peaks which correspond to the \{111\} reflexes of the silicon crystal. The size of the QD is roughly 17 nm.

Figure 3.7.: TEM analysis of a 20 nm silicon quantum dot. The bright field image (left) and a reduced FFT image (right).

The TEM results for the SOI nanodiscs are given in figure 3.8. The sample for this investigation was prepared by Carsten Waltenberg at the Carl Zeiss SMT AG with a focused ion beam (FIB) system. On the left a bright field image of a silicon nanodisc on top of the 110 nm thick buried oxide layer is shown. Below the BOX the silicon substrate can be seen. On the right a magnified view of the disc together with a reduced FFT image of its core is depicted. The FFT image shows two reflexes corresponding to the \{022\} plane of silicon indicating a crystalline disc. The discs are about 38 nm thick and have a diameter of 95 nm.

Besides the silicon dots and discs also gold residues were found on some of the samples. In figure 3.9 (a) a bright field (BF) image of a 50 nm QD is printed next to its dark field counterpart. The dark spots in the bright field correspond to the bright areas in the dark field image. The bright color in the dark field image marks a large Z value and indicates the presence of gold. In the BF image of the 20 nm QD 3.9 (b)) a brighter crystalline part in the center can be seen in between two darker crystals. As the reduced FFT analysis in (c) shows, the bright lattice belongs to the silicon QD
while the dark part shows a gold peak. The gold is most probably a residue of the colloidal etch mask. One reason why the gold was not removed during the I₂KI etch might be that it was covered by a protection layer deposited during the RIE process by sputtering of silicon oxide.

From the TEM investigations we can conclude that we were able to fabricate crystalline silicon quantum dots on an amorphous silicon oxide surface. The quantum dots were intended to be individually contacted with nano-electrodes as described in section 4.2.6 and used as an island in SET devices. As the dots are still quite large, no quantization effects are expected to be observable. Nevertheless the dots will be referred to as quantum dots in the following chapters. If the technique is extended to 10 nm dots or smaller in the future, confinement effects will start to play an important role.
3. Quantum dot preparation

3.2. Colloidal CdSe/ZnS-QDs

As second approach, colloidal quantum dots were attached to gold electrodes by linker molecules. The QDs used for this work had a CdSe core and a ZnS shell and they were produced by Colin Heyes and Vladimir Breus from the Biophysics Department at the University of Ulm. A short summary of their fabrication process is given in section 3.2.1. These QDs were then self-assembled onto gold electrodes with a technique described in section 3.2.2. In section 3.2.3 the QDs are characterized by transmission electron microscopy (TEM) and photoluminescence (PL) spectroscopy.

3.2.1. Synthesis of colloidal QDs

The preparation of CdSe/ZnS-core/shell QDs consists of two steps. In the first step the CdSe core has to be grown and in a second step the core is covered with the ZnS shell.

For the CdSe core synthesis Colin Heyes and Vladimir Breus employed the methods of Talapin et al.\cite{115} and Peng and Peng\cite{93}. Therefore cadmium oxide was used as precursor, dissolved in stearic acid and heated to about 200 °C. Then a solution of trioctylphosphine oxide (TOPO) and hexadecylamine (HDA), acting as coordinating solvents to stabilize the cadmium ions in reverse micelles, was injected into the reaction mixture and the temperature was further increased to 310 °C. At this temperature a solution of selenium in trioctylphosphine (TOP) was injected while quickly stirring. The rapid injection raises the precursor concentration above the nucleation threshold and a chemical reaction between the Cd and Se ions leads to immediate nucleation and subsequent growth of CdSe nanoparticles. After a short nucleation burst the supersaturation is partially relieved and as long as the consumption of precursors by the growing colloidal nanocrystals is not exceeded by the rate of precursor addition to the vessel, no further nucleation will take place. This growth from solution is followed by an Ostwald ripening phase where individual nanocrystals coalesce and form larger QDs. The nucleation and growth sequence is sketched in figure 3.10. By taking aliquots after different time intervals, QD samples with different sizes can be obtained. The quantum dots were then dispersed in cold toluene. More details about the synthesis process can be found in reference\cite{27} and\cite{26}.

In the second step the CdSe dots were capped with a ZnS shell. Therefore the uncapped quantum dots were mixed with TOPO and HDA and heated to 165 °C. At this temperature a Zn-S injection solution consisting of diethylzinc (Zn(C₂H₅)) in toluene and hexamethylidisilathiane (HMDST) in TOP was added in a dropwise fashion. The amount of Zn and S precursors needed for capping the CdSe dots depends on the
3.2. Colloidal CdSe/ZnS-QDs

Figure 3.10.: Illustration of the nucleation and growth process for the CdSe core synthesis in the framework of the La Mer model (after Murray et al. [82]).

size of the core and the desired shell thickness and can be calculated by the required increase in volume [27].

In this work quantum dots with a CdSe core of about 3 nm diameter and a ZnS shell of nominally 8 monolayers (ML) were used. The overall diameter of the core/shell QDs was about 8 nm.

### 3.2.2. Attachment of QDs to gold electrodes

The colloidal quantum dots provided by Colin Heyes and Vladimir Breus were dissolved in toluene. To be contacted by nano-electrodes or for integration into a device the QDs had to be dispersed onto a substrate. For SET devices additionally a controlled barrier to the electrodes is needed. One method to achieve this is by utilizing chemical linker molecules such as hexanedithiol [66].

The hexanedithiol molecule is an alkane chain with two thiol (−HS) groups at its ends. These thiol groups are known to have a strong affinity to gold and form self-assembled monolayers (SAMs) on it [31]. Thereby one of the thiol groups binds to the gold surface while the other one is directed away from it. When the so functionalized surface is now exposed to the QD solution, these extended thiol groups may substitute some of the QD’s stabilizing ligand molecules and thus immobilizing the quantum dots. Besides attaching the QDs the hexanedithiol molecules with their length of 1.2 nm also provide a well defined tunneling barrier. A self-assembled hexanedithiol monolayer on a pair of gold electrodes as well as a SET configuration where one QD is bound to both electrodes are schematically shown in figure 3.11.
3. Quantum dot preparation

![Diagram of a self-assembled hexanedithiol monolayer on a pair of gold electrodes (a) and a SET configuration with one CdSe/ZnS-QD bridging both electrodes (b).]

In the experiments samples with gold electrodes or nanowires predefined by electron beam lithography (see section 4.1) were cleaned in a N₂ plasma. Then the samples were immersed into a 123 mM hexanedithiol solution in isopropanol for 24 hours. After rinsing with isopropanol and drying with nitrogen the samples were placed in a quantum dot solution for 5 days. Before immersing the samples the QD solution was heated to 140 °C until it was clear to dissolve conglomerates of dots. For the QD solution different dilutions from pure to $\frac{1}{100}$ of the original aliquot were tested. The best results were obtained for a dilution ratio of $\frac{1}{10}$. After 5 days the samples were taken out of the solution, rinsed with toluene and dried with nitrogen. Finally the samples were characterized with an atomic force microscope (AFM). An exemplary measurement is shown in figure 3.12.

![AFM scan of CdSe/ZnS core/shell quantum dots self-assembled onto a predefined gold nanowire with hexanedithiol linker molecules.]

The scan shows a predefined gold nanowire with side gate electrodes onto which the
CdSe/ZnS quantum dots were self-assembled. All over the yellowish metal structure one can see little bright spots corresponding to the attached QDs. The larger bumps are due to the roughness of the metal film.

In this case the quantum dots were deposited onto a gold nanowire which was subsequently broken by a controlled electromigration process (see chapter 4.2) to yield two separated electrodes with a distance below 5 nm. The idea behind this procedure is that after electromigration a QD might end up between the two emerging electrodes bound to either of them with one or more hexanedithiol molecules as depicted in figure 3.11 (b). The opposite approach is to first break the nanowire or use any other method to fabricate a pair gold electrodes with sub-5 nm separation and only then deposit the QDs. This strategy has the advantage that the nano-electrodes can be electrically characterized before the QD deposition which may be taken as reference for the measurements with dots. The downside is, however, that sample cool down and surface energy relaxation processes of the nano-electrodes may modify the system between reference characterization and actual measurement. Hence, the value of such a reference measurement is questionable and the probability to fabricate a working device is reduced. Therefore the preferred sequence for this work was QD deposition before breaking the electrode.

3.2.3. Characterization of QDs with TEM and optical spectroscopy

After synthesis of the CdSe core and after capping with a ZnS shell the quantum dots were investigated with a transmission electron microscope (TEM) to analyze their size and the size distribution [27]. Furthermore, optical absorption and emission spectroscopy was used to investigate the electronic structure of the quantum dots.

For the TEM measurements the QDs were dispersed onto a carbon-coated copper grid [26]. Two exemplary TEM images of uncapped and capped QDs are shown in figure 3.13 (a) and (b), respectively. From such TEM images size histograms, as shown in figure 3.13 (c), were extracted.

In the histogram the blue bars depict the occurrence of uncapped CdSe QDs with corresponding diameter. The distribution is nearly Gaussian and centered around roughly 3 nm. The width of the distribution is on the order of 1 nm. Therefore we conclude that the CdSe cores of our particles have a diameter of about 3 nm.

The red bars correspond to the capped QDs. As expected, the distribution is shifted to larger diameters, but it is also much broader than that of the uncapped dots. The shown distribution has its maximum at about 6.5 nm diameter, which corresponds to a ZnS shell of 5 monolayers (ML). The quantum dots used in this work had a slightly
3. Quantum dot preparation

Figure 3.13.: TEM images of (a) uncapped and (b) capped CdSe quantum dots and (c) the corresponding size distribution histograms (from [27], reproduced with permission).

thicker shell of 8 ML with an expected size of about 8 nm.

For further characterization the QDs were analyzed by means of optical absorption and emission spectroscopy [27, 26]. The results from optical spectroscopy are of particular importance as they provide information about the confinement energies of the QDs that may be compared to electrical measurements and simulation data. For the emission spectra an excitation wavelength of 500 nm was used. Both, emission and absorption measurements are shown in figure 3.14.

Figure 3.14.: Room temperature absorption (dotted lines) and emission (solid lines) spectra of uncapped (blue) and capped (red) CdSe quantum dots (from [27], reproduced with permission).

The emission spectra of uncapped and capped CdSe quantum dots show a relatively narrow symmetric peak. The peak position of the uncapped QDs is located at 540 nm.
while the peak of the capped dots is red-shifted by about 13 nm [27]. Both peaks correspond to the transition from the electron ground state to the hole ground state of the quantum dots. For the capped dots the transition is shifted to lower energies as the wave functions can penetrate into the ZnS shell and are therefore less localized. The energy gap between electron and hole ground state is about 2.24 eV, whereas the bandgap of bulk CdSe is only 1.74 eV [39]. The additional 502 meV of the QD energy gap are the sum of electron and hole quantization energies. As the quantization energy is approximately inverse proportional to the effective mass, the electron confinement energy can be estimated to 390 meV while the hole part is only about 113 meV. In this estimation the different band offsets for electrons of 1.55 eV and for holes of 0.66 eV are not yet considered, which is expected to even slightly increase this asymmetry. For comparison, the calculated ground state quantization energies for a CdSe core of 2.4 nm radius with a 2 nm ZnS shell are 402 meV and 114 meV for electrons and holes, respectively. The width of the peaks in figure 3.14 is caused by the size distribution of the QDs.

In the absorption spectra the ground state transition is also visible, but Stokes-shifted to lower wavelength. Again the spectra of uncapped and capped QDs are offset by about 13 nm. In principle, absorption measurements also show transitions of excited levels as the absorbance has a local maximum each time the wavelength of the incident light matches with a transition in the dot. The strength of the transition depends on the corresponding matrix element. In figure 3.14, with fantasy, one might perceive some more features at higher energies, but there are no clear peaks. This is most probably due to the fact that the measurement was performed on an ensemble of QDs with the size distribution described above. As the position of the energy levels strongly depends on the size of the dots, peaks of individual QDs will average out.
4. Electrode fabrication

In order to make nano-objects, such as the quantum dots discussed in the previous chapter, actually usable for nano-electronics, they need to be electrically contacted and integrated into a device. Therefore nano-electrodes with a separation of only a few nanometers are necessary. Besides giving us the ability to contact individual QDs, nano-electrodes have a wide range of additional applications, like e.g. molecular electronics, and show interesting properties themselves. For that reason a large fraction of this work was spent to establish fabrication techniques for nano-electrodes.

A whole range of different approaches can be found in literature and in the following a short overview of the most prominent ones is given. The most obvious and straightforward way to fabricate nano-structures is electron beam lithography (EBL) discussed in section 4.1. It is a well established technique and very flexible, but it is also time consuming and expensive. Furthermore its resolution is at the moment limited to about 10 nm. Therefore different alternative approaches have been investigated in the past decade.

In this work two alternative approaches were examined and established. The controlled electromigration method is based on the usually undesired electromigration effect in conductors at high current densities as explained in section 4.2. With it a predefined metal nano-wire is opened to yield two separated electrodes with nanometer separation.

The second technique is based on electrochemical deposition and it is dealt with in section 4.3. Here two initially separated electrodes were grown together by depositing metal onto the electrode templates. The conductance between the electrodes was used to monitor the process and to achieve electrode separations in the nanometer range.

There is a variety of other techniques for nano-electrode preparation mentioned in literature. Beside scanning probe methods [12, 94], which have a completely different application scenario, the mechanically controllable break junction (MCJB) technique is the most prominent candidate. Here initially connected electrodes are patterned onto a flexible substrate and then broken by bending the substrate with a mechanical mechanism [123, 98, 104]. The mechanical displacement ratio allows one to adjust the electrode distance in the sub-nanometer range. The disadvantage of this method is a high experimental effort as well as severe limitations in the device integration.
4. Electrode fabrication

4.1. Electron beam lithography

Electron beam lithography (EBL) is the standard technique to write nano-patterns. Together with evaporation and a lift-off process it was used to fabricate the nano-electrodes for this work. The process parameters were optimized to yield a minimum electrode separation as outlined in section 4.1.1. In section 4.1.2 the resolution achieved with this recipe and the resulting electrode gap is analyzed. Even though the minimum separation was still about 10 nm, electron beam lithography served as the basis for both alternative approaches. In the electromigration experiments EBL was used to pattern the required metal nano-wires, whereas electrode templates with a separation of about 200 nm were prepared for electrochemical deposition. In both cases a similar recipe as for the nano-electrodes was used.

4.1.1. Fabrication process

The basis of electron beam lithography is a resist sensitive to irradiation with high voltage electrons which is used to cover the substrate. By irradiating the resist with a focused electron beam its chemical structure is locally modified. When then developed with an appropriate agent, the resist is removed in either the irradiated or the unirradiated areas, depending on the type of resist and the developer. If the exposed area is cleared the resist is said to be positive otherwise negative. The resulting resist structure can either be used as an etch mask or as template for a lift-off process as done in our experiments. Therefore metal is evaporated onto the partially covered sample and subsequently removed from the areas which were masked with the resist. As electron beam writing is a time consuming process and the metalization thickness is limited by the thin resist layer used for nano structures, the nano-electrodes were then contacted in a second, conventional lithography step. An overview of the fabrication process is sketched in figure 4.1 a) to f). The resolution of the process is thereby limited by the spot size of the focused electron beam as well as by the grain size and the layer thickness of the resist. The process was used to pattern separated nano-electrodes and metal nano-wires as depicted in the SEM micrographs in figure 4.1 g) and h).

Resist

For the experiments two different high resolution positive electron beam resist stacks based on polymethyl methacrylate (PMMA) were employed. A thin bilayer resist was optimized for extremely small structures while a thicker stack was used for patterns in the micrometer range when a thicker metalization layer was desired. In both cases two resist layers with different sensitivity to electron irradiation were used to obtain
4.1. Electron beam lithography

Figure 4.1.: Schematic overview of the EBL nano-electrode fabrication process: a) Substrate, b) PMMA bi-layer resist spin-on, c) exposure and development, d) evaporation of metal, e) lift-off, and f) contacting with standard photolithography. SEM micrographs of a contact pair g) and a metallic nanowire h) fabricated with this process.
4. Electrode fabrication

an undercut profile, which is necessary for the subsequent lift-off process.

The parameters used for the nano resist stack are compiled in table 4.1. To obtain the desired undercut profile PMMA molecules of different chain length and respective molecular weight were deposited, resulting in different sensitivities. First the bottom layer with lower molecular weight was spun onto the samples. The shorter PMMA molecules had a molecular weight of 50k (which means 50000 times the proton mass) and were dissolved in ethyl lactate with a concentration of 4 %. The spin on process was performed with the parameters given in table 4.1 and followed by a soft bake at 180 °C on the hot plate for 5 min. This resulted in a bottom layer thickness of about 80 nm.

Table 4.1.: Parameters for the bilayer EBL resist used for nanometer sized patterns.

<table>
<thead>
<tr>
<th></th>
<th>bottom layer</th>
<th>top layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resist</td>
<td>50k PMMA</td>
<td>950k PMMA</td>
</tr>
<tr>
<td>Solvent</td>
<td>ethyl lactate</td>
<td>ethyl lactate</td>
</tr>
<tr>
<td>Concentration</td>
<td>4 %</td>
<td>1 %</td>
</tr>
<tr>
<td>Spin on</td>
<td>4000 rpm</td>
<td>2000 rpm</td>
</tr>
<tr>
<td>Bake temperature</td>
<td>180 °C</td>
<td>180 °C</td>
</tr>
<tr>
<td>Bake time</td>
<td>5 min</td>
<td>5 min</td>
</tr>
<tr>
<td>Thickness</td>
<td>80 nm</td>
<td>40 nm</td>
</tr>
</tbody>
</table>

The top layer consisted of PMMA molecules with a higher molecular weight of 950k. To deposit the molecules onto the samples they were also dissolved in ethyl lactate with a concentration of 1%. After spin-on and soft-bake with the parameters given in table 4.1 the second PMMA layer was about 40 nm thick. According to the resist data sheets, the 50k PMMA bottom layer is supposed to have a 20 % higher sensitivity to electron irradiation than the 950k top layer. This resist configuration was used for all exposures where an ultimate resolution was necessary. The electrode templates needed for electrochemical deposition were patterned using a slight modification of this process, which produced a 240 nm thick 50k PMMA bottom layer and a 120 nm thick 950k PMMA top layer (for details see 43).

For structures with larger dimensions, e.g. the gold bond pads for the magnetic nickel nano-electrodes or the contact patterns to select individual SOI SETs, a different resist stack was employed. Here a copolymer PMMA/MA dissolved in 1-methoxy-2-propanol was used as sensitive bottom layer. With the spin-on parameters given in table 4.2 a layer thickness of 750 nm was achieved. For the top layer again 950k PMMA was used, but this time with a higher concentration. After the PMMA was spun onto the samples with 6000 rpm, a 120 nm thick top layer had developed. Because of its specific chemical properties the copolymer resist has a 3-4 times higher sensitivity compared...
4.1. Electron beam lithography

to PMMA. Furthermore, the thick bottom layer allows one to evaporate 300 nm of metal and more, which was important in some of the experiments to reduce the lead resistivity.

Table 4.2.: Parameters for the bilayer EBL resist used for larger structures with thicker metalization.

<table>
<thead>
<tr>
<th></th>
<th>Bottom layer</th>
<th>Top layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resist</td>
<td>Copolymer PMMA/MA</td>
<td>950k PMMA</td>
</tr>
<tr>
<td>Solvent</td>
<td>1-methoxy-2-propanol</td>
<td>ethyl lactate</td>
</tr>
<tr>
<td>Concentration</td>
<td>33 %</td>
<td>3.2 %</td>
</tr>
<tr>
<td>Spin on</td>
<td>3000 rpm</td>
<td>6000 rpm</td>
</tr>
<tr>
<td>Bake temperature</td>
<td>180 °C</td>
<td>180 °C</td>
</tr>
<tr>
<td>Bake time</td>
<td>5 min</td>
<td>5 min</td>
</tr>
<tr>
<td>Thickness</td>
<td>750 nm</td>
<td>120 nm</td>
</tr>
</tbody>
</table>

As the substrates were typically non-conducting, the samples had to be additionally covered with a thin (3-4 nm) layer of germanium (not shown in the sketch) to avoid a charge pile-up distorting the electron beam.

Exposure

The samples were then exposed with a Leica EBPG 5 HR electron beam writer. For the acceleration voltage of the electrons 50 kV and 100 kV was used, where the experiments with 50 kV yielded better results. With the 50 kV acceleration voltage doses ranging from 185 $\mu$C/cm$^2$ to 1400 $\mu$C/cm$^2$ were tried. At a dose of 310 $\mu$C/cm$^2$ and below the samples were underexposed resulting in resist residues in the exposed areas. At doses over 450 $\mu$C/cm$^2$ the structures started to become overexposed, which led to a rounding effect at corners and ultimately to a short between the nano-electrodes. The best results were achieved with the parameters given in table 4.3 which were used for most samples presented in this work. Here the fine electrode tips were written with a smaller dose than the coarse leads. The minimum spot size of the electron beam was on the order of 35 nm and the minimum exposed feature size of the machine was 20 nm.
4. Electrode fabrication

Table 4.3.: Exposure parameters used for high resolution EBL.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage</td>
<td>50 kV</td>
</tr>
<tr>
<td>Dose (fine structures)</td>
<td>350 $\mu$C/cm$^2$</td>
</tr>
<tr>
<td>Dose (coarse structures)</td>
<td>380 $\mu$C/cm$^2$</td>
</tr>
<tr>
<td>Spot size</td>
<td>$\sim$ 35 nm</td>
</tr>
<tr>
<td>Beam current</td>
<td>0.316 nA</td>
</tr>
</tbody>
</table>

Development

After exposure the germanium was removed in $\text{H}_2\text{O}_2$ diluted in deionized water with a $\text{H}_2\text{O}_2$ : DI ration of 1:5. Then the samples were developed using a methyl isobutyl ketone (MIBK) based developer until the PMMA was removed from the exposed areas. A summary of the development parameters is given in table 4.4. The degree of development was determined under an optical microscope and typical development times were on the order of 60 s. As the low molecular weight PMMA has a much higher development rate than the high weight one, the apertures in the thin top PMMA layer are underetched yielding the desired undercut as sketched in figure 4.1 c). After development the samples were rinsed in isopropyl alcohol and blown dry with nitrogen. Finally, PMMA residues on the exposed areas were removed by a 30 s oxygen plasma.

Table 4.4.: Parameters used for germanium removal and resist development.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Germanium etch</td>
<td>$\text{H}_2\text{O}_2$ : $\text{H}_2\text{O}$ (1:5)</td>
</tr>
<tr>
<td>Developer</td>
<td>MIBK:IPA (1:3)</td>
</tr>
<tr>
<td>Development time</td>
<td>55-60 s</td>
</tr>
<tr>
<td>Rinsing</td>
<td>IPA</td>
</tr>
</tbody>
</table>

Evaporation

For most samples gold was used as electrode material. If gold is directly evaporated onto silicon oxide, the adhesion is very poor and the structures tend to fall off the sample. Therefore an adhesion layer of titanium was evaporated onto the silicon oxide before depositing the gold. Care has been taken that the vacuum was not broken between the two deposition processes as titanium quickly oxidizes and the adhesion of gold on titanium oxide is also very poor. For the nano-electrodes typical thicknesses for the Ti adhesion layer were 3 to 5 nm, while the gold layer was chosen to be between 13 and 25 nm. For the evaporation a Temescal FC1800 electron beam evaporator was
4.1. Electron beam lithography

used. In those areas of the samples previously exposed to the electron beam and cleared from the resist, the metal was directly deposited onto the silicon oxide surface while in the other areas the metalization sat on top of the sacrificial PMMA layer as shown in figure 4.1(d).

Lift-off

In the next step the unwanted metal was removed in a lift-off process. Therefore the PMMA resist was dissolved in 1-methyl-2-pyrrolidone (1M2P) at a temperature of 180 °C. After a few minutes the metal on top of the resist came off the samples in little flakes and could be washed away with a syringe leaving the desired metal structures on the sample surface (see figure 4.1(e)). In case of an incomplete removal of the flakes ultrasound was used to get rid of the remnants. Afterwards the samples were rinsed with acetone and isopropyl alcohol and dried with nitrogen. Figures 4.1 g) and h) show a pair of nano-electrodes and a nanowire, respectively, after the lift-off process. Additionally, two side gates patterned in the same EBL step are visible. The distance from the side gates to the center of the electrode gap was 400 nm.

Photolithography and bonding

In order to electrically access the nano-electrodes, the EBL structures were finally contacted with a standard photolithography step as depicted in figure 4.1(f). The samples were then glued onto a chip carrier and electrical contact was established with gold bond wires. A photograph of a chip carrier with bonded sample can be seen in figure 4.2.

Figure 4.2.: Nano-electrode sample glued and bonded to a chip carrier.
4. Electrode fabrication

4.1.2. Characterization and resolution limit

After fabrication the nano-electrodes were characterized by means of scanning electron microscopy (SEM) and atomic force microscopy (AFM). The AFM proved to be not appropriate to determine the electrode separation as the dimensions of the tip lay in the same range as the gap to be analyzed.

The SEM images were taken with a LEO DSM 982 Gemini cold field emitter microscope with a nominal resolution of 2.5 nm at an acceleration voltage of 5 kV. The actually achieved resolution was slightly lower due to the insulating substrate and vibration problems. The distance between the electrodes was measured either with the SEM software on the machine or offline with the image analysis software ImageJ. Depending on nominal geometry and applied EBL dose electrode separations down to about 10 nm were achieved. Also electrode pairs with even smaller gaps were observed, however it was often not clear from the SEM images whether the electrodes were still separated or already connected for distances below 10 nm.

Figure 4.3 shows a diagram connecting the design electrode distance to the actually measured separation. The data points depicted as circles were all taken from one sample, while the two triangular data points were obtained from a different sample processed with the same parameters. The inset shows a SEM micrograph of an electrode pair with a separation of 12 nm. As for all other data shown in the plot, the electrodes were written with an acceleration voltage of 50 kV and a dose of $350 \mu\text{C/cm}^2$. The nominal separation was 50 nm.

![Figure 4.3](image)

Figure 4.3.: Measured electrode separations plotted against the corresponding design values. Data obtained from two different samples are shown. Inset: SEM micrograph of an electrode pair with a measured separation of 12 nm.

As one can see from the diagram, for the circles a minimum electrode separation...
is achieved with a design distance of 40 nm. When the design distance is reduced to 30 nm, the electrodes are already connected. These 30 nm roughly correspond to twice the spot radius of the electron beam.

For one design distance the measured data points have a spread of a few nanometers even within one sample. The data points from the second sample show that although processed under the same nominal conditions an even larger sample to sample variance is present. Therefore always a range of fields with different nominal electrode separation was patterned onto one sample and the fields with the desired gap size were chosen after the lift-off process.

For the nano-wires design widths of 70 and 100 nm were tested. The corresponding measured wire widths were about 105 nm and 175 nm, respectively. For most electromigration experiments described in this work nanowires with a nominal width of 70 nm were used. The width variation from sample to sample turned out to be noncritical.

To wrap this section up, it was shown that our electron beam lithography patterning together with the lift-off process is capable of producing nano-electrodes with separations down to about 10 nm. If electrodes with an even smaller separation are desired, alternative methods need to be employed. Two of these alternatives, the controlled electromigration and electrochemical deposition, are the topics of the following sections. The metallic nano-wires and template electrodes needed for these unconventional techniques are typically prepared with the EBL fabrication process outlined in this section.

4.2. Electromigration

Electromigration has long been known as an undesired effect in integrated circuits causing device failure due to the movement of material in a conductor at high current densities. The effect was first discovered in molten alloys of lead-tin and mercury-sodium by the French scientist Gerardin in 1861, but it took until the late 1960ies when the first integrated circuits became available that electromigration was further investigated by Black and others [56, 22, 16]. One result of this research was Black’s equation, which describes the mean time to failure (MTTF) of an integrated circuit due to electromigration as an activated process.

Only recently it was discovered that electromigration can also be used to obtain nano-electrodes with a separation of less than 5 nm [88, 69, 19, 113, 38, 117]. Therefore one starts from a thin metallic nano-wire and applies an increasing voltage. At some threshold voltage electromigration will set in at the narrowest part of the wire, mass will be removed there and deposited elsewhere. As a consequence the wire eventually breaks leaving a more or less small gap depending on the process parameters.
4. Electrode fabrication

In section 4.2.1 the underlying theory is discussed and consequences for the process control are drawn. In section 4.2.2 this knowledge is used to establish a controlled electromigration scheme to reproducibly fabricate nano-electrodes with a separation of only a few nanometers. Before the nano-wire finally breaks, transport undergoes a transition from the diffusive to a ballistic regime showing conductance quantization, which is discussed in section 4.10. After the wire is broken, transport switches further to the tunneling regime. The properties of these resulting nano-electrodes are investigated in 4.2.4. As also reported in literature, artifacts in the electronic characteristics of the tunnel junctions may occur due to metallic clusters unintentionally created during the electromigration process. This problem is addressed in section 4.2.5. Furthermore, the controlled electromigration was applied to metallic nano-wires patterned onto predefined silicon QDs making use of a self-alignment effect. This aspect is covered in 4.2.6. Finally, the electromigration process was extended to ferromagnetic electrodes with specific geometries to control the relative magnetization taking advantage of the shape anisotropy effect (section 4.2.7).

4.2.1. Theory of electromigration

When a voltage is applied to a metallic conductor, the metal atoms are subject to two different forces. One force, the so-called direct force is caused by the electric field acting on the positively charged metal ions and pointing in the field direction. The second force is referred to as electron-wind force and is due to a momentum transfer from the conduction electrons to the atoms via scattering processes. This force is directed into the opposite field direction as sketched in figure 4.4 (a). Both forces are proportional to the electric field and the resulting effective force is the driving force for electromigration. It can be written as

$$F_{\text{eff}} = F_d + F_w = e Z^* E = e Z^* \rho j$$

with $Z^*$ being the effective ionic charge [52, 77]. This means that due to the momentum transfer from the electrons the atoms behave like if they had a charge $Z^*$). For noble metals such as Au, Ag and Cu the wind force is typically 5 to 10 times larger than the direct force and dominates electromigration. Thus $Z^*$ is negative and atoms move in the same direction as the electron flow [77, 121, 117].

The driving force causes the atoms to drift with an average velocity, which is proportional to the electric field and hence to the current density.

$$v_d = \mu F_{\text{eff}} = e Z^* \rho j$$

(4.1)
4.2. Electromigration

Figure 4.4.: (a) Schematic illustration of the direct and the electron-wind force in a metallic conductor and (b) displacement of metal ions due to a resulting effective force.

The mobility $\mu$ describes the interaction of the moving atoms with the static lattice, which can be interpreted as a friction force that balances the driving force and leads to a constant drift velocity. It can be expressed in terms of the diffusion coefficient $D$ via the Einstein relation.

$$\mu = \frac{D}{k_B T} = \frac{D_0}{k_B T} \rho e^{-\frac{E_a}{k_B T}}$$

Diffusion of metal atoms is an activated process and the diffusion coefficient has an Arrhenius type of dependence on the temperature [56]. Here $D_0$ is the maximum diffusion coefficient (at infinite temperature) and $E_a$ is the activation energy. Typically, this activation energy is much higher for atomic motion in bulk material than for motion on the surface. Hence, in nano-structures the dominant mass flow takes place at grain boundaries and surfaces [52, 77] and the bulk mass flow can be neglected. For gold the activation energy for surface diffusion is about 0.12 eV [117].

Substituting the mobility into equation 4.1 and multiplying with the atom concentration $c$, one obtains an expression for the atom flux $J$ caused by the current density $j$ [117, 17].

$$J = cv_d = c\rho e^{Z^*} \frac{D_0}{k_B T} \rho e^{-\frac{E_a}{k_B T}}$$

From the equation we see that mass transport depends linearly on the current density and roughly exponentially on the temperature. On the other hand, one has to keep in mind that the current density is also coupled to the temperature via Joule heating.

Besides the atomic flux induced by the current there are also other contributors to the total flux caused e.g. by a concentration gradient, a temperature gradient or by mechanical stress. It was shown by Blech [17] that the mass transport in aluminum
4. Electrode fabrication

films caused by mechanical stress balances the atom flux due to an applied current and prevents electromigration up to a critical current density \( j_{\text{crit}} = \frac{\Omega \Delta \sigma_{\text{max}}}{2 e \rho L} \), which depends on the mechanical yield strength \( \Delta \sigma_{\text{max}} \) of the material, the length \( L \) of the conductor and the atomic volume \( \Omega \) [17] [117]. Only above this critical current density the aluminum deforms plastically and electromigration takes place.

Mahadevan and Bradley modeled and simulated the void evolution due to electromigration [77]. They also found that below a critical current density surface irregularities smooth out over time as surface-self-diffusion is the dominant effect. However, when the critical current density is reached, surface electromigration becomes dominant, an edge perturbation becomes instable and evolves into a slit-shaped void. In these simulations as well as in experiments the slits “lean” into the electron-wind.

From the arguments above we conclude that two conditions need to be met for a net material transport to takes place: Firstly, the current density driving electromigration has to exceed a critical value to be dominant over other transport processes caused by diffusion or mechanical stress. Secondly, the temperature has to be high enough to provide the mobility for substantial atom motion. Thereby the threshold junction temperature \( T_{\text{start}} \), above which electromigration was observed, is nearly independent of the temperature of the sample environment. If the sample was kept at lower temperatures, more electrical power was needed to increase the local temperature via Joule heating and start electromigration [117]. Threshold temperatures ranging from 345 to 500 K have been reported by different authors [69] [117] [53], even when the sample was kept in a liquid helium cryostat. Depending on the temperature of the sample environment, the current at which EM sets in is therefore either determined by the amount of heat to achieve the required temperature or by the critical current density.

Moreover, it is obvious from the thermally activated behavior that electromigration will tremendously increase when the junction temperature rises above the threshold value. It will therefore be very important, as noted by many authors [69] [38] [113] [54] [116] [129], to control the junction temperature if one wants to achieve a reproducible electromigration process. This will be the main goal of the next section.

4.2.2. Controlled electromigration scheme

As outlined in the previous section, one has to control the junction temperature in order to perform a reproducible electromigration process. When a voltage is applied to a break junction and steadily increased, the current also increases as one would expect, but the overall conductance of the junction decreases. This reversible effect is due to a local Joule heating of the junction [69] [38] [113].

The electrical power dissipated in the junction is \( P_J = I^2 R_J \), where \( R_J \) is the junc-
4.2. Electromigration

Electromigration resistance. Initially the junction resistance is very small and most of the applied voltage drops over the lead resistance $R_L$. However, when electromigration sets in, the junction resistance increases and therefore a larger fraction of the voltage drops over the junction. This will in turn heat the sample, accelerate electromigration and further increase $R_J$. If the lead resistance $R_L$ is too large, this positive feedback causes a thermal runaway leading to an uncontrolled and instable EM. Such a thermal runaway causes the nano-wire to “blow up” and results in gaps much larger than 10 nm and gold particles in the gap [116].

In figure 4.5 a breaking curve taken at room temperature without active feedback to control the dissipated power is illustrated. It can be seen that when electromigration sets in at around 1.06 V, the conductance abruptly drops to 0 and no more current can pass through the junction. The insets shows an AFM scan taken after electromigration. A relatively large gap between the two electrodes is visible and it seems as if some of the gold in the junction was melted and subsequently resolidified in a drop-like structure on the upper electrode. This is an indication for the presence of very high temperatures during the EM process. Furthermore the junction showed no tunneling conductance after EM.

![AFM Image](image.png)

Figure 4.5.: Current-voltage characteristics of an electromigration process without active control of the junction temperature. Inset: AFM image of the resulting junction.

The junction temperature $T_J$ can be expressed in terms of the environment temperature $T_0$ and the dissipated power $P_J$ as [38]

$$T_J = T_0 + \Delta T = T_0 + P_J R_\lambda$$

(4.2)
4. Electrode fabrication

where $R_\lambda$ is the thermal resistance from the junction, where the power is dissipated, to the reservoir with temperature $T_0$. To prevent thermal runaway during electromigration, the change in temperature with junction resistance $dT_J/dR_J$ must be negative [38].

$$
\frac{dT_J}{dR_J} \propto \frac{dP_J}{dR_J} = \frac{d}{dR_J} \left( \frac{R_J}{(R_J + R_L)^2} U^2 \right) < 0
$$

Here it was assumed that the thermal resistance $R_\lambda$ from the junction to the heat sink does not depend on the electrical resistance of the junction. The inequality is only satisfied if

$$R_J > R_L.$$

As this condition is typically not met, an uncontrolled electromigration process is not performed along a curve of constant power. Consequently the dissipated power is much higher, the junction temperature far exceeds the threshold value and the junction is “burnt” [129].

From the above considerations two major consequences can be drawn for the development of an advanced electromigration scheme. First, one has to choose a sample layout which minimizes the lead resistance, and second, an active feedback is needed to keep the applied power to the junction and thus the junction temperature constant [38, 113, 54].

To meet the second demand it was proposed by some authors [38, 113, 54] to measure a reference conductance of the junction at a relatively low voltage. Then the voltage is steadily increased until the conductance falls below a set fraction of this reference value. Next the voltage is ramped down by a set amount, a new reference conductance is determined and the procedure is repeated until the desired conductance is reached.

In our experiments, however, we found that the absolute conductance is not the most adequate criterion to detect the onset of electromigration. One reason for this is that the conductance is already reduced by Joule heating of the junction when still in a reversible regime. As a consequence, setting the fraction of the reference conductance too high results in the feedback loop always reacting on the conductance decrease due to Joule heating and never entering the EM regime. On the other hand, setting the fraction too low holds the risk of missing the point when EM sets in. This is especially crucial in our setup, because the feedback is established over a computer interface which is very slow.

It turned out to be much more beneficial to use the local gradient of the breaking curve as control parameter, which was calculated from the currents measured at the active ($I$) and the previous ($I_{prev}$) voltage setpoint to $dIdV = \frac{I-I_{prev}}{V-V_{prev}}$. Note that this
4.2. Electromigration

parameter is not just the discrete version of the differential conductance, as it also
includes the temporal evolution of the current between the two measurements. It only
weakly reacts on Joule heating as this is a smooth and steady process. Electromigration,
however, causes an abrupt decrease of the conductance and a kink in the breaking curve,
which is perfectly captured by the local gradient. Therefore it is perfectly suited to
detect the onset of electromigration. When the electromigration process had progressed
to a certain extend, the parameter $dI/dV$ became quite unstable and sometimes even
took negative values. At this stage the feedback parameter was switched back to the
absolute conductance. A detailed description of the feedback algorithm is given in
appendix A.3.

With this two step process it was possible to reproducibly break metallic nano-wires
in a controlled manner even with our slow experimental setup. An exemplary breaking
curve taken at room temperature is shown in figure 4.6. Initially the current rises with
increasing bias voltage until the onset of electromigration. When the onset is detected
by the feedback system, the voltage is reduced and ramped up again. Thereby the
current passed through the junction is steadily reduced without the occurrence of an
abrupt drop.

![Figure 4.6](image)

Figure 4.6.: Breaking curve obtained during a controlled electromigration process per-
formed at root temperature. The red line shows a calculated curve of
constant power dissipation in the junction.

Also a line of constant power dissipation in the junction $P_J$ was drawn into the I-V
diagram in figure 4.6 by plotting the current $I = \sqrt{P_J/R_J}$ over the applied voltage
$V = (R_J + R_L)I$ for different values of the junction resistance $R_J$. The parameters
for calculating the curve were a power dissipation in the junction of 170 $\mu$W, a lead
resistance of 147 $\Omega$ and the junction resistance was varied from 5 $\Omega$ to 5 k$\Omega$. Comparing
the calculated curve to the breaking curve one can see that the electromigration process was actually performed at a constant power. This indicates that the electromigration rate was dominated by the junction temperature and the feedback scheme was able to control this temperature \[38\].

Further electromigration experiments were performed at room temperature, at about 225 K and at 4.2 K and the breaking curves were also analyzed by fitting with a curve of constant power dissipation. In figure 4.7 the resulting power dissipation is plotted as a function of sample temperature. From the diagram it is obvious that for lower sample temperatures a higher electrical power needs to be dissociated in the junction for electromigration to take place. Together with the data points a linear fit is plotted.

![Figure 4.7. Dissipated power in the EM junction as a function of sample temperature.](image)

Rearranging equation 4.2 for \(P_J\) one obtains a linear dependence on the sample temperature, which corresponds to the linear fit from figure 4.7.

\[
P_J = -\frac{1}{R_\lambda} T_0 + \frac{T_J}{R_\lambda}
\]

Under the assumption that \(R_\lambda\) is roughly independent of the sample temperature, a junction temperature \(T_J\) of 350.2 K and a thermal resistance of \(3.85 \times 10^5 \text{ K m}^2 \text{ W}^{-1}\) were extracted from the fit. This means that independent of the environment temperature, the electromigration is performed at a constant junction temperature.

To crosscheck these findings the thermal resistance and along with it the junction temperature are estimated in the following. Therefore the geometry of our EBL electrodes is approximated by three rectangles with corresponding width \(w_i\) and length \(l_i\) as illustrated in figure 4.8. The thickness of the electrodes \(d = 25 \text{ nm}\) is the same for.
all rectangles. The thermal resistance of each part is now calculated with

\[ R_{i,\text{Au}}^i = \frac{l_i}{\lambda_{\text{Au}} w_i d}. \]

<table>
<thead>
<tr>
<th>i</th>
<th>length ( l_i )</th>
<th>width ( w_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>88 nm</td>
<td>110 nm</td>
</tr>
<tr>
<td>2</td>
<td>400 nm</td>
<td>340 nm</td>
</tr>
<tr>
<td>3</td>
<td>29.5 ( \mu )m</td>
<td>3 ( \mu )m</td>
</tr>
</tbody>
</table>

Figure 4.8.: Geometric dimensions of the electrode resistance model.

Here \( \lambda_{\text{Au}} \) is the thermal conductance of gold. Additionally, heat can be conducted from the junction via the silicon oxide layer into the silicon substrate. Here the thermal resistance for each rectangle is calculated to

\[ R_{i,\text{SiO}_2}^i = \frac{d_{\text{SiO}_2}}{\lambda_{\text{SiO}_2} w_i l_i}. \]

The silicon substrate and the thick photolithography contact pads are assumed to behave as perfect heat sinks with a temperature \( T_0 \). To calculate the thermal resistance for one electrode the partial resistances of the gold leads have to be connected in series while the resistances corresponding to the silicon oxide layer are connected in parallel. The total thermal resistance is then obtained by division with 2 as the two different electrodes are connected in parallel. Insertion of the parameters for our sample geometry into the calculation results in a total thermal resistance of \( 2.90 \cdot 10^5 \text{ Km W} \) which compares well to \( 3.85 \cdot 10^5 \text{ Km W} \) obtained by the linear regression above, in particular considering the crude approximation. When this thermal resistance is used to calculate the junction temperature with the dissipated power obtained from figure 4.6, the result of 349.3 K is also in good agreement with the value from above. Furthermore, our results are consistent with temperature data given in literature [117, 53].

The conductance evolution during the electromigration process is depicted in figure 4.9. It can be seen that the conductance is smoothly reduced during the process from initially about 7.5 mS down to about 2 mS. By stopping the electromigration process at any point, the junction conductance can be tuned to the desired value.

Until now, the discussion only referred to this first part of the electromigration process. Here electromigration is said to be in a diffusive regime where the junction dimensions are much larger than the mean free path of the electrons. In this regime we found that electromigration is dominated by the electron-wind force and triggered
4. Electrode fabrication

Figure 4.9.: Conductance evolution during a controlled EM process performed at room temperature.

at a constant temperature of about 350 K. Furthermore we showed that the feedback scheme introduced in this section is capable to control the junction temperature.

However, when the conductance in figure 4.9 falls below about 2 mS, which corresponds to a resistance of 500 Ω, the trace becomes non-monotonic and the conductance seems to jump between different plateaus. In this phase of the breaking process electromigration has already proceeded to a point where the junction is constricted such that its size is comparable to the electron mean free path and transport has entered the ballistic regime. How the break junctions behave in this regime and the consequence arising for electromigration will be discussed in the following section.

4.2.3. Quantized conductance in electromigrated junctions

As we have seen in the previous section, the conductance of the junction was smoothly reduced during electromigration in the diffusive regime via the feedback scheme. However, as the junction conductance falls below a certain value, which is on the order of 1/500 Ω for EM experiments performed at room temperature, it is observed in most samples that the conductance does not evolve in a continuous way anymore, but jumps between more or less defined plateaus.

For the interpretation of this step-like behavior it is assumed that the junction is already constricted to a point where its dimensions are comparable or smaller than the electron mean free path and the resistance is not determined by scattering anymore. In this regime the conductance may no longer be described by a macroscopic conductor with a uniform specific conductance, but depends on the exact configuration of the
4.2. Electromigration

lattice atoms. When the electromigration process changes the configuration, this is reflected by a jump in the conductance. Between such events, the conductance stays more or less unchanged.

In some breaking curves, as the one shown in figure 4.10, it was found that these steps clearly coincide with integer multiples of the conductance quantum $G_0 = 2e^2/h$. This is the distinct fingerprint of a quantum point contact [1] as discussed in section 2.2.2.

![Conductance Trace](image)

Figure 4.10.: Conductance trace during a controlled electromigration process at room temperature right before wire breakage. Steps corresponding to integer multiples of the conductance quantum $G_0 = 2e^2/h$ are clearly visible.

From the conductance taking preferentially integer multiples of $G_0$ we conclude that at this stage of the electromigration process only a few metal atoms are bridging the nano-electrodes. Depending on the number of atoms in the junction and on their actual configuration, a specific number of channels is available for electron transport. The conductance of the junction is then governed by the number of channels and the corresponding transmission rates according to Landauer’s formula 2.2. When the atomic configuration is such that the transmission values of all channels participating in transport are approximately 1, the overall conductance is an integer multiple of the conductance quantum.

On the other hand, also conductance values differing from this scheme may be measured in metallic QPCs. One possible reason is that channels with a transmission rate smaller than 1 are involved in transport. A second explanation can be given from a measurement point of view: if the junction switches between two configurations within the integration time of the conductance measurement, the measurement yields an average over the individual conductance values, which would also be no multiple of $G_0$. 

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4. Electrode fabrication

It has to be mentioned that conductance quantization has already been reported by different authors for electromigrated break junctions \[113, 112, 117\] as well as for mechanically controllable break junctions (MCBJs) \[123, 32, 104\].

In the ballistic regime we found that electromigration is considerably slowed down, but it does still continue. Furthermore, the process does not follow a curve of constant power dissipation anymore and the bias voltages needed to finally break the wires are rather high (up to 1 V and sometimes even above). These findings are consistent with the results published by other authors \[113, 129\]. Also atomic rearrangements may take place during the process, which can lead to an increase of the junction conductance and sometimes results in a rather chaotic breaking curve as depicted in figure 4.11. This behavior is especially pronounced at low sample temperatures.

Figure 4.11.: Electromigration breaking curve for a junction in the ballistic regime recorded at room temperature. Due to atomic rearrangements the junction conductance sometimes abruptly increases.

These observations are not surprising as ballistic transport implies that scattering in the junction region is rare and therefore only little momentum is transferred from the conduction electrons to the metal atoms. In addition Joule heating is expected to be drastically reduced in the junction and the resistance should only slightly depend on \(T\) \[129\]. This also means that our temperature estimation from the previous section does not hold in this regime. Considering all these aspects the question arises, why electromigration does actually continue at all in the ballistic regime.

Even though it won’t be possible to answer this question completely, three aspects will be discussed in the following. The first point is considering the driving force of electromigration and its behavior in the ballistic regime. As the junction is narrowed
the direct force is believed to become more dominant compared to the electron-wind force. The ratio of electron-wind force and direct force

\[
\frac{F_w}{F_d} \propto \frac{a}{Z} \sigma
\]

as derived in references [97] and [109], is proportional to the radius of the constriction \(a\). Here \(\sigma\) denotes the scattering cross section for the scattering process and \(Z\) the valence of the associated defect. Hence, when the junction is strongly constricted and \(a\) becomes very small, the direct force will dominate the wind force and thus electromigration.

The second aspect to be discussed here is the junction temperature at which EM is performed in the ballistic regime. As already mentioned, the temperature estimation from the previous section does not hold anymore. Instead, one has to consider non-equilibrium conditions where electrons and defects have a much higher temperature than the lattice of the junction [97, 29]. For the maximum electron temperature \(T_{el,max}\) in the junction Chen and Sorbello derived the expression

\[
T_{el,max} = \frac{3}{8} T_0 + \frac{5}{16} \frac{eV}{k_B} \coth \left( \frac{eV}{2k_B T_0} \right).
\]

based on a stationary harmonic oscillator model coupled to the electrons via inelastic scattering [29]. For a junction with a bias voltage of 0.5 V at room temperature, the formula yields an electron temperature of 1926 K, which is already much larger than the melting point of gold of 1337 K. On the other hand, the lattice temperature, which is the relevant temperature for melting, is supposed to be much smaller and approximately equal to the environment temperature \(T_0\) [29].

The temperature governing atom motion and hence electromigration is the defect temperature \(T_d\), which lies somewhere between the electron and the lattice temperature as both act like a thermal bath for the defects. The actual value of \(T_d\) depends on the coupling of the defect to the electrons and the lattice and is difficult to determine. It is reported to be typically two to five times smaller than the electron temperature [97, 116]. For the example give above the temperature for atom motion would lie somewhere between 385 and 963 K. This result suggests that the temperature is high enough to provide the atom mobility necessary for electromigration to take place if a driving force is present.

The third point to be discussed here is regarding the scattering length and momentum transfer in the junction. From our point of view it is questionable if the concept of an electron mean free path and a scattering length, which was originally derived for a bulk lattice with defects, can also be applied to a situation where only individual atoms are
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responsible for electron transport. To get a clearer picture on how electrons behave in such structures, how they are scattered and the amount of momentum transferred to the atoms, ab initio calculations might give more insight.

In this section it was shown that electromigration can be controlled such that contacts bridged by only a few gold atoms and exhibiting conductance quantization can be fabricated. From these metallic quantum point contacts electromigration can be further continued, even though the EM process for this regime is not yet completely understood. Once the conductance drops below the conductance quantum $G_0$, transport undergoes another transition to the tunneling regime, which is the topic of the next section.

4.2.4. Tunneling characteristics of nano-electrodes

As soon as the conductance falls below the conductance quantum $G_0$, it is assumed that the electrodes are separated from each other and electron transport takes place via tunneling. In the experiments the tunneling current was measured as a function of bias voltage right after the electromigration process to characterize the junction. According to the stage at which electromigration was stopped, the measurements yielded tunneling curves corresponding to resistances from a few tens of kiloohms up to hundreds of gigaohms. Depending on the resistance and individual tunnel junction I-V curves with shapes ranging from close to linear to pronounced non-linear were observed. In general, the non-linearity increased with higher tunneling resistances.

In figure 4.12 an I-V trace measured after electromigration at room temperature is shown. The resistance for small bias voltages is about $6.6 \, \text{G}\Omega$ and the curve exhibits a strong non-linear, s-shaped characteristic typical for tunneling junctions. For higher bias voltages the current increases disproportionately.

In order to analyze the electrode separation, the measured data was fitted with the Simmons formula \( (2.9) \) for tunneling currents. The fit is plotted together with the measured curve in figure 4.12. As fitting parameters an electrode separation $s = 1.46 \, \text{nm}$, a barrier height $\varphi = 1.2 \, \text{eV}$ and a contact area $A = 1.1 \times 10^{-16} \, \text{m}^2$ were used.

The barrier height is much lower than one would expect for tunneling from gold to gold via vacuum as the work function of gold is about 4.7 eV. This may have a number of reasons: Firstly, tunneling might occur not through vacuum or air, but through the insulating substrate, which would yield a lower tunneling barrier. Secondly, Simmons formula was derived from a 1D model, while the actual contact has a 3D geometry. The result of a 1D fit to the 3D contact would be an effective barrier width overestimating the actual electrode separation and an effective barrier height underestimating the real one \[69\]. Thirdly, in such thin barriers the image force, which was not taken into
4.2. Electromigration

Figure 4.12.: I-V curve measured after electromigration and fitted with the Simmons formula. The fitting parameters were a spacing \( s = 1.46 \) nm, a barrier height \( \varphi = 1.2 \) eV and a contact area \( A = 1.1 \cdot 10^{-16} \) m\(^2\).

account for the simple Simmons formula, will not be negligible. And finally, samples are typically covered with a thin water film when kept at ambient conditions. This film might also reduce the barrier height between the electrodes.

Even though the origin of the low work function is not quite clear, the fit to the measured data indicates that the distance between the two electrodes is rather small. We therefore conclude that our electromigration process is capable of producing electrode pairs with a separation of about 2 nm and below. This is in good agreement with values reported in literature which range from a few Å to about 5 nm \[88, 69\].

When first entering the tunneling regime, the junction resistance is typically on the order of 100 kΩ corresponding to a very small separation. However, one can proceed with the electromigration process to further separate the electrodes by applying even higher voltages. In the tunneling regime atoms are believed to migrate either due to the strong electric field present in the gap or due to field emission currents \[63\]. An exemplary breaking curve for electromigration performed in the tunneling regime is depicted in figure 4.13.

When the voltage is initially ramped up, the non-linear I-V characteristics of the tunnel junction can be observed. In contrast to electromigration in the diffusive regime, where the conductance was reduced with increasing bias voltage due to Joule heating, here the conductance increases at higher voltages. At some threshold voltage the electric field becomes large enough to modify the junction configuration and the conductance abruptly changes. Usually the conductance is reduced due to the modification, but as evident from figure 4.13 at a bias voltage of 1.11 V and 1.38 V, the
4. Electrode fabrication

Figure 4.13.: Breaking characteristics of an electromigration process in the tunneling regime.

reconfiguration sometimes also may lead to a higher conductance. By proceeding with electromigration, the junction resistance can be further reduced to the desired value. To achieve this typically quite high voltages up to 4 V are required.

When electromigrated junctions are kept under ambient conditions for several days or weeks, it can be observed that their electric properties change over time. Typically the conductance decreases, which is also reported in literature where Strachan et al. [112] investigated electromigrated gold junctions under a transmission electron microscope (TEM) over a period of three to four month. They observed a degradation of the nano-gaps over time and ascribed the effect to the surface tension of gold, which causes features with high curvature to be smoothed out.

A similar effect occurs when samples are broken at low temperatures and heated up afterwards or vice versa. After annealing or cooling down the tunneling conductance typically had changed. Sometimes the contacts showed metallic conductance in the 200 Ω range again, while with other samples a lower conductance was measured than before the thermal cycle. The reason may again be relaxation processes taking place during annealing or a difference in thermal expansion coefficients of substrate and electrode material.

Besides the typical tunneling current one would expect for broken junctions, some of the contacts show additional features in their I-V characteristics. These artifacts are presumably caused by metallic grains created within the gap during electromigration and are subject to the next section.
4.2.5. Artifacts due to metallic residues

Even though most of the break junctions show either normal tunneling behavior or no conductance at all after electromigration, sometimes nonlinear feature-rich I-V curves were measured. Figure 4.14 shows an exemplary I-V trace taken at cryogenic temperatures directly after the electromigration process.

![I-V Characteristics](image)

Figure 4.14.: I-V characteristics measured at 42 K directly after electromigration on a sample without intended conducting islands. The curve exhibits clear Coulomb blockade and Coulomb staircase features. Inset: AFM scan recorded after the electric measurements.

On this sample neither quantum dots nor metallic particles were deposited on purpose. Nonetheless, the I-V curve shows a plateau around 0 V bias, which can be attributed to current suppression caused by Coulomb blockade. At higher negative as well as positive bias voltages the current increases in a step-like fashion known as the Coulomb staircase (see chapter 2.4). Both features indicate that an undesired conducting island was present in the gap between the two nano-electrodes. The plateau has a width of about 400 mV and the spacing of the steps is roughly 200 mV. Assuming a corresponding Coulomb energy of 200 meV, an island capacitance of 0.4 aF can be calculated. From this capacitance value we expect an island with a size of a few nanometers.

The island was presumably composed of metallic grains which were created unintentionally during the electromigration process. This assumption is supported by the AFM scan depicted as inset in figure 4.14, which was taken after the electrical measurement. The image shows a drop-like structure on the top electrode as already observed for uncontrolled electromigration, from which a very high junction temperature and
4. Electrode fabrication

the melting of gold during the process can be inferred. Taking a closer look at the gap between the electrodes, also smaller droplets can be seen which may potentially act as Coulomb island. It might be important to note that this was an electromigration carried out in the early stage of the development when the process was not yet as elaborated as the one presented in the previous sections.

Metallic grains introduced during the electromigration process and resulting artifacts in the electric characteristics of the tunnel junctions were also reported by other authors [110, 122, 112, 116]. Zant et al. [122] for example wrote that electromigration actually produces a whole range of different I-V characteristics including asymmetric I-Vs, Coulomb blockade, and Coulomb staircases as also observed in our experiments. The occurrence of these artifacts was reported to be on the order of 30 % of the junctions, which seems to be a lot higher than what we experienced. On the other hand, some of the authors attribute the unintentional creation of metallic particles during electromigration to a poor process control and an overheating of the junction. Taychatanapat et al. [116] reported that if the series resistance is kept low to prevent thermal runaway as outlined in section 4.2.2, no gold particles were found in the gap. This is consistent with the observations made in this work. In later experiments when the electromigration process was well controlled barely any junction showed unexpected artifacts.

We conclude that one can try to avoid the creation of undesired metallic islands within the break junction by optimizing the process control. Nevertheless one has to bare in mind that measurements performed on quantum dots or molecules directly after electromigration might still be related to artifacts caused by the process. The only way to avoid this is to first break the junction, next electrically characterize it, and only then deposit the nano-objects to be investigated. Unfortunately this is very inconvenient as it means that the sample has to be further processed and probably annealed or cooled after the nano-electrodes were fabricated. This may again change the properties of the junction as discussed in the previous section.

4.2.6. Electrode alignment to QDs

As shown in section 4.2.1, electromigration strongly depends on the current density and typically starts at the position in the conductor with the least cross sectional area. This property was used to align the evolving nano-electrodes to predefined quantum dots already present on the sample [127].

Therefore silicon quantum dots were fabricated by etching into a silicon on insulator (SOI) substrate using a self-assembled etch mask according to chapter 3.1. Next, gold nano-wires were patterned onto the sample covered with silicon QDs using electron
beam lithography and subsequent thermal evaporation as outlined in section 4.1. An AFM scan of such a metallic nano-wire on top of the QDs is shown in figure 4.15 (a).

Figure 4.15.: AFM scan and sketched cross-section of a gold nano-wire patterned onto SOI-based silicon QDs before (a,b) and after (c,d) EM.

The amount of material per area normal to the sample surface deposited during the metalization process is constant. Therefore the presence of the QDs leads to a locally reduced metal film thickness at the edge of the dots, as sketched in figure 4.15 (b). Hence, the nano-wire is likely to have its cross-section with the least area for the current to pass at a position of a QD. When the electromigration process is now performed on such a wire, the current density will have a maximum at the position of a dot and wire breakage will preferentially take place there. As a result, the evolving gap between the two electrodes is aligned to the quantum dot as desired. Devices fabricated with this technique will be characterized in section 5.2.

4.2.7. Electromigration on ferromagnetic nickel electrodes

Electromigration experiments were also performed on ferromagnetic nickel electrodes. The aim was to obtain a pair of two electrodes with different switching behavior for spin-dependent transport measurements. Therefore the shape anisotropy effect discussed in section 2.6.3 was utilized and several different electrode geometries were investigated. First, numerical simulations were carried out to estimate the switching behavior for different geometries. Then samples were fabricated with the most promising geometries, electromigration was performed and the transport properties were measured.
Numerical simulations

To find an optimized geometry for ferromagnetic electrodes to be switched between parallel and antiparallel magnetization, as described in section 2.6.3, numerical simulations were carried out similar to those reported by Pasupathy and Bolotin et al. [92, 20]. For the calculations the micromagnetic OOMMF code [34] was used. This software allows one to define a nearly arbitrary 2D geometry for a ferromagnetic object and to apply and change an external magnetic field. To calculate the magnetization $M$, the solver of this software package integrates the Landau-Lifshitz equation

$$\frac{dM}{dt} = -|\tilde{\gamma}| M \times H_{eff} - |\tilde{\gamma}| \alpha \frac{1}{M_s} M \times (M \times H_{eff}).$$

This equation describes the time evolution of the magnetization subject to an external field where $\tilde{\gamma}$ is the Landau-Lifshitz gyromagnetic ratio and $\alpha$ is the damping coefficient. The effective field $H_{eff}$ can be written as

$$H_{eff} = -\mu_0 \frac{1}{2} \frac{\partial E}{\partial M}.$$  

Here the average energy density $E$ is a function of $M$ specified by Brown’s equations, including anisotropy, exchange, self-magnetostatic (demagnetization) and applied field (Zeeman) terms [34].

We have studied a whole range of different geometries which showed substantial deviations in the difference of coercive field strength of upper and lower electrode. The coercive field strength associated with an electrode determines the external field at which its magnetization is switched. Another important point to look at was the direction of the local spins in the contact region, which did not always coincide with the average magnetization of the overall structure. An overview of the simulated electrode geometries is given in figure 4.16.

Geometries (b), (c) and (d) did not match the demands at all, because the coercive field strength for upper and lower electrode nearly coincided. For the very small field range where the average magnetizations were antiparallel, the local magnetization in the contact region was ill defined. Geometry (a) showed a relatively large difference in the magnetic switching field of the two electrodes, however the spin direction in the contact region was also not in good agreement with the electrode average. From the simulations, geometry (e) yielded the most promising results with respect to the difference in coercive field strength as well as the spin alignment in the contact region.

For geometry (e) the upper electrode had a rhombic shape with a length of 2 $\mu$m and a width of 1 $\mu$m and showed a relatively small coercive field of about 13 mT. Its easy magnetization direction lay in parallel with the long axis. The lower electrode
was a rhombus of the same size but truncated in width to 0.25 µm, and its magnetization switched in the simulations at a much higher magnetic field of about 35 mT. The structures were simulated to be 30 nm thick and made of nickel with a saturation magnetization $M_S = 490 \cdot 10^3$ A/m and an exchange stiffness $A = 9 \cdot 10^{-12}$ J/m. The crystalline anisotropy was neglected for the simulations as the electrodes in the experiment were polycrystalline and crystalline anisotropy effects were assumed to average out over all crystallites. The magnetization curve obtained from the numerical simulations for this geometry is depicted in figure 4.17.

Coming from large negative magnetic fields and passing 0 T the magnetization curve shows an abrupt jump at about 13 mT corresponding to the magnetization switching in the upper electrode. The insets show that the spins in the contact region change from a clean parallel (left-most inset) to a well defined antiparallel (second inset from right) configuration. At about 35 mT a second jump in the curve occurs and the magnetization of second electrode flips around. The right-most inset shows that the electrodes are now parallelly magnetized again, but in the opposite direction. The down-sweep shows exactly the same behavior.

The behavior of the electrodes with respect to coercive field strength and spin alignment in the contact region can be understood in the following way. The upper electrode has a much wider body with no edge parallel to the electrode axis, which makes it relatively easy to turn the magnetization from one axis direction to the antiparallel one. The lower electrode is very narrow with a long edge parallel to its axis. This leads to a higher stray field energy for magnetization perpendicular to the axis and therefore involves a higher switching field. Moreover, the angle of the electrode tips, which will
4. Electrode fabrication

Figure 4.17.: Simulated magnetization curve for optimized electrode geometry (e). The insets show the alignment of individual spins in the contact region for different magnetizations.

be the contact region after electromigration, is relatively sharp. This aspect leads to a “focusing” effect of the local spins towards the tips and results either in a clean parallel or an antiparallel configuration in the contact region.

Electromigration experiments

After finding the “optimal” geometry from the simulations, corresponding nano-electrodes were fabricated by electron beam lithography (see section 4.1). To avoid contact problems due to the oxidation of nickel, the macroscopic gold bond pads were patterned in advance and the nickel electrodes were aligned to them with the electron beam writer. A colorized SEM micrograph of a pair of nickel electrodes (purple) patterned on top of the bond pads on a SOI QD sample is shown in the inset of figure 4.18.

To obtain ferromagnetic electrodes with nanometer separation, electromigration was conducted on the initially connected electrode pairs with the scheme introduced in section 4.2.2. A typical breaking curve is depicted in figure 4.18. In comparison to gold, nickel showed a much higher reversible increase in resistance due to Joule heating when current was passed through the junction. This can be seen from the curvature of the initial voltage ramp and leads to difficulties with the feedback scheme. The breaking curve even turned horizontal at very low temperatures and therefore the breaking process had at least to be started at room temperature.

The I-V diagram shows three different traces, because the breaking process was repeatedly stopped to characterize the junction at different resistances. Before electro-
4.2. Electromigration

Figure 4.18.: Breaking curve of an electromigration process performed on nickel electrodes at room temperature. The electromigration was stopped three times to characterize the junction. Inset: colorized SEM micrograph of a nickel electrode pair with optimized electrode geometry.

Electromigration the sample had a resistance of 128 Ω and showed a magnetoresistance curve with a sharp symmetric minimum around 0 T like the rectangular reference samples. At a resistance of 350 Ω this characteristic was still visible, but much less pronounced. At 5 and 200 kΩ only a random, field independent switching between resistance values was observed and the measured curves were very noisy. This was attributed to a thermal rearrangement of the junctions.

Because of the instability of the resistance and the noise, the sample was cooled from room temperature to 4.2 K in a liquid helium bath cryostat. During cool down the conductance was recorded and is depicted in figure 4.19.

At the begin of the measurement the sample was still at room temperature and a switching between two discrete conductance values could be observed. These two values are assumed to correspond to two atomic configurations of the tunnel junction, between which the contact switched back and forth. Then, after about 600 s the sample was cooled down and the conductance gradually decreased. Finally, when reaching 4.2 K the conductance settled to a constant value, the switching disappeared and the noise was largely reduced.

Under these conditions magnetic measurements were performed on the sample by sweeping a magnetic field parallel to the current direction from about -0.4 to 0.4 T and back. The resistance was offset by the resistance at the begin of the sweep and normalized to that value. The resulting tunneling magnetoresistance (TMR) is measured in % and plotted in figure 4.20.
4. Electrode fabrication

![Conductance vs. Time Graph](image)

Figure 4.19.: Conductance of a nickel junction after EM during cool down from room to liquid helium temperature.

From the diagram it can be seen that at high negative magnetic fields the resistance in the up-sweep starts from the same value that it ends in the down-sweep. Also at high positive fields the resistance has the same value independent of the sweep direction. However, the resistance for high positive and negative fields differs, which is not yet understood. At lower magnetic fields a hysteresis is observed, which manifests itself in different resistance values for up and down-sweep.

Roughly speaking, the junction had a lower resistance at high magnetic fields and exhibited an intermediate increase in resistance after passing 0 T from either direction. This general behavior is in agreement with what we expect from the model in section 2.6.1 where high external fields lead to a parallel magnetization of the two nano-electrodes resulting in a low tunneling resistance. When the field is then swept from high negative values over 0 T into the positive region, the resistance suddenly increases. The increase can be attributed to the first electrode’s magnetization being switched and a subsequent antiparallel magnetization of the two electrodes. By sweeping the field to even higher positive values, the resistance dropped again, presumably coinciding with the switching of the second electrode and a restored parallel configuration. The down-sweep shows a similar behavior and can be understood in an analog way.

Despite this rough structure, also minor jumps and kinks can be seen in the curves, which are not so easy to interpret. Especially when the resistance is falling from the value assigned to the antiparallel configuration to the value for parallel magnetization, it first drops to a resistance even below that observed at high magnetic fields. Inter-
Figure 4.20.: Tunneling magnetoresistance measured at 4.2 K after electromigration. The red trace was recorded during an up-sweep, the green one during a down-sweep.

Interestingly, similar features can also be seen in the measurements reported by Pasupathy et al. [92] on nickel electrodes with a different geometry.

Even though these findings may not be completely explained at the moment, the following aspects could play a role. Possibly the two electrodes did not behave like two distinct domains, as suggested by the simulations, but rather consisted of multiple domains. This assumption is corroborated by the fact that the nickel electrodes were patterned on top of the relatively thick gold pads, which causes a step in the evaporated nickel film. The step was not accounted for in the 2D micromagnetic simulations, but could have a strong influence on the shape anisotropy of the electrodes and hence their switching behavior. Compared to the results of the simulations our measurements also yielded somewhat higher switching fields, which might be a related issue. Maybe also the exact grain structure in the contact region, which is of course not known, plays an important role in the transport properties. One other effect that cannot completely be ruled out is magnetostriction, which might have caused a tiny change in the shape of the electrodes due to the applied magnetic field [21] and thereby altered the tunnel coupling.

In this section we have shown that patterning initially connected nickel electrodes with a geometry optimized for shape anisotropy and subsequent electromigration yields a pair of nano-electrodes whose relative magnetization may be switched from a parallel to an antiparallel configuration by applying an external magnetic field. These electrodes can be used to perform spin-dependent transport measurements on nano-objects. Together with the preparation scheme for silicon quantum dots given in section 3.1 they
4. Electrode fabrication

in principle provide everything needed to fabricate a QD spin valve. However, further investigations will have to follow to clarify the additional features in the tunneling magnetoresistance curves that are not yet understood.

4.3. Electrochemical deposition

Besides electromigration, also electrochemical deposition was employed to fabricate nano-electrodes. It is a process typically used to coat metallic surfaces with other metals or to metalize conduction lines on printed circuit boards. Therefore the sample is immersed into an electrolyte solution containing ions of the desired metal. These ions are then reduced by either a chemical reaction or the application of an electric voltage and thereby deposited onto the surface. The basic theoretical background of this process is briefly summarized in section 4.3.1.

A few years ago it was realized that electrochemical deposition, also known as electroplating, can be used to fabricate nano-electrodes [81, 118, 119, 64]. Therefore two well separated electrodes were used as a template onto which metal was electrochemically deposited. Thereby the distance between the two electrodes was gradually reduced. At the same time the process could be monitored by measuring the conductance between the two electrodes.

The setup used for the electrochemical deposition experiments in the present work largely resembles the ones in the references above and is described in section 4.3.2. A positive deposition voltage led to a deposition of material and reduced the electrode separation until the electrodes eventually grew together. By applying a negative voltage, the process could be reversed and the electrodes were etched again. When the deposition voltage was repeatedly switched between positive and negative values, a cyclic closing and opening of the electrodes could be achieved (see section 4.3.3). As the electrodes were grown together slowly, conductance quantization was observed like in the electromigrated break junctions. This is shown in section 4.3.4. Before the electrodes actually touched each other or if they were reopened again by a negative deposition voltage, tunneling currents were measured after rinsing and drying the sample. These electrochemically fabricated tunnel junctions are characterized in section 4.3.5. Besides the deposition of gold, which was the material used for all experiments mentioned to this point, also ferromagnetic cobalt electrodes were deposited for potential spintronic applications (section 4.3.6). Finally, by slightly modifying the experimental setup, it was possible to deposit metal only onto one of the two template electrodes while still monitoring the conductance between them. This allowed for the fabrication of hetero-electrodes of two different materials with interesting possible applications, which is outlined in section 4.3.7.
4.3. Electrochemical deposition

4.3.1. Electrochemical background and electrolytes used

Electrochemistry is dealing with chemical reactions taking place at the surface of an electron conductor (e.g. a metal) immersed into an electrolyte solution, which involve the transfer of electrons between the electrode and species in the solution. A chemical reaction where the reactant gains electrons is called reduction, while the loss of electrons is referred to as oxidation. In normal chemical reactions oxidation and reduction are present at the same time and electrons are transferred between the different reactants leading to a redox reaction. However, it is also possible to spatially separate the two processes by introducing an external electric circuit, which then locally supplies or removes electrons. This situation is then called an electrochemical reaction and can either produce a voltage like in a battery or it can be driven by a voltage like electrolysis.

When two different metals are submerged in an electrochemical cell with appropriate electrolytes containing the positively charged ions of the metals, the less noble electrode will experience galvanic corrosion while material will be deposited onto the nobler one. The difference in nobility can be measured as a voltage drop between the two electrodes in an open circuit configuration. By comparing different elements and their ions or rather comparing each of them to a common reference like the standard hydrogen electrode (SHE), the galvanic series also known as the standard electropotential series can be obtained. Table 4.5 shows an excerpt of this series with some materials relevant to this work. The higher an element is positioned in the table the nobler it is and the harder it is to oxidize.

Table 4.5.: Standard electropotential series for some selected elements [5, 75].

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxidized form</th>
<th># of electrons</th>
<th>Reduced form</th>
<th>Standard potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (H$_2$O)</td>
<td>O$_2$(g) + 4 H$_3$O$^+$</td>
<td>4 $e^-$</td>
<td>6 H$_2$O</td>
<td>+1.23 V</td>
</tr>
<tr>
<td>Platinum (Pt)</td>
<td>Pt$^{2+}$</td>
<td>2 $e^-$</td>
<td>Pt</td>
<td>+1.20 V</td>
</tr>
<tr>
<td>Iodide (I$^-$)</td>
<td>I$_3^+$</td>
<td>2 $e^-$</td>
<td>3 I$^-$</td>
<td>+0.53 V</td>
</tr>
<tr>
<td>Gold (Au)</td>
<td>[AuI$_2$]$^-$</td>
<td>$e^-$</td>
<td>Au$_{(s)}$ + 2 I$^-$</td>
<td>+0.58 V</td>
</tr>
<tr>
<td>Gold (Au)</td>
<td>[AuI$_4$]$^-$</td>
<td>3 $e^-$</td>
<td>Au$_{(s)}$ + 4 I$^-$</td>
<td>+0.56 V</td>
</tr>
<tr>
<td>Hydroxide (OH$^-$)</td>
<td>O$_2$(g) + 2 H$_2$O</td>
<td>4 $e^-$</td>
<td>4 OH$^-$</td>
<td>+0.40 V</td>
</tr>
<tr>
<td>Hydrogen (H$_2$)</td>
<td>2 H$^+$</td>
<td>2 $e^-$</td>
<td>H$_2$</td>
<td>0 V</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>Fe$^{3+}$</td>
<td>3 $e^-$</td>
<td>Fe</td>
<td>-0.04 V</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>Ni$^{2+}$</td>
<td>2 $e^-$</td>
<td>Ni</td>
<td>-0.23 V</td>
</tr>
<tr>
<td>Cobalt (Co)</td>
<td>Co$^{2+}$</td>
<td>2 $e^-$</td>
<td>Co</td>
<td>-0.28 V</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>Fe$^{3+}$</td>
<td>2 $e^-$</td>
<td>Fe</td>
<td>-0.44 V</td>
</tr>
<tr>
<td>Water (H$_2$O)</td>
<td>2 H$_2$O</td>
<td>2 $e^-$</td>
<td>H$_2$ + 2 OH$^-$</td>
<td>-0.83 V</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>K$^+$</td>
<td>$e^-$</td>
<td>K</td>
<td>-2.93 V</td>
</tr>
</tbody>
</table>
4. Electrode fabrication

From the standard electropotential series one can in principle calculate the voltage between two electrodes of arbitrary material placed in an electrochemical cell, also known as the electromotive force (EMF). However, this is only possible if the standard conditions for temperature (25 °C), pressure (1 atm) and concentrations (1 mol/kg) are met. Especially the concentrations are non-standard in typical experiments. To still calculate an electrode potential $E$ for non-standard conditions, the Nernst equation

$$E = E^0 + \frac{RT}{nF} \ln \left( \frac{c_{ox}}{c_{red}} \right) \quad (4.3)$$

may be used [72]. Here $E^0$ is the electrode potential for standard conditions, $R$ the universal gas constant, $n$ the number of electrons involved in the reaction, and $F$ is the Faraday constant ($F = 96.485 \text{ C/mol}$). Furthermore, $c_{ox}$ denotes the product of all concentrations of oxidizing agents participating in the reaction, and $c_{red}$ of all reducing agents. Often activities are used rather than concentrations, which can be interpreted as effective concentrations.

The redox reactions taking place on a pair of electrodes immersed in an electrolyte solution can be influenced by applying an external voltage between them. If the bias voltage is high enough, metallic ions from the electrolyte will be reduced with electrons provided by the cathode. The resulting metal atoms precipitate on the negative electrode and therefore the process is referred to as electrochemical deposition or electroplating. On the other hand, metal atoms may be oxidized at the anode by extraction of electrons. The metal ions go into solution and the anode experiences corrosion.

The amount of material electrodeposited (or etched) is proportional to the charge transferred through the external circuit as already discovered by Faraday in 1834. The proportionality factor consists of the molecular mass $M$ of the deposited material, the valence number $n$ of the substance as an ion in solution and the Faraday constant $F$.

$$m = \frac{Q M}{F n}$$

To describe the kinetics of an electrochemical reaction, the Butler-Volmer equation can be used [3]. It was derived from chemical kinetics and states that the current density, and therefore the reaction or deposition rate, exponentially depends on the applied voltage $V$.

$$j = j_0 \left\{ \exp \left[ \frac{(1 - \alpha) nF}{RT} (V - V_{eq}) \right] - \exp \left[ -\frac{\alpha nF}{RT} (V - V_{eq}) \right] \right\} \quad (4.4)$$

The equilibrium potential $V_{eq}$ corresponds to the electrode potential $E$ calculated with the Nernst equation. If the voltage $V = V_{eq}$ is externally applied, equilibrium conditions are adjusted and oxidation and reduction rates are balanced. A deviation
4.3. Electrochemical deposition

\( V - V_{eq} \) from the equilibrium potential is called overpotential. The exchange current density \( j_0 \) equals the equilibrium oxidation and reduction current densities and is a measure for how much overpotential is needed to obtain a noticeable deposition. Furthermore, \( n \) is again the number of electrons involved in the reaction and \( \alpha \) is the so-called transfer coefficient or symmetry factor, which corresponds to the difference in activation energy for oxidation and reduction and reflects the structure of the double layer at the electrode surface. The equation is valid when the reaction is controlled by the charge transfer at the electrode rather than by the mass transfer to or from the electrode surface.

In the experiments presented here two different electrolyte solutions were used. For the electrochemical deposition of gold a gold saturated iodine potassium iodide solution was employed, while cobalt was deposited from a buffered \( \text{CoSO}_4 \) solution. In the following these electrolytes are discussed in more detail.

**Gold saturated \( I_2\text{KI} \) solution**

For the electrochemical deposition and etching of gold a recipe introduced by Umeno and Hirakawa [119, 118] based on a gold saturated \( I_2\text{KI} \) solution was used. Elementary iodine \( I_2 \) is nearly not soluble in water, however, if iodide ions \( I^- \) are already present in the solution, \( I_2 \) can be dissolved under formation of polyiodide ions [95, 96].

\[
I^- + I_2 \rightleftharpoons I_3^- \\
I^- + I_3^- \rightleftharpoons I_4^- \\
I_5^- + I_2 \rightleftharpoons I_7^-
\]

Polyiodide ions with more I atoms are also possible, but typically \( I^- \) and \( I_3^- \) are the prevailing species. In our recipe the initial \( I^- \) ions necessary to dissolve elementary iodine are provided by the potassium iodide KI. An even higher solubility of iodide is achieved if the solvent contains some ethanol.

In the experiments 2 % by weight of potassium iodide KI were dissolved in 70 % by volume of ethanol the remainder being deionized water. Next, 3 % by weight of elementary iodine \( I_2 \) was added to the solution at 110 °C under constant stirring, resulting in a dark red tincture. Similar mixtures are typically used to etch gold.

Iodide solutions are capable of dissolving gold, because gold forms Au(I) and Au(III) complexes with halides and in particular with iodide [95]. Thereby the (anodic) oxidation process is described by
4. Electrode fabrication

\[ \text{Au} + 2 \text{I}^- \rightleftharpoons [\text{AuI}_2]^- + e^- \]

while the (cathodic) reduction follows the following reaction equation.

\[ \text{I}_3^- + 2 e^- \rightleftharpoons 3 \text{I}^- \]

The overall redox reaction can thus be obtained by stoichiometrically combining the above equations \[95, 83\].

\[ 2 \text{Au} + \text{I}_3^- + \text{I}^- \rightleftharpoons 2 [\text{AuI}_2]^- \]

In this reaction gold atoms from the solid phase are oxidized to the very stable \([\text{AuI}_2]^-\) complex which then goes into solution. In a similar reaction also the less stable complex \([\text{AuI}_4]^-\) may be created. As the reaction equation describes an equilibrium, the back reaction where the complexed gold is reduced to the elementary form is also always present. Thereby the relative rates for forth and back reaction are determined by the concentration of \([\text{AuI}_2]^-\) ions and hence the amount of gold already dissolved.

To obtain a solution capable of dissolving and depositing material, the I\textsubscript{2}KI tincture had to be saturated with gold. The amount of gold needed was estimated to be 0.44 g/l by setting the Nernst equation for the corresponding redox reaction to zero and solving it for the \([\text{AuI}_2]^-\) concentration. Typically gold was added in excess to guarantee the saturation of the solution. When enough gold had been dissolved, the rates for dissolution and deposition compensated each other and effectively no more gold was etched. Under these equilibrium conditions the balance between the two process directions could be influenced by an external voltage applied between the working electrode that should be etched or deposited upon and a counter electrode. In most cases gold was used as electrode material for both electrodes.

The gold saturated I\textsubscript{2}KI solution was characterized by varying the bias voltage between two immersed gold electrodes from -1 to 1 V. As expected, nearly no deposition current was measured at 0 V bias and hence gold was neither etched nor deposited. When the voltage between the electrodes was increased a roughly exponential increase in the deposition current was observed. As the applied voltage was switched from positive to negative also the deposition current changed its sign. Evidently, deposition and etching of gold on the working electrode was possible depending on the sign of the deposition voltage. The measured deposition current was further fitted with the Butler-Volmer equation 4.4 where an exchange current density \(j_0\) of about 2 mA/cm\(^2\) and a symmetry parameter \(\alpha\) of 0.46 were found.
For the electrochemical deposition of cobalt a recipe from Deshmukh et al. [33] based on an aqueous solution of cobalt sulfate (CoSO₄) was adopted. In the experiments a CoSO₄ concentration of 0.22 M was used. Furthermore, 0.2 M citric acid and 0.12 M potassium citrate were added to the mixture acting as a buffer system to adjust the pH value and increasing the conductivity of the solution [33]. From the acidity constant of citric acid, its concentration and the concentration of its conjugate base, the citrate, a pH of 2.9 is expected.

In solution the cobalt sulfate dissociates into the Co²⁺ and the two times negatively charged sulfate ions. At the cathode the cobalt ions can be reduced to elementary cobalt

\[ \text{Co}^{2+} + 2e^- \rightarrow \text{Co} \]

which thereby precipitates onto the electrode. For the counter electrode typically inert platinum or gold electrodes were used in our experiments. Therefore the first anodic reaction energetically accessible to provide the electrons needed for the reduction of Co²⁺ ions is the electrolysis of water molecules into hydronium ions (H₃O⁺) and oxygen (O₂).

\[ 6 \text{H}_2\text{O} \rightarrow \text{O}_2(\text{g}) + 4 \text{H}_3\text{O}^+ + 4e^- \]

The overall redox reaction is again obtained by stoichiometrically combining the two equations.

\[ 2 \text{Co}^{2+} + 6 \text{H}_2\text{O} \rightarrow 2 \text{Co} + \text{O}_2(\text{g}) + 4 \text{H}_3\text{O}^+ \]

With the standard electrode potentials from table 4.5 the Co²⁺ concentration and the pH value the electrode potential for the redox reaction can be calculated using Nernst’s equation 4.3. The calculation yields a value of 1.36 V, which is the least voltage between working and counter electrode necessary for cobalt deposition. The actual voltage needed for observable deposition is expected to be even slightly higher due to overpotentials caused for example by the serial resistance of the electrolyte. In the experiments we found that a voltage of 1.4 V was needed to obtain a decent deposition.

In this section we have seen that metal can either be deposited upon or etched from a working electrode by an electrolyte solution depending on the voltage applied with respect to a counter electrode. With the electrolytes introduced above, material was deposited onto two nano-electrode templates acting as one working electrode while
monitoring the conductance between them. This is shown in the next section.

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4.3.2. Symmetric deposition of gold

As basis for the electrochemical deposition experiments template electrodes were patterned onto a silicon wafer covered with a 200 nm insulating silicon oxide layer by means of electron beam lithography (as described in section 4.1). After evaporation of 10 nm titanium as adhesion layer and 90 nm gold as electrode material a lift-off was performed to obtain the templates. The process yielded electrode pairs with an initial separation of about 200 nm as can be seen from the SEM micrograph depicted in figure 4.22(b) taken before electrochemical deposition.

Next, most of the electrodes was covered with resist to protect it from the electrolyte solution. Only a small area around the initial gap was omitted to be accessible for the deposition. It turned out that not all resists were able to withstand the ethanolic electrolyte solution and some were dissolved during the process. The best results were obtained with the very imperishable PMGI-SF8 resist (MicroChem Corp.), which was either deposited manually under a binocular microscope or with an additional photolithography step. The function of this resist cover was not only to protect the electrodes but also to reduce the ionic current background in the monitoring circuit. The so-prepared electrodes were then immersed into the electrolyte solution. For the deposition of gold the gold saturated iodine potassium iodide solution discussed in the previous section was used. As counter electrode a gold covered glass sheet was employed in our setup.

For the actual deposition process both nano-electrodes were connected to the same DC potential while the deposition voltage was applied with respect to the counter electrode. Sometimes also a potentiostat setup was employed where the voltage is currentlessly measured at a reference electrode to eliminate the serial resistance of the electrolyte solution. At the same time an AC voltage was applied between the two nano-electrodes and the corresponding current was measured with a lock-in amplifier over a 100 Ω shunt resistance. An additional 150 Ω resistance was introduced into the second branch to compensate for the internal resistance of the AC voltage source and the shunt resistance and realize a symmetrical setup. With an asymmetric setup typically also an asymmetric deposition was observed. A sketch together with images of the actual setup is shown in figure 4.21.

For the deposition of gold from the I\textsubscript{2}KI solution deposition voltages between 20 and 200 mV were applied. The AC voltage was kept as low as possible which typically was 10 mV at a frequency of about 1 kHz. Figure 4.22(a) shows an overview of the electrical signals recorded during a typical gold deposition process. After about 200 s
4.3. Electrochemical deposition

![Diagram of electrochemical deposition setup]

Figure 4.21.: (a) Schematic illustration and (b) photographic images of the experimental setup for symmetric electrochemical deposition.

The deposition voltage, shown in the upper diagram, was switched on to a value of 60 mV and a corresponding deposition current was measured. During the deposition process the current, which is assumed to be proportional to the electrode area and a measure for the material deposited, slowly increased. This can be attributed to an increase of the sample surface, which is corroborated by the SEM micrograph in figure 4.22 (c) taken after deposition. It shows a much rougher surface covered with gold crystallites compared to the reference image 4.22 (b) taken before the deposition. Finally, after about 18 min the conductance depicted in the lower diagram steeply increased indicating that the nano-electrodes had grown together.

If one takes a closer look at the monitoring conductance at the begin of the process, which is done in figure 4.23, one can see that there are two distinct jumps. Between 0 and 100 s the sample was not yet immersed into the electrolyte solution and the conductance measured at that point mainly reflects the noise floor of our setup. After about 100 s the sample was immersed into the electrolyte, which coincides with the first step in the conductance. At this time the deposition voltage was still switched off and the increase in the monitoring conductance can be attributed to the ionic conductance of the electrolyte between the 200 nm separated electrodes. The height of this step depended on the area of the electrodes exposed to the electrolyte, which was therefore kept as small as possible. After about 200 s the deposition voltage was switched on, which caused a second step in the monitor conductance. At first glance the reason for this is not obvious as the DC deposition voltage should not influence the AC monitoring circuit. On the other hand the electrostatic potential induced by the deposition voltage will cause the ions in the electrolyte to move and locally change their concentration. This change in concentration between the nano-electrodes is then reflected in the AC monitoring current. It is important to note that at this stage of
Figure 4.22.: (a) Electrical signals recorded during the electrochemical deposition of gold: the deposition voltage (blue), the corresponding deposition current (red) and the monitor conductance (green). SEM micrographs of an electrode pair (b) before and (c) after the deposition process.
the process the monitor conductance was still clearly below the conductance quantum $G_0 = 2e^2/h$, at least when the electrodes were properly protected by PMGI-SF6 resist. This is important, because the conductance rising over $G_0$ is taken as a criterion that the electrodes touch each other.

With the process illustrated in this section it was possible to grow two separated electrodes together where the speed of growth could be controlled by the deposition voltage. The process was monitored via an AC conductance measurement between the two electrodes. When this conductance exceeded the conductance quantum $G_0$ it was assumed that the electrodes had joined and the main electric transport occurred by metallic conductance. In the next section it is shown that the electrodes could be separated again by applying a negative deposition voltage and thereby etching away material.

### 4.3.3. Cyclic deposition and etching

In the previous section it was shown that applying a positive voltage with respect to the counter electrode results in a positive deposition current and hence in the deposition of gold onto the working electrodes. However, when the deposition voltage was set to negative values also the deposition current became negative corresponding to the oxidation and dissolution of gold atoms. Thereby the separation between the two nanoelectrodes was increased or the electrodes could be opened again after they had grown together.
4. Electrode fabrication

Figure 4.24 (a) shows an excerpt of the electrical signals recorded during a process where the deposition voltage was switched between -30 mV and 80 mV each time the monitor conductance reached a lower \((0.2G_0)\) or an upper \((7G_0)\) threshold value indicated by horizontal lines in the lower diagram. Thereby, the electrodes were cyclically closed and re-opened.

Figure 4.24.: (a) Electric signals recorded during a cyclic deposition and etching process: the deposition voltage (blue), the corresponding deposition current (red) and the monitor conductance (green). In the conductance diagram the threshold values are indicated by horizontal lines. (b) SEM micrographs of an electrode pair after a deposition process with 60 cycles.

One can also observe that the deposition current was slowly rising throughout the process. From the findings in the previous section it can be concluded that the electrode surface had increased even though the conductance between the electrodes was always kept in the same range. This process can therefore be regarded as quasi-reversible, because the contact can be closed and re-opened and the distance between the electrodes can either be reduced or increased, but this is accompanied by an irreversible change of the electrode morphology. This change is also evident from the SEM micrographs in figure 4.24 (b) taken after a cyclic deposition and etching process with 60 cycles.

It was not only possible to close and re-open the nano-electrodes, as outlined in this section, but we were also able to very accurately control the coalescence process by setting an appropriate deposition voltage. This control could be extended to a regime
where single atoms arranged between the two electrodes giving rise to conductance quantization.

**4.3.4. Quantized conductance in electrochemically grown electrode pairs**

In this section a closer look at the monitor conductance is taken in the phase where the electrodes finally grow together. When the deposition voltage was kept low enough and therefore the deposition of gold atoms was slow, some samples showed a step-like evolution of the conductance similar to that observed in electromigration. One exemplary conductance trace is shown in figure 4.25.

![Conductance trace](image)

**Figure 4.25.:** Monitor conductance recorded during the coalescence phase of a slow electrochemical gold deposition process. The conductance increases in steps of integer multiples of $G_0 = 2e^2/h$.

The monitor conductance was recorded during a gold deposition process performed according to the specifications given in section 4.3.2 and driven with low deposition voltages between 20 and 70 mV. It can be seen from the diagram that the conduction increased roughly in steps of integer multiples of the conductance quantum $G_0 = 2e^2/h$. Prominent steps are visible at 2, 6, 10, 14 and $15G_0$. Another very common way to plot the data is a conductance histogram where the occurrence is plotted over the corresponding conductance value. A conductance histogram gained from the data in figure 4.25 is depicted in figure 4.26.

In this representation the cumulative occurrence of integer multiples of $G_0$ is even more obvious. Following the same interpretation as in the case of electromigration, each step in the conductance trace or each peak in the histogram is attributed to an atomic
4. Electrode fabrication

Figure 4.26.: Conductance histogram for the coalescence phase of a slow electrochemical gold deposition process. The conductance preferentially takes values of integer multiples of $G_0$.

configuration of the nano-junction with only a few atoms bridging the electrodes. The conductance of the junction is then again governed by the number of transport channels and the corresponding transmission rates, as already outlined in section 4.2.3. From these observations we conclude that besides electromigration also our electrochemical deposition process is suited to prepare metallic quantum point contacts. Conductance quantization in electrochemically grown nano-electrodes was also reported by Morpurgo et al. \[81\] and He et al. \[51\].

The fact that conductance quantization has been observed during the fabrication of the nano-electrodes indicates how accurate the control of the deposition process was. This degree of control should also allow us to prepare separated electrodes with a very small distance and adjust their separation. Therefore the two electrodes were first grown together. After the conductance had reached a few $G_0$, the deposition voltage was set to a small negative value until the integrated deposition current, which corresponds to the amount of material electrochemically etched, had reached a preset amount and the junction was re-opened. This approach yields the advantage that one does not directly depend on the monitor conductance as measure for the electrode separation, which is influenced by many parameters like for example the exposed electrode area. Often connected electrodes with a conductance of a few $G_0$ also spontaneously re-opened when the deposition voltage was switched off and the sample was removed from the electrolyte, rinsed and dried. The resulting tunneling junctions are analyzed in the following section.
4.3.5. Tunneling characteristics of nano-electrodes

After rinsing with deionized water and drying with nitrogen many electrode pairs showed a conductance clearly below $G_0$ and had a typical tunneling I-V characteristic. This was either the case when the electrodes were deliberately re-opened by electrochemical etching or sometimes just happened spontaneously during sample removal from the electrolyte. An exemplary I-V curve is depicted in figure 4.27.

![I-V characteristic of an electrode pair after electrochemical deposition showing tunneling behavior. The solid line shows a fit with Simmons formula using an electrode separation $s = 1.00 \text{ nm}$, a barrier height $\varphi = 3.58 \text{ eV}$, and a contact area $A = 4.81 \cdot 10^{-17} \text{ m}^2$ as fit parameters. Inset: SEM micrograph of the respective junction.](image)

The currents measured in this sample were in the pA regime and the curve shows the s-shaped characteristic typical for tunneling junctions. In the diagram also a fit with Simmons formula (2.9) is plotted. The parameters for the calculated curve were a barrier width $s = 1.00 \text{ nm}$, a barrier height $\varphi = 3.58 \text{ eV}$, and a junction cross section $A = 4.81 \cdot 10^{-17} \text{ m}^2$. The barrier height is again a little bit lower than the expected work function of gold, but this can be attributed either to the simplicity of Simmons’ model or to electrons tunneling through the SiO$_2$ substrate. For a more detailed discussion regarding the barrier height see the respective electromigration section 4.2.4. Even though the reason for the low barrier height is not completely elucidated yet, this analysis implies that the distance between the two electrodes is rather small. We therefore conclude that the electrochemical deposition scheme yields nano-electrodes with a separation of less than 2 nm.

Very often also much higher tunneling currents were observed after electrochemical...
deposition. However, the corresponding I-V curves could not satisfyingly be fitted with the Simmons formula. The reason for this might be the break down of Simmons’ model for very thin barriers or the presence of a thin water film on the sample.

In this section we have seen that electrochemical deposition is capable of producing nano-electrodes with a separation of less than 2 nm, which is comparable to the results accomplished with electromigration. In the experiments discussed so far a I$_2$KI electrolyte solution was used and the material deposited was gold. However, the electrochemical deposition process was also extended to other electrolytes suitable to deposit different metals. In particular it was possible to deposit ferromagnetic cobalt, which will be the topic of the next section.

4.3.6. Symmetric deposition of ferromagnetic cobalt

With the setup presented in the previous sections it is in principle also possible to deposit ferromagnetic metals such as cobalt or nickel. In the following experiments we used the buffered CoSO$_4$ solution from reference[33] introduced in section 4.3.1. Deshmukh et al. had shown that cobalt could be deposited with this electrolyte.

For the deposition process voltages up to 1.5 V were used while the monitoring AC voltage was kept constant at 10 mV. In figure 4.28 (a) the electrical signals recorded during an exemplary cobalt deposition are depicted. In this experiment the deposition voltage was set to 1.4 V and a positive deposition current was measured indicating the deposition of cobalt onto the template electrodes. This is in good agreement with the electrochemical consideration in section 4.3.1, which predict a minimum required deposition voltage of 1.36 V.

The monitor conductance plotted in the lower diagram showed a relatively pronounced increase when the deposition voltage was switched on. As outlined earlier, this effect is presumably related to a change in the ion concentrations around the nano-electrodes due to the deposition voltage, which causes an increase in the ionic conductance. After the step-like increase at 110 s process time the conductance stabilized to about $0.1G_0$ until it steeply skyrocketed at 430 s to values clearly above $G_0$ indicating a connection between the two electrodes. The steepness of the rise shows that the growth was very fast and not as controlled as in the case of gold deposition. Also smaller voltages have been tried to achieve a better control over the deposition, but this usually resulted in electrode pairs not growing together at all. This is, however, not surprising when we consider the expected minimum deposition voltage of 1.36 V. Further experiments have to be performed and the electrolyte recipe needs to be optimized to improve the control over this process. One strategy might be to use a sacrificial cobalt counter electrode, which would be dissolved during the deposition
Figure 4.28.: (a) Electric signals recorded during the electrochemical deposition of cobalt: the deposition voltage (blue), the corresponding deposition current (red) and the monitor conductance (green). (b) SEM micrograph of an electrode pair after the deposition process.
4. Electrode fabrication

process. This is expected to largely reduce the electrode potential and resembles the situation present for the deposition of gold.

Figure 4.28 (b) shows a SEM micrograph of the electrode pair taken after the deposition process. It can be seen that the original gold templates were covered by cobalt crystallites.

Until now it was shown that electrochemical deposition is capable of fabricating nano-electrodes of magnetic and non-magnetic material. With these results it is on par with the electromigration process, however it is a much more laborious process and involves the not so well controlled transfer of the electrodes out of the electrolyte solution. In the following section an asymmetric deposition process is discussed, which permits to produce hetero-electrodes of different materials. This is not possible with any other method and might make up for the bigger effort of the process.

4.3.7. Asymmetric deposition - fabrication of hetero-electrodes

For an asymmetric deposition of material, the experimental setup introduced in section 4.3.2 had to be slightly modified. To prevent the deposition onto one of the electrode templates this electrode was decoupled from the DC circuit by introducing a capacitor as proposed by Deshmukh et al. Consequently, on average no charges could enter or leave the electrode via the external circuit and no material was deposited or etched. On the other hand, the capacitor is permeable for AC currents with higher frequencies, which allowed us to still monitor the conductance between the nano-electrodes as a measure for their separation. A schematic of this modified setup is depicted in figure 4.29 (a).

Figure 4.29.: (a) Schematic of the experimental setup used for asymmetrical deposition with the right template electrode decoupled by a capacitor and (b) a colorized SEM micrograph of a pair of platinum electrode templates after asymmetric deposition of gold onto the left electrode.
4.3. Electrochemical deposition

For the capacitance typically a film capacitor with 4.7 $\mu$F was used. Together with a frequency of 1.23 kHz for the AC monitoring voltage (typically 10 mV) an AC resistance of about 10 $\Omega$ was calculated. Therefore the monitoring current could pass the capacitor nearly unaffected and it was still possible to determine the conductance between the nano-electrodes.

For the first experiment platinum electrodes were used as template and gold was deposited from the I$_2$KI electrolyte introduced in section 4.3.1. The deposition voltage was again set to values between 80 and 120 mV. Figure 4.29 (b) shows a SEM micrograph of such a platinum electrode pair after asymmetric deposition of gold. The image was additionally colorized to emphasize the different materials. The original platinum electrodes were colored in gray, while the crystallites presumably deposited during the process were colored yellowish as they are assumed to be gold. The underlying silicon oxide substrate was colored in green.

From the image one can clearly see that gold was only deposited onto the left electrode while the right electrode, which was attached to the capacitor, is still untouched. However, not the whole area of the left electrode is covered with gold. Most of the material was deposited close to the tip of the electrode. This phenomenon did not occur in all experiments but was observed on several samples. One possible explanation is that there was a strong field enhancement effect at the sharp tip of the electrodes due to their different potential, which was not present when they were kept at the same DC potential. As the effect was not always observed, the remaining process parameters also seem to have an influence. One strategy to avoid selective deposition at the tip might be to apply a high deposition voltage at the begin of the process to generate seed crystals everywhere on the electrode and to reduce the bias later on to achieve a controlled deposition.

The control over the asymmetric deposition process is comparable to that for the symmetric one. Figure 4.30 shows a monitoring conductance trace recorded during an asymmetric gold deposition process with a deposition voltage of 120 mV. In the diagram again steps at integer multiples of the conductance quantum $G_0$ are visible. As discussed earlier, these steps correspond to specific configurations of the junction at the atomic level and show the excellent control over the process.

In a second experiment the asymmetric deposition of magnetic material was investigated. Therefore the setup introduced above was used together with the buffered cobalt sulfate solution from section 4.3.6. As material for the electrode templates gold was chosen. For the process again a deposition voltage of 1.4 V was employed and the conductance was monitored with a 10 mV AC voltage. Two SEM micrographs of an electrode pair after asymmetric deposition of cobalt are shown in figure 4.31.

The images show that cobalt crystallites were only deposited onto the left electrode
while the right one, which was decoupled by the capacitor, remained unaltered. The upper SEM micrograph shows a top view of the electrode pair, whereas the lower one was taken under an angle of 70 to 80°. In addition, the lower image was colorized to illustrate the different materials on the sample. Green represents again the silicon oxide from the substrate, yellow was used for gold, and purple for cobalt.

The crystallites deposited onto the left electrode show a very rough morphology. This might have disadvantages if one wants to place nano-objects between the two electrodes and image them either by SEM or by scanning probe techniques. As a work around one could start from templates with a smaller electrode separation, which would reduce the required deposition time and hence the thickness of the deposited film. Another approach is to work with reduced deposition speed as it was reported that a slower deposition tends to yield smoother films [33]. Finally, special additives are known from the electrochemical filling of microvias and interconnects to improve the morphology and roughness of the deposited film. Further experiments have to be carried out to optimize the process in terms of film quality following the approaches mentioned.

In this section a fabrication technique for hetero-electrodes made from two different materials with a very good control over the electrode separation was demonstrated. These hetero-electrodes open very interesting possibilities for further experiments.

The gold platinum electrode pairs may for example be used to contact bi-functionalized molecules. By means of organic chemistry it is possible to synthesize molecules with distinct functional groups such as thiols and isonitriles [125]. If one now takes a...
4.3. Electrochemical deposition

Figure 4.31.: SEM micrographs of a pair of golden electrode templates after asymmetric deposition of cobalt. Cobalt crystallites were only deposited onto the left electrode, while the right one remained untouched.

molecule with one group preferentially binding to gold (e.g. a thiol group) and a second group with an affinity to platinum (e.g. a isonitrile group), an oriented deposition onto the hetero-electrodes is conceivable. This scheme would be a large step into the direction of single molecule electronics.

On the other hand, ferromagnetic hetero-electrodes offer an interesting tool for spintronic applications. If e.g. nickel electrodes had been taken as template in the experiment above, the result would have been a pair of two ferromagnetic electrodes with a separation of only a few nanometers and with different magnetic properties. In particular, the coercive fields of cobalt and nickel differ by a factor of more than ten and hence the electrode magnetization is expected switch at different external fields. This feature is the prerequisite to observe tunneling magnetoresistance as discussed in 2.6.1. If such a pair of electrodes is employed to contact a quantum dot, a QD spin valve may be realized (see section 2.6.2).

In this chapter two alternative techniques besides electron beam lithography were introduced to fabricate nano-electrodes. Both methods were compared and their individual advantages and drawback were pointed out. The prepared nano-electrodes open a wide field of possible applications including single-electronics, molecular electronics, and spintronics. According to the requirements of the desired experiment the appropriate technique can be chosen. In this work nano-electrodes were used to contact individual semiconductor quantum dots. Thereby the electromigration scheme was used to fabricate most of the devices presented in the next chapter.
5. Electrical measurements

Different combinations of the techniques introduced in the previous two chapters were employed to fabricate nano-electronic single-electron devices. In this chapter the electrical characterization of these devices is addressed and their properties are compared to numerical simulations and similar experiments in literature.

In section 5.1 the measurement setup used to characterize the samples at cryogenic temperatures is briefly illustrated. Section 5.2 covers the electrical measurements on samples based on silicon-on-insulator quantum dots (SOI-QDs). Finally, in section 5.3 the results on CdSe/ZnS core/shell quantum dot based devices are presented.

5.1. Measurement setup

To electrically characterize the samples, they were glued and bonded onto a custom made chip carrier. The chip carriers consisted of a little PCB with bond pads for 18 signals, a sample back contact and an electric shield plane. The 20 leads of the chip carrier were designed to fit the corresponding socket on the sample holder depicted in figure 5.1(b), which allowed us to connect the signals within a liquid helium bath cryostat. It was possible to contact up to 14 devices in parallel on the same sample.

The transport experiments were carried out at low temperature, typically at 4.2 K. Therefore the samples were mounted in a liquid helium bath cryostat. The cryostat was equipped with a liquid helium reservoir and a liquid nitrogen shield as sketched in figure 5.1(a). The sample was placed in the sample chamber and the liquid helium inlet was controlled via a manual valve. Furthermore, a diode to measure the temperature and an electrical heater were connected to a feedback control system, which in principle allowed to adjust and hold a desired chamber temperature. However, it was found that the electrical heater would interfere with the low current measurements and was therefore switched off during the actual data acquisition.

For plain I-V measurements a Model 236 Source-Measure Unit (SMU) from Keithley Instruments Inc. was used. This device had a variety of different integration and filtering settings and, provided the adequate adjustment of these parameters, it was capable of sourcing voltages down to 0.5 mV and at the same time measuring currents...
5. Electrical measurements

Figure 5.1.: (a) Schematic illustration of the setup used to directly measure the differential conductance of a device mounted in a liquid helium bath cryostat and (b) an image of the respective sample holder with sample.

in the pA range. For measurements in this regime long integration times were required accumulating to about 15 min for an I-V trace with 201 points.

From the measured I-V curves the differential conductance could be obtained by numerical differentiation. Therefore the delta in current between two subsequent data points was divided by the corresponding delta in the applied voltage. Unfortunately, the noise present in the measured I-V data was amplified by this technique, especially when the points on the voltage axis were very dense and the difference in current was small. To circumvent this problem the measured data was smoothed by a numerical low-pass filter before differentiation. Care was taken not to distort the original shape of the curves or to smear out features that were of interest by the filtering procedure.

Alternatively, the differential conductance could be measured directly with a lock-in amplifier technique. The setup for this technique is sketched in figure 5.1 (a). Again a Keithley SMU was used to source the bias voltage across the device under test (DUT). This bias voltage was then superimposed with an AC voltage from the internal oscillator of a Stanford Research SR830 lock-in amplifier by a summation operational amplifier circuit. As depicted in the sketch, this sum signal was then connected to one lead of the DUT, while the other lead was connected to a current amplifier which converts the current through the device into a voltage. This voltage was fed into the lock-in amplifier input jack. The lock-in amplifier correlates (multiplies) the input voltage with its internal reference oscillator and thereby filters the part in the signal which changes
with the frequency of the oscillator and rejects the DC part and any other frequency components. If this periodic change in the current through the device is divided by the amplitude of the oscillator, the result equals the differential conductance for the bias adjusted at the SMU. At the same time, the voltage from the current amplifier was measured with a second SMU whose internal filters extracted the DC part of the signal and provided a parallel I-V measurement. The lock-in amplifier was typically operated with an oscillator frequency of 12.3 Hz and an amplitude of 10 mV.

One main advantage of directly measuring the differential conductance was a strong suppression of noise due to the lock-in technique. In addition, no further noise amplification was generated during numerical differentiation. Hence, the quality of these differential conductance curves easily outperformed those obtained from direct I-V measurements. On the other hand, an even longer measurement time was necessary. Depending on the date on which an experiment was performed and on its requirements with respect to measurement time, either one of the above setups was employed. Earlier experiments were typically carried out with direct I-V measurements, while the lock-in setup was used in more recent investigations when applicable.

5.2. Measurements on SOI-SiQDs

Single-electron devices based on SOI-QDs were fabricated employing the techniques described in the previous chapters. Samples covered with silicon quantum dots and quantum discs were obtained by etching into a SOI substrate according to section 3.1. To utilize these silicon nanostructures as islands in SET devices they had to be contacted with nano-electrodes. Therefore electrodes were fabricated either by direct writing with electron beam lithography (section 4.1) or with the electromigration technique described in section 4.2.6. In the former case an array of thousands of nano-electrode pairs was written onto the QD covered sample and promising devices were selected by SEM investigation and contacted with bond pads in a second EBL step. In the latter case metallic nano-wires were patterned on top of the QDs and broken with electromigration such that the gap preferentially aligned to the QDs already present on the sample. In both cases the native oxide on the silicon structures served as tunneling barrier.

The electrical measurements presented in the following sections were performed at 4.2 K. First, I-V and dI/dV-V measurements were conducted at a constant or without a gate voltage to characterize the devices (section 5.2.1). Next, if a sample showed single-electron tunneling behavior, the bias voltage was kept constant and the gate voltage was swept (section 5.2.2). Finally, I-V and dI/dV-V curves were taken for a range of different gate voltages and a so-called stability diagram was obtained for the
5. Electrical measurements

Sample as shown in section 5.2.3.

5.2.1. I-V measurements

Samples with 100 nm silicon quantum discs were contacted by direct electron-beam writing. After the selected devices had been equipped with bond pads, the samples were attached to a chip carrier and mounted in the liquid helium bath cryostat for the measurements. Then the current through each device was measured as a function of the applied bias voltage. Many devices showed no current at all in the voltage range from -3 V to 3 V. Some of these devices expressed a Fowler-Nordheim tunneling behavior when even higher voltages were applied. However, a few devices showed feature-rich I-V and dI/dV-V curves even at voltages below 0.2 V. An exemplary dI/dV-V trace recorded with the lock-in amplifier technique is depicted in figure 5.2.

![dI/dV-V curve measurement](image)

Figure 5.2.: dI/dV-V curve measured at 4.2 K on a 100 nm silicon quantum disc contacted with EBL electrodes. Together with the measurement a calculated curve is shown. Inset: SEM micrograph of the device. On the right there is a band diagram illustration of the device in the Coulomb blockade regime (A) and at a the positive threshold voltage (B), where the first state becomes available for transport. In (C) the same voltage with negative sign is applied.

The curve shows a plateau around 0 V bias with a width of about 50 mV. On the negative voltage side, the conductance starts to rise at a threshold voltage of...
5.2. Measurements on SOI-SiQDs

-15 mV and subsequently exhibits 4 fairly equidistant peaks with a mean spacing of about 50 mV. On the positive voltage side, the conductance is set on at a voltage of about 27 mV. Here one strong conductance peak is followed by a weaker one partially obstructed by a general increase in conductance. The peak spacing on the positive side can be estimated to be on the order of 80 mV.

These findings can be interpreted the following way: The SET island consists of a boron-doped silicon quantum dot which has an acceptor binding energy of 45 meV. Therefore, the Fermi level is expected to lie close to the valence band edge as depicted in sketch (A) of figure 5.2. The actual position of the Fermi level is also influenced by the background polarization charge $Q_p$. When a positive bias voltage is applied to the device as sketched in (B), the Fermi level of the left reservoir is lowered while the right one is increased. The fact that the positive threshold voltage is higher than the negative one indicates that the voltage drop across the two tunneling barriers is slightly asymmetric, expressed by a voltage division ratio $\eta = C_1 / (C_1 + C_2)$ above $\frac{1}{2}$. The Fermi level of the left reservoir is scanned through the valance band of the silicon island, while the right one is driven into the band gap. As soon as the left Fermi level reaches far enough into the valence band to provide the Coulomb charging energy $E_C$, one electron can tunnel out of the island into the left reservoir. When the island state is unoccupied, an electron from the right reservoir may tunnel into the island reoccupying the state and the sequence is repeated. This effect is called sequential tunneling as discussed in section 2.4. By further increasing the voltage, the island may be charged with additional electrons providing independent transport channels and leading to a peak in the conductance trace. When the same voltage is applied with a negative sign, the Fermi level of the left reservoir is elevated into the band gap while the right one is reduced. Due to the voltage division ratio the right Fermi level reaches further into the valance band as the left one did with the same positive voltage. Therefore the conductance sets in at a lower threshold voltage, the states are scanned faster and the peak spacing is reduced.

The electrical behavior of the device was simulated employing the orthodox theory approach outlined in section 2.4.2, which was originally developed for metallic islands [76]. However, the island in our experiment was a silicon quantum dots, which has two major consequences. Firstly, a quantum dot usually shows discrete energy levels due to the confinement of the electrons. In the present case the size of the quantum dots was very large compared to the exciton Bohr radius of silicon, which is about 4.3 nm. Therefore confinement was expected to be weak and discrete energy levels should not be observable. Secondly, as silicon is a semiconductor, the island should have an energy gap $E_G$ where no states are available enclosed by parabolic conduction and valence bands. Hence, for the calculations presented here the orthodox theory had
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to be extended to account for an appropriate, energy dependent density of states on
the island (appendix A.1).

For the calculations a capacitance \(C_1 = 2.91\ \text{aF}\) for barrier 1 and \(C_2 = 1.56\ \text{aF}\) for barrier 2 was used. This corresponds to a division ratio \(\eta \approx 0.65\) and a Coulomb charging energy \(E_C = \frac{e^2}{2C}\) of 18 meV. Furthermore, a background polarization charge \(Q_p\) of \(-0.8\ e\) had to be assumed to obtain the right plateau width around 0 V bias. The calculated \(\frac{dI}{dV}\) curve is plotted as solid line together with the measured data in figure 5.2. From the diagram it can be seen that the peak positions of the measurement are reflected reasonably well by the calculated curve. However, the agreement in terms of actual amplitude of the conductance is rather poor. The reason for this discrepancy may be a dependence of the tunneling coefficient on the bias voltage, which is not completely captured in the model.

From the overall capacitance of the island \(C = 4.47\ \text{aF}\) extracted from the calculations one can estimate the island size. Therefore the island is modeled as a conducting sphere in a homogeneous dielectric medium with an effective permittivity \(\varepsilon\). The capacitance of such a sphere is given by \(C = 4\pi\varepsilon R\). For the vacuum permittivity \(\varepsilon_0\) an island radius of 40 nm is obtained. As the SiO\(_2\) substrate has a relative static permittivity \(\varepsilon_r\) of 4.5, the effective permittivity will be roughly a factor of 2 higher than the vacuum value leading to an island radius of about 20 nm. Considering the simplicity of this model, the result is in reasonably good agreement with the nanodisc thickness of 38 nm and the diameter of 95 nm found in section 3.1.4. Furthermore, a study published by Franceschetti and Zunger [40], which determines the Coulomb energy by calculating the polarization self-energies from the wave functions in a silicon QD, also shows good agreement with the capacitance model.

As the fabrication of devices with islands smaller than the nanodiscs by direct electron-beam writing proved to be rather difficult, the self-aligned electromigration technique was used to contact samples with nominally 50 nm silicon quantum dots [128]. The electromigration process was performed in the liquid helium bath cryostat at 4.2 K and electrical measurements were conducted directly afterwards to characterize the devices. Besides tunneling current behavior and open contacts, some devices showed \(I-V\) curves with current suppression around 0 V bias, presumably due to Coulomb blockade. The plateau was typically between 50 and 100 mV wide. In addition, some contacts also showed a Coulomb staircase with several steps. In figure 5.3 an exemplary \(I-V\) trace is depicted. The curve shows a clear plateau around 0 V bias with a width of about 50 mV. The positive threshold voltage for the current to set in is about 20 mV and the negative one is -30 mV.

Together with the gate dependent measurements presented in the following sections it was found that the device exhibits a behavior similar to metallic SETs. This may be
5.2. Measurements on SOI-SiQDs

Figure 5.3.: I-V measurement taken at 4.2 K on a 50 nm SOI-QD sample directly after electromigration [128]. Together with the measurement a calculated curve is shown. Inset: SEM micrograph of the device. On the right there is a band diagram illustration of the device in the Coulomb blockade regime (A) and at the positive threshold voltage (B) where current sets in.

explained by a large negative background polarization charge $Q_p$, which is shifting the island potential upwards such that the Fermi levels of the electrodes become situated in the valence band. For a situation like this the characteristics of the device are expected to be equivalent to a metallic SET with the exception of a smoothly changing density of states on the island.

In the Coulomb blockade regime around 0 V bias the Fermi levels of the two electrodes were both situated between one always filled and another always empty level on the island separated by the Coulomb charging energy $E_C$. The situation is depicted in the schematic band diagram labeled (A). When the bias voltage was increased over a threshold value labeled (B), current flow set in. Now one level on the island was energetically enclosed by the positions of the two electrode Fermi levels and electron transport became possible via sequential tunneling. The actual positive and negative threshold voltages are determined by the voltage division ratio and the background polarization charge. When the bias is further increased, more island states are enclosed by the reservoir Fermi levels offering additional transport channels. Contrary to the situation at the band edge discussed above, here the spacing of steps is equal for positive and negative bias voltages.

The electrical characteristic of the device was again modeled with the orthodox theory extended for the non-constant density of states on the island. The calculated
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I-V curve is plotted as solid line together with the measured data in figure 5.3. For the calculation a capacitance $C_1 = 1.38 \, \text{aF}$ for barrier 1 and $C_2 = 2.76 \, \text{aF}$ for barrier 2 was used, which corresponds to a Coulomb charging energy $E_C$ of 19.4 meV. For the background polarization charge $Q_p = -3.875 \, e$ was assumed. The diagram shows that the orthodox theory curve agrees well with the measured data.

From the calculation an overall island capacitance of 4.1 aF could be extracted, which was again used to estimate the island size. The self-capacitance of a sphere model yields a diameter of 74 nm for the vacuum permittivity. With a realistic value for the effective permittivity a diameter between 30 and 50 nm is expected. This is again in very good agreement with the device dimensions of 40 nm found in section 3.1.4.

Comparing our results to experiments in literature one finds that also other groups have measured I-V curves with similar properties. Klein et al. [66, 65] for example contacted CdSe nanocrystals with EBL electrodes and obtained I-V curves with a plateau width of a few ten millivolts, which is much smaller than the band gap of CdSe. Thereby they proved that the background polarization charge is actually capable of moving the island potential such that the electrode Fermi levels energetically lie in the valence band of the semiconductor and the SET behaves like a metallic one. Compared to our experiments the plateau was narrower and therefore the capacitance larger even though the quantum dots were smaller. On the other hand the authors write that they would have expected a slightly larger charging energy. Furthermore, not only the size of the island but also the actual geometry of the electrodes has an influence on the device’s capacitance.

Choi et al. [30] also contacted silicon quantum dots synthesized by a conventional low pressure chemical vapor deposition process with EBL electrodes. They observed a plateau of roughly 180 mV in their I-V measurements and concluded that their silicon dot might have a size of about 7.3 nm. Considering the smaller plateau in our measurements this is in good agreement with the results presented above. In their analysis Choi et al. also treated the silicon island device like a metallic SET.

Hu et al. [55] used a top down approach to pattern a full silicon SET into a SOI substrate. The island was reported to be about 20 nm in size and the plateau width observed in the measurements was up to 30 mV. From that the authors concluded that the overall capacitance was 10 aF. This value is about 2.5 times higher than what we observed, even though our islands were a factor of 2 larger. On the other hand the authors report a gate capacitance of up to 3.2 aF, which adds to the overall capacitance. In our experiments the gate coupling is much weaker (see next section).

The group around Saitoh [101, 100] also prepared silicon SET devices and observed a plateau in the I-V characteristic with a width of 270 mV. Their island was believed to have a diameter of about 5.3 nm. Again, considering a factor of about 7.5 in size,
the plateau width and charging energy is comparable but slightly less than what we observed in our experiments.

Zhuang et al. [131] also fabricated a device fully based on a SOI substrate. The authors claimed to have an island with a size of about 16 nm and saw a charging energy of 98 meV corresponding to a maximum plateau width of about 200 mV. These results are also in accordance with our measurements, even though their estimated charging energy is slightly lower.

In summary our results do generally agree well with a large spread of experiments reported in literature. The charging energy with respect to island size that we have observed seems to lie on the upper end of the range. This might be due to the fact that our islands were among the largest ones in the comparison.

Besides devices like the ones discussed above, a few contacts prepared with the electromigration technique showed Coulomb blockade behavior with much higher charging energies. These I-V curves could not numerically be reproduced with a reasonable size for the silicon QDs. They are assumed to be caused by small metal islands created during the electromigration process, which also happened on samples with no silicon QDs present (see section 4.2.5).

5.2.2. Gate-dependent measurements

Our devices were also equipped with two lateral gate electrodes and additionally the silicon substrate was used as a back gate. Typically these three gate electrodes were connected to have the same potential. On all devices that showed an interesting I-V characteristic gate dependent measurements were performed. Therefore the source-drain voltage was kept at a constant value and the gate voltage was varied. Gate voltages from -15 to 15 V were typically applied unless a noticeable leakage current was detected.

Many of the devices that exhibited single-electron tunneling behavior and a Coulomb blockade in the I-V measurements did not react to a variation of the gate voltage. However, some samples showed a gate dependent modulation of the conductance. Figure 5.4 shows a plot of the source-drain conductance as a function of applied gate voltage for the 50 nm SOI quantum dot device introduced in the previous section.

The conductance trace shows a very low base value and distinct peaks with a nearly periodic spacing of 5 V. In the band diagram illustration on the right the low conductance (A) corresponds to a Coulomb blockade situation where the electrode Fermi levels were both located between one always filled and another always empty level on the island separated by the Coulomb charging energy $E_C$. When the gate voltage is increased the island potential is shifted downwards. A peak like (B) occurs each time
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Figure 5.4.: Source-drain conductance of a 50 nm SOI-QD device as a function of applied gate voltage for a fixed source-drain voltage of 10 mV. Together with the measurement a calculated curve is shown. On the right there is a band diagram illustration of the device in the Coulomb blockade regime (A) and when one level on the island is aligned to the source and drain Fermi levels (B) and resonant transport is possible.

an island state aligns with or falls in between the two electrode Fermi levels. Hence, the peak spacing corresponds to the Coulomb charging energy divided by the gate capacitance $C_g$. This conductance modulation is typical for SET devices and allows one to switch the device from a non-conducting into a conducting state. The irregular peak around -4.5 V is attributed to a temporal charge rearrangement in the electrostatic environment of the island. This interpretation is corroborated by the fact that the feature did not appear in the stability diagram measurements presented in the next section.

From the peak spacing of this measurement and the Coulomb energy $E_C = 19.4 \text{meV}$ obtained in the previous section the gate capacitance was calculated to be 0.0325 aF. With these parameters the gate dependent conductance of the device was numerically simulated again employing the extended orthodox theory code. The calculated curve is plotted as solid line together with the measured data in figure 5.4. The peak positions of the simulated curve generally coincide well with the measured ones, however, the absolute height is not reflected. The reason for this discrepancy is not yet understood.

The gate capacitance found in the measurements is comparatively small and means that the coupling efficiency of the gate is low. As a consequence, the voltages that need to be applied to switch the device are rather high. For future devices a better coupling of the gates to the island would be desirable. This can either be achieved by decreasing
the distance of the lateral gates to the island. However, this approach involves a strong complication in electron beam lithography and holds the risk of causing shorts between the gates and source or drain. One alternative approach would be a thinner buried oxide of the SOI substrate. This would decrease the distance of the back gate electrode to the island and is the more promising strategy. The disadvantage is that one relies on the SOI manufacturer to provide substrates with an appropriate BOX thickness. Another alternative is to process a top gate electrode separated by a few nanometer thin oxide layer. Investigations on this method were started but did not yield any usable results yet.

As mentioned at the beginning of this section, many devices showed no gate dependence at all. This implies that besides the geometry under control of the electron beam writer and the BOX thickness also details of the device structure, which arise either from electromigration or from the coincidental alignment of the electrodes on top of the quantum dots, play an important role for the gate coupling. At the moment there is no method available to control these parameters so that the only possibility is to generally improve the gate efficiency as outlined above.

Comparing the gate activity of our devices to examples from literature one has to distinguish two cases. SETs fabricated on top of an oxidized aluminum back gate typically show a very good gate efficiency due to the accurate control on the thickness of the aluminum oxide [19]. Unfortunately, this technique is not applicable for SET islands patterned into a SOI substrate. In the case of SOI based devices and when lateral gates were used, voltages of several volts necessary to switch the devices from one state to another are quite common [100].

5.2.3. Stability diagram

Devices exhibiting gate activity were further characterized by recording a stability diagram. Therefore $I_{SD} - V_{SD}$ curves were collected for a range of gate voltages and their numerical derivatives were calculated. Then a color (brightness) corresponding to this differential conductance was assigned to each point of a 2-dimensional plot over gate and source-drain voltage. The result is the so-called stability diagram. Figure 5.5 (top) shows the stability diagram for the 50 nm SOI quantum dot device analyzed in the previous two sections.

In this diagram dark colors correspond to a low and bright colors to a high differential conductance. The dark diamond shaped areas mark stable configurations of the device where the number of electrons on the island is constant and no current can flow due to Coulomb blockade. Because of their shape they are referred to as “Coulomb diamonds”. From the periodicity of the diamonds with the gate voltage the gate capacitance $C_g =$
Figure 5.5.: Top: measured stability diagram of a 50 nm SOI-QD single-electron transistor. Bottom: simulated stability diagram for a boron-doped silicon island SET with the parameters $C_1 = 1.38 \, \text{aF}$, $C_2 = 2.76 \, \text{aF}$, $C_g = 0.0325 \, \text{aF}$ and $Q_p = -3.875 \, e^{128}$. 
0.0325 aF can again be extracted. The width of the diamonds on the other hand corresponds to twice the Coulomb charging energy $E_C = 19.4$ meV.

With the parameters already obtained in the previous two sections, a stability diagram was calculated. Therefore boron-doped silicon was used as island material and parabolic bands were assumed to calculate the density of states. The result is depicted in figure 5.5 (bottom) and shows an excellent agreement with its measured counterpart. Taking a closer look at the conductance for higher bias voltages one can see that it decreases with increasing gate voltage. This decrease in the calculated conductance is caused by the electrode Fermi levels being scanned through the density of states of the silicon island. When the gate voltage is increased the island potential is shifted downwards and the Fermi levels approach the band edge of the valance band where the density of states drops. The same characteristic gradient can be observed in the measured diagram. A calculated stability diagram for a metallic SET would be perfectly periodic in $V_g$ and the conductance does not show this decrease.

To conclude, single-electron transistors based on SOI quantum dots were fabricated and electrically characterized. The devices show Coulomb blockade around 0 V bias and Coulomb staircase features at higher bias voltages. The plateau width and therefore the Coulomb charging energy roughly agrees with the geometrical properties of the devices. Some of the devices exhibit gate activity and can be switched from a non-conducting into a conducting state by applying a gate voltage. The stability diagram of the devices show Coulomb diamonds typical for SETs.

### 5.3. Measurements on CdSe/ZnS-QDs

The second type of devices investigated in this work was based on the CdSe/ZnS core/shell quantum dots introduced in section 3.2. For these devices a standard silicon wafer covered with a 200 nm layer of sputtered silicon oxide was used as substrate onto which gold nano-wires were patterned with electron beam lithography according to section 4.1.1. On top of these wires CdSe/ZnS QDs were deposited with the linker molecule technique outlined in 3.2.2. Then the wires were broken at cryogenic temperatures with the controlled electromigration process sketched in section 4.2.2 to yield electrode pairs with only a few nanometer separation. Thereby the intention was that one of the previously deposited CdSe/ZnS QDs may by coincidence end up lying between the two electrodes attached to either of them by one or more linker molecules.

In comparison to the SOI-QD based devices treated in the previous section, the transistor character was not the main aspect for the investigations on the CdSe/ZnS QD samples. The primary goal in these experiments was to determine the electronic...
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structure and the transport properties of the CdSe/ZnS core/shell quantum dots.

5.3.1. I-V measurements

The gold nano-wires covered with CdSe/ZnS QDs were broken via electromigration in a liquid helium bath cryostat at 4.2 K. Directly after breaking the wires the devices were characterized by measuring their I-V and dI/dV-V characteristic with the techniques outlined in section 5.1. Most of the junctions showed either tunneling behavior or current suppression around 0 V bias with additional features at higher bias voltages. The width of the plateau differed from sample to sample but was generally much smaller than the bulk band gap of CdSe. After current onset the peak spacings were comparable for different samples, which makes us confident that the features in the measurements actually originate from the CdSe/ZnS quantum dots and not from random gold particles unintentionally created during electromigration. In figure 5.6 an exemplary I-V characteristic together with its numerical derivative is shown.

![I-V characteristic and differential conductance](image)

The I-V curve has a 410 mV wide plateau around 0 V and several distinct steps at higher negative and positive bias voltages. The corresponding peaks in the differential conductance show that the the first three steps on the positive voltage side are equidistant while the spacing on the negative side is irregular. The negative current onset occurs at -130 mV while the positive threshold voltage is 280 mV.

The fact that the plateau is much smaller than the band gap of CdSe and roughly symmetric suggests that at zero bias the Fermi level is either located within the band
5.3. Measurements on CdSe/ZnS-QDs

gap and close to one band edge or between a set of electron or hole states. We further conclude that the capacitances $C_1$ and $C_2$ are distributed fairly symmetric and therefore the Fermi levels of electrode 1 and 2 are scanning the same states at roughly opposite bias voltages. This implies that the peaks on the positive and negative voltage side are caused by transport through the same set of states. When a positive voltage is applied to the configuration, the Fermi level of the drain electrode is lifted with respect to the energy states on the island while the source level is lowered according to the capacitive voltage divider. As soon as one of the electrode Fermi levels reaches a state in the dot, current is set on and a peak in the differential conductance occurs. The Fermi level of the other electrode is situated somewhere in the energy gap. When the bias voltage is reversed, the source level is lifted and the drain level lowered. This time the state on the island is reached by the other electrode Fermi level, but at a slightly different bias voltage. The difference in voltage is caused by the asymmetry of the voltage drop over the capacitances $C_1$ and $C_2$.

Comparable tunneling spectra with similar symmetries have also been reported for CdSe quantum dots by other authors [11] [114]. Bakkers and Vanmaekelbergh obtained their data with a scanning tunneling microscope on 4.3 nm CdSe quantum dots at different tip-to-dot separations, which allowed them to measure in asymmetric as well as symmetric configurations. In the asymmetric configuration nearly all voltage dropped across one of the barriers such that the Fermi level of the opposite electrode was quasi fixed with respect to the states on the island while the Fermi level of the other electrode is scanned through the states. In this configuration the valence band states were observed on one side of the differential conductance curve while the conduction band states were observed on the other. By further approaching the quantum dot with the tip the authors switched to a relatively symmetric configuration presumably similar to the one in our experiments. The curves measured in this configuration were similar to the ones we obtained.

Despite one voltage side being stretched compared to the other due to the voltage division ratio, some peaks seem to be enhanced on one side while being suppressed or completely missing on the opposite side. This effect is attributed to the distribution of the tunneling resistances $R_{t1}$ and $R_{t2}$. If the resistances are very different, the quantum dot may either be full or empty of electrons, depending on the direction of the applied voltage. In case of an empty dot, every peak in the differential conductance corresponds to an additional excitation state of the quantum dot. Such a spectrum is then called excitation or shell-tunneling spectrum and reflects the electronic energy levels of the dot. For a partially or completely filled quantum dot additional peaks appear each time the bias voltage allows to charge the island with one additional electron that may tunnel into an already occupied but degenerated state. In principle a single state may
show as many peaks as its degeneracy, which can thus be determined. This type of spectrum is referred to as addition or shell-filling spectrum \[10, 13\].

To further analyze the differential conductance spectrum the capacitance distribution parameter \( a = \frac{C_1}{C_2} = \frac{|V_+|}{|V_-|} \) is determined by dividing the positions of the first peak to either side of the current gap, which corresponds to the first accessible state. From the peak positions in figure 5.6 a value of 0.46 was obtained and with it the voltage division ratio \( \eta = 0.32 \) could be calculated. In figure 5.7 the differential conductance curve is plotted in a slightly modified way. The positive part of the curve was compressed by a factor of \( \eta \) along the x-axes while the negative part was compressed by \( (1 - \eta) \). This operation corrects the data for the voltage division due to the capacitances \( C_1 \) and \( C_2 \) in series and yields peak positions for the island states on an energy scale with respect to the equilibrium Fermi level.

\[
\begin{align*}
\Delta \epsilon_3 &= 107 \text{ meV} \\
\Delta \epsilon_2 &= 158 \text{ meV} \\
\Delta \epsilon_1 &= 200 \text{ meV} \\
E_C &= 56 \text{ meV} \\
E_C &= 53 \text{ meV} \\
\Delta \epsilon + E_C &= 88 \text{ meV} \\
\Delta \epsilon + E_C &= 88 \text{ meV}
\end{align*}
\]

Figure 5.7.: Left: Energy spectrum obtained by applying the voltage division ratio \( \eta \) to the differential conductance curve. The green curve originates from positive and the red from negative bias voltage side of the original curve. Right: Band diagram illustration of the transport mechanisms in case of an empty and a full quantum dot.

On the positive side of the spectrum the three equidistant peaks now show a spacing of about 55 meV. Because of the first peak having two neighbors with twice the same spacing this energy is interpreted as the Coulomb charging energy \( E_C \). The second and third peak occurs at an energy where a second and a third charge, respectively, may be loaded onto the island into the same state that lead to the first peak. This requires the state to be at least three times, most probably four or six times degenerate. The
fourth peak on the positive side has a different spacing and is therefore attributed to the next state becoming accessible. It is separated about 200 meV from the first peak on the positive side, which coincides with the distance of the first two peaks on the negative side and is therefore allocated to one single electron on the island occupying the first excited state.

In many measurements the separation of the first two peaks on the negative side was the same as on the positive side, which means that the first state was also charged with multiple charges when a voltage with opposite sign was applied. Hence, both sides of the spectrum consist of peaks caused by multiple charging of one state and peaks that occur when a new state is reached. This makes an assignment of the peaks very difficult. The curve in figure 5.7 was explicitly chosen, because it does not show a charging peak on the negative side. This is the case when the tunneling resistances $R_{t1}$ and $R_{t2}$ are distributed very unevenly as depicted in the sketches on the right. When a negative voltage is applied to such a configuration and the first state becomes accessible for transport, a charge tunnels slowly through the thick barrier into the island and immediately leaves it through the thin barrier on the right. Therefore the island is empty again and the next charge coming from the left electrode is not blocked. When the voltage is further increased until two charges may be loaded onto the island at the same time, this does barely happen as the island is empty most of the time anyway and therefore no peak occurs. Only when the voltage is increased such that the next state is reached a new transport channel becomes available leading to a peak in the spectrum. If, on the other hand, a positive voltage is applied, a charge easily enters the island through the thin barrier on the right and stays there for a long time until it eventually leaves through the thick barrier on the left. As long as the island is occupied by one charge, tunneling is blocked for successive charges. When the voltage is increased in this case, the island may be charged with one additional electron tunneling into the already occupied but degenerated state, which provides an independent transport channel and therefore leads to a peak in the differential conductance. The degeneracy is thereby lifted due to electron-electron Coulomb interaction.

The peaks on the positive side of the spectrum in figure 5.7 are therefore interpreted as addition or shell-filling spectrum and those on the negative side as excitation or shell-tunneling spectrum. The latter reflects the electronic energy levels of the island. From the peak spacings in the spectrum the corresponding level spacings on the island $\Delta \varepsilon_1 = 200 \text{ meV}$, $\Delta \varepsilon_2 = 158 \text{ meV}$ and $\Delta \varepsilon_3 = 107 \text{ meV}$ were extracted.

Furthermore, the position of the first peak on the positive or negative side provides information about the distance $\Delta \varepsilon$ of the equilibrium Fermi level to the first accessible state. The position has to be corrected for the Coulomb energy $E_C$, which has to be additionally spent for the first electron to tunnel into or out of the island. From the
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peak position of ±88 meV and $E_C = 55$ meV an offset of 33 meV is obtained.

From the measurements it can not be definitely determined whether transport takes place via conduction or valence band states. To gain more insight the electron and hole energy levels for a CdSe/ZnS core/shell QD were calculated as a function of core radius as outlined in appendix A.2. In the radius range of the quantum dots two possible interpretations for the experimentally determined level spacings were found.

On the one hand, the experimental peak spacings could be explained by transport through valence band states. In this case the equilibrium Fermi level would have been situated in the bandgap 33 meV above the hole ground state. The first peak in the dI/dV-V curve is then allocated to this ground state. The calculated level spacings qualitatively agree well with the measured data, however, they are slightly larger.

On the other hand, the spectrum may be explained by transport through electron states. As the electron ground state is localized in the CdSe core and has a large distance to the first excited state only confined to the shell (see figure 5.8), it is assumed that the equilibrium Fermi level is located between these two states, 33 meV below the excited state. In this case the first peak in the spectrum is allocated to the first excited state and the successive peaks on the negative side to even higher energy levels. The ground state is not accessed in the measurement due to its large energetic distance of 610 meV. The agreement between calculation and measurement is quantitatively good, only the position of the third excited state, which is of d-type, is not exactly met.

From the dI/dV-V measurements it can not be unambiguously determined which of the two interpretations is the correct one. However, the gate dependent measurements

![Figure 5.8.](a) Calculated electron energy levels as a function of core radius for a CdSe/ZnS core/shell QD with 2 nm shell and (b) the corresponding radial wave functions for the case of a 1.3 nm core radius.

From the dI/dV-V measurements it can not be unambiguously determined which of the two interpretations is the correct one. However, the gate dependent measurements
5.3. Measurements on CdSe/ZnS-QDs

presented in the next section corroborate that transport occurred via conduction band states. Hence, the following analysis is focused on that interpretation. In figure 5.8 (a) the calculated electron states of a CdSe/ZnS core/shell QD are plotted as a function of core radius. The best agreement of the calculated level spacings to the measured data was found for a radius of 1.3 nm, which is close to the maximum of the size distribution of our CdSe cores. For this radius the wave functions corresponding to the energy levels are depicted in figure 5.8 (b).

From the diagram the level spacings $\Delta \varepsilon_1 = 190$ meV, $\Delta \varepsilon_2 = 78$ meV, and $\Delta \varepsilon_3 = 177$ meV were extracted. Compared to the measured spacings $\Delta \varepsilon_2$ is too small by about 80 meV while $\Delta \varepsilon_3$ is too large by a similar amount. Taking both together means that the energy level $\varepsilon_{l=2,n=0}$ is situated slightly too low. Considering the simplicity of the model that was used to calculate the spectrum, the agreement is still astonishing.

The calculated spectrum was used together with the voltage division ratio $\eta = 0.32$ and the Coulomb charging energy $E_C = 55$ meV to calculate a differential conductance curve according to appendix A.1. Furthermore, a tunneling resistance ratio $R_{t1}/R_{t2} = 999$ was used to realize an empty quantum dot on the negative bias side and a full dot on the positive side. In figure 5.9 the calculated curve is compared to its measured counterpart.

![Figure 5.9](image)

From the diagram it can be seen that the positions of the first three peaks of the
addition spectrum on the right are perfectly reproduced by the calculation. The fourth peak on the positive side of the measurement is not exactly met. This is not surprising as it was allocated to one single electron on the dot occupying the first excited state. Such a peak is strongly suppressed in the calculation due to the high tunneling resistance ratio. Instead two more Coulomb replicas of the first state are visible.

Taking a look at the shell-tunneling spectrum on the negative bias side we see that the positions of the excitation peaks are also well reflected by the calculation. Only the third peak, which corresponds to the d-state already discussed above, seems to be displaced to the right as expected. The peak heights were not correctly predicted by the calculation, which is once again attributed to the voltage dependence of the tunneling coefficient not included in the model.

Similar level spacings were also identified in other measurements where addition and excitation spectrum were not as clearly separated as in the measurement presented above. However, the plateau width and the Coulomb charging energy varied between samples and measurements. The differences in charging energy can be explained by a variation in the effective permittivity due to the actual sample geometry. The width of the plateau, on the other hand, is determined by the position of the equilibrium Fermi level with respect to the energy spectrum on the island. As the island potential is shifted by the background polarization charge, the plateau width is expected to differ from sample to sample. We conclude that the different curves originate from the same energy spectrum specific to the quantum dots when they are placed in slightly different configurations and electrostatic environments.

To our knowledge there is no tunneling spectroscopy data on CdSe/ZnS core/shell quantum dots in literature. Therefore our results are compared to results from bare CdSe QDs. Bakkers et al. \[10\] reported a measured spacing of 173 meV from the $\epsilon_1^s$ to the $\epsilon_1^p$ level for a 4.7 nm dot. Considering a $1/r^2$ dependence of the energy levels, this would correspond to a spacing of about 566 meV for a 2.6 nm QD, which is in good agreement with the 610 meV that we obtained from our calculations. The higher energy levels are not directly comparable, as the order of the states changes with the size of the core (see figure 5.8 (a)). As Coulomb charging energy Bakkers et al. extracted 60 meV from their measurements. This value is on the same order as what we found, however, their quantum dots were smaller by roughly a factor of two. On the other hand, figure 5.8 (b) shows that the excited states in our quantum dots are localized in the ZnS shell, which might increase the effective island size and reduce the charging energy.

Alperson et al. \[2\] employed scanning tunneling spectroscopy on 3 nm CdSe QDs and found a $\epsilon_1^p - \epsilon_1^s$ spacing of 520 meV. They compare their results to a theory value of 530 meV published by Ekimov et al. \[37\]. Both values are again in accordance with
what we found, especially when taking the difference in size into account.

5.3.2. Gate-dependent measurements

After measuring the I-V and dI/dV-V characteristics at a constant or without applied gate voltage, also the gate dependence of the transport properties was investigated. Therefore a gate voltage was applied to the two lateral side gates connected with the silicon substrate used as a back gate electrode. Then dI/dV-V traces were measured for different gate voltages either with the lock-in amplifier technique outlined in section 5.1 or by measurement and numerical differentiation of I-V curves. Again the color corresponding to the differential conductance for a combination of gate and source-drain voltage was plotted in a 2-dimensional diagram. Unfortunately, only a few samples showed any gate-dependence at all. In figure 5.10 one of the differential conductance diagrams is depicted.

In the upper four diagrams the measured data is plotted with different color scales to visualize features in both, the low and the high differential conductance rage. The diagrams show an area around 0 V bias with a width of about 1.5 V where no noticeable conductance was measured. At higher bias voltages several lines can be seen, which correspond to peaks in the differential conductance curves discussed in the previous section. As the lines are inclined, these peaks change their position as a function of the applied gate voltage. In particular, the gate voltage shifts the potential on the quantum dot and therefore the position of available states with respect to the equilibrium Fermi level of the electrodes. Hence, the states become accessible at different bias voltages corresponding to the positions of the differential conductance peaks. Also the crossing of lines with different inclination can be observed on both bias sides in the diagrams.

From numerical simulations it was found that such a crossing of lines only occurs at the edges of Coulomb diamonds, but not in the region of the band edge. Therefore it was concluded that the differential conductance diagram shows a section of a Coulomb diamond. From the width of the diamond, which corresponds to twice the sum of Coulomb charging energy and energy level spacing, a level spacing of about 600 meV was estimated. This value is in good agreement with the separation of the electron ground state and the first excited state for a CdSe/ZnS core/shell quantum dot with a 1.3 nm radius core, as calculated in the previous section. As the hole states showed much smaller spacings in the calculation, it was ruled out that the stability diagram was caused by transport over VB states.

The bottom diagram in figure 5.10 shows a calculated differential conductance diagram. For the calculation the electron spectrum of the 1.3 nm radius core CdSe/ZnS QD from the previous section was used and the equilibrium Fermi level was placed close
Figure 5.10.: Differential conductance diagram of a CdSe/ZnS-QD device. The four upper plots were generated with different color scales to visualize features in the high as well as in the low differential conductance range. The bottom diagram was calculated with the electron states of a CdSe/ZnS QD with 1.3 nm radius core and a Coulomb energy of 120 meV.
5.3. Measurements on CdSe/ZnS-QDs

to the first excited state. In this case a Coulomb energy of 120 meV and a tunneling resistance ratio of 1 were chosen. When the calculated diagram is compared to its measured counterpart, qualitatively many features like the crossing lines can be identified, even though the exact inclinations and spacings of the lines were not perfectly reproduced.

Unfortunately the gate efficiency in our samples was poor. Even though gate voltages of up to 15 V had been applied, no complete Coulomb diamond could be recorded. If the sample layout was improved, e.g. by introducing an aluminum back gate [9, 19], and the gate coupling sufficiently increased, it would be possible to adjust the quantum dot potential from the valence band states to the conduction band states with respect to the electrode Fermi level. This would provide even more solid and comprehensive information about the QD level structure and make it possible to unambiguously determine the position of electron as well as hole states.

In this section it was shown that nano-electrodes, especially if combined with an effective back gate, are a promising approach to characterize the energy states of semiconductor QDs, but in principle also of single molecules. Compared to scanning tunneling spectroscopy (STS), which of course offers a much higher degree of flexibility, the main advantage is the additional information that can be obtained by gate dependent measurements. To really access all VB as well as CB states in the QD, the sample setup has to be further improved with respect to the gate coupling.
6. Conclusion

In this thesis semiconductor quantum dots were contacted with nano-electrodes to fabricate single-electron devices. Therefore a whole range of techniques to prepare quantum dots and to form nano-electrodes has been developed and implemented. The devices that were created by applying combinations of these techniques were then electrically characterized.

Semiconductor quantum dots were fabricated following two different approaches. On the one hand, colloidal CdSe/ZnS core/shell quantum dots were deposited onto gold electrodes with an already established method based on hexane dithiol linker molecules. This procedure yielded a sub-monolayer coverage of QDs with a 3 nm CdSe core and a 2.5 nm ZnS shell.

On the other hand, a completely new top-down technique was developed to prepare silicon quantum dots. Therefore a self-assembled gold colloidal etch mask was deposited onto a thin silicon-on-insulator substrate. After a reactive ion etch of the top silicon layer and a subsequent etch mask removal, silicon quantum dots were obtained on top of the insulating buried oxide. As TEM investigations have shown, it was possible with this technique to prepare nanodots with diameters of 20 and 50 nm as well as nanodiscs with a diameter of 95 nm and a thickness of 38 nm.

To contact individual quantum dots, nano-electrodes with an ultra small separation were needed. Therefore three different techniques were established. Electron beam lithography was used as basis technology and its resolution was optimized to yield electrode separations down to 10 nm.

For electrodes with even smaller gaps two alternative approaches were taken. First, a controlled electromigration process was developed to break a predefined metallic nanowire. This process was optimized to an extend that conductance quantization was observed before wire breakage indicating that only a few atoms were bridging the electrodes. Thereby a metallic quantum point contact was realized. After breakage a tunneling current was measured between the electrodes, which allowed us to estimate the electrode separation to be on the order of 2 nm. When electromigration was used on nanowires patterned on top of SOI-QDs, a self-alignment effect due to an increased current density at the positions of the QDs could be utilized. Electromigration was also performed on specially shaped ferromagnetic electrodes, which exhibited signs of
6. Conclusion

tunneling magnetoresistance after breakage.

Another method that was implemented to achieve electrodes with a sub-10 nm separation was controlled electrochemical deposition. In this process material was electrochemically deposited from an electrolyte solution onto well separated electrode templates while monitoring the conductance between the electrodes. Thereby the electrodes were slowly grown together and the conductance monitoring allowed to stop the process in the desired configuration. With this technique also tunneling currents were measured before the electrodes actually touched and conductance quantization was observed after contact. Furthermore, the technique was extended to asymmetrically deposit material onto only one electrode. The hetero-electrodes fabricated by this method provide interesting new possibilities such as an oriented deposition of bifunctionalized molecules or magnetic switching in spintronic devices.

These fabrication schemes for nano-electrodes may not only be used to contact semiconductor quantum dots, but have a wide range of further possible applications. Especially in the field of molecular electronics they can be used to contact single molecules.

Different combinations of the above techniques were applied to fabricate two types of single-electron devices. The first type was a SOI-QD based single electron transistor, while the second type was a device employing the colloidal CdSe/ZnS core/shell quantum dots as Coulomb island. Furthermore, a setup was established to measure the I-V and dI/dV-V characteristics of the devices at cryogenic temperatures with a resolution in the picoampere range.

The SOI-QD devices showed Coulomb blockade and Coulomb staircase features in their I-V and dI/dV-V traces corresponding to a Coulomb charging energy of about 18 meV. The island size associated with this energy via a capacitance model was found to be in good agreement with the dot dimensions of 50 nm. Due to the relatively large size of the silicon dots, quantization effects did not play a role in these devices. When a voltage was applied to the gate electrodes, conductance oscillations were observed and the devices could be switched from a non-conducting to a conducting state. The stability diagram showed several Coulomb diamonds typical for single-electron transistors.

The devices based on CdSe/ZnS core/shell quantum dots also showed Coulomb blockade and additional features in their I-V and dI/dV-V curves. The purpose of measurements on these devices was to characterize the electronic properties of the CdSe/ZnS QDs. From the shell-filling part of the dI/dV-V spectra a Coulomb charging energy of 55 meV was extracted, whereas the shell-tunneling part was used to obtain the energy level spacings of the quantum dot. These spacings were compared to theoretical energy level calculations for CdSe/ZnS core/shell quantum dots and the best accordance was found for a QD with 2.6 nm core. By gate-dependent measure-
ments it was further determined that transport in our devices took place over excited electron states and it was possible to assign the features in the spectra to three of these states.

Finally, numerical simulations were performed with the parameters deduced from the measurements and the results were compared to the experimental I-V and dI/dV-V curves. The SOI-based SET devices were well described within the framework of the orthodox theory extended to account for the non-constant density of states on the silicon island. To simulate the dI/dV-V characteristics of the CdSe/ZnS QD devices the energy spectrum calculated for the 2.6 nm core QDs was used. In both cases the peak positions of the resulting curves showed a good agreement with the measurements.
A. Appendix

A.1. Numerical simulation of single-electron devices

To calculate the current through a single-electron device, the distribution function $\rho(n)$, which describes the probability to find the system with $n$ charges on the Coulomb island, needs to be determined. It is governed by the master equation, which can be simplified to

$$\left[\Gamma_1^+(n) + \Gamma_2^+(n)\right]\rho(n) - \left[\Gamma_1^-(n+1) + \Gamma_2^-(n+1)\right]\rho(n+1) = 0$$

for the steady state. Depending on the electronic properties of the island the tunneling rates $\Gamma_{1,2}$ into and out of the island through barrier 1 and 2 were calculated according to one of the recipes given below. To numerically compute $\rho$ the master equation was used in the matrix notation $\mathbf{\Gamma} \rho = 0$ and the $\mathbf{\Gamma}$-matrix was composed as follows.

$$\mathbf{\Gamma} = \begin{pmatrix}
\cdots & \cdots & \cdots & \cdots & 0 \\
0 & \Gamma_1^+(n-1) + \Gamma_2^+(n-1) & \cdots & \cdots & 0 \\
\cdots & 0 & \Gamma_1^+(n) + \Gamma_2^+(n) & \cdots & \cdots & 0 \\
\cdots & \cdots & \cdots & \cdots & \cdots \\
\end{pmatrix}$$

As the full matrix has an infinite number of rows and columns, it had to be properly truncated. Therefore, the relevant charge states for the system were educatedly guessed and the resulting set of linear equations was solved with the numerical software package GNU Octave [36]. The orthonormal basis of the null space of $\mathbf{\Gamma}$ corresponds the desired probability distribution vector $\mathbf{\rho}$. With $\mathbf{\rho}$ the current through the device was calculated to

$$I = e \sum_n \left[\Gamma_1^-(n) - \Gamma_1^+(n)\right] \rho_n.$$ 

Figure A.1 shows an exemplary I-V curve, which was calculated with the tunneling rates from the standard orthodox theory. For selected voltages the probability distribu-
A. Appendix

The differential conductance was obtained by calculating the numerical derivative of the I-V curves.

Figure A.1.: I-V curve for a single-electron device calculated with the orthodox theory. For selected voltages the probability distribution $\rho$ is depicted on the right.

Depending on the type of the island, and in particular on its density of states, one of the following three approaches was chosen to calculate the tunneling rates.

**Orthodox theory (metallic islands)**

If the density of states on the island could be assumed as constant, like e.g. for metallic SET devices, the standard orthodox theory was applied. In this case Fermi’s golden rule can be integrated out and the tunneling rates become

$$\Gamma_j^\pm = \frac{1}{e^2 R_{tj}} \frac{\Delta E_j^\pm}{1 - e^{-\Delta E_j^+/k_B T}}$$

with $\Delta E_j^\pm$ being the change in energy caused by the corresponding tunneling event (equations 2.11).

**Non-constant DOS (SOI-QDs)**

When the density of states on the island cannot be assumed as constant, but is also not determined by a set of discrete states, Fermi’s golden rule needs to be integrated numerically. This was for example the case in our SOI-QD based devices, because they
A.1. Numerical simulation of single-electron devices

had a silicon island with an energy gap and parabolic valence and conduction bands, but the size was still too large to observe quantization effects. The rate for tunneling into the island through barrier 1 is then given by

\[ \Gamma^+_1 = \frac{2\pi}{\hbar} \sum_{E_m} dE |T|^2 D_1(E_m) D_i(E_m) f(E_m + E_C - E_{F_1}) [1 - f(E_m - E_{F_1})]. \]

Here, \( E_{F_i} \) and \( E_{F1} = E_{F_i} - \frac{e^2}{2C} [(C_g + C_2) V - C_g V_g - Q_p] \) denote the Fermi levels of the island and electrode 1, respectively, and \( E_C = \frac{e^2}{2C} \) is the charging energy. \( E_m \) are the elements of a vector with equidistant energy values between \( E_{F1} - 10k_BT \) and \( E_{F1} + 10k_BT \) whereas \( dE \) is the interval of these interpolation points. Note that in principle also the tunneling coefficient may be energy-dependent with this approach. The other tunneling rates are calculated in an analogous way.

**Discrete DOS (CdSe/ZnS-QDs)**

In case of a discrete density of states on the SET island, as e.g. for the CdSe/ZnS-QD devices, a third way to calculate the tunneling rates had to be implemented. Because the DOS can be treated as a comb of delta functions here, the integration of Fermi’s golden rule is converted into a sum over the energy levels \( \varepsilon_i \) on the island. Therefore,

\[ \Gamma^+_1 = \frac{2\pi}{\hbar} \sum_{\varepsilon_i} |T|^2 D_1 \varepsilon_i D_i(\varepsilon_i - \Delta E^+_1 - E_{F1}) [1 - g(n, \varepsilon_i)] \]

is obtained as rate for charges tunneling into the island through barrier 1. \( E_{F1} \) is again the Fermi level of reservoirs 1, \( \Delta E^+_1 \) is the energy change taken from equation 2.11 and \( g \) is the Gibbs distribution function (equation 2.15). As it is very time-consuming to calculate this distribution, it was replaced by the Fermi function if \( k_BT \) was much smaller or larger than the average interval between the energy levels. The other tunneling rates could again be calculated by similar means.
A.2. Numerical calculation of quantum dot states

In order to calculate the energy spectrum of the CdSe/ZnS core/shell quantum dots, the matrix method proposed by Uria et al. \[120\] to solve the 1-dimensional Schrödinger equation was adapted to the radial equation 2.14 for a spherical potential. Therefore, the radius $r$, the radial potential $V(r)$, the mass $m(r)$ and the radial wave functions $R(r)$ were represented by vectors. The first spatial derivative of the radial wave functions was approximated by the difference quotient $\frac{R_{i+1} - R_{i-1}}{2dr}$ and the second derivative by $\frac{R_{i+1} - 2R_{i} + R_{i-1}}{dr^2}$. The radial equation thus became

$$-\frac{\hbar^2}{2m_i} \left( \frac{R_{i+1} - 2R_{i} + R_{i-1}}{dr^2} + \frac{2}{r_i} \frac{R_{i+1} - R_{i-1}}{2dr} - \frac{l(l+1)}{r_i^2} \right) + V_i R_i = \epsilon R_i. $$

By sorting for the different components of $R$, this finite-difference equation can be written in a matrix form $MR = 0$ with the matrix

$$M = \begin{pmatrix}
\cdots & 0 & \cdots & \cdots \\
\cdots & -\frac{\hbar^2}{2m_i} \left( \frac{1}{dr^2} - \frac{1}{r_i dr} \right) & \cdots & \cdots \\
\cdots & \cdots & -\frac{\hbar^2}{2m_i} \left( -\frac{2}{dr^2} - \frac{l(l+1)}{r_i^2} \right) + V_i & \cdots \\
\cdots & \cdots & \cdots & -\frac{\hbar^2}{2m_i} \left( \frac{1}{dr^2} + \frac{1}{r_i dr} \right) & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots
\end{pmatrix}. $$

After filling the matrix, GNU Octave \[35\] was used to find its eigenvectors and eigenvalues. The eigenvalues correspond to the energy levels of the QD states whereas the vectors represent the corresponding wave functions. By sorting the eigenvalues, the ground and first excited states were identified. The procedure was repeated for different orbital angular momentum numbers $l$ to obtain the spectra for $s$, $p$, $d$ and $f$-type states.

This method allows one to calculate the energy spectrum and the wave functions for an arbitrary spherical potential. In figure A.2 (a) the energy levels for a CdSe quantum dot were computed as function of the dot radius. The corresponding radial wave functions for a QD with 3 nm radius are depicted in figure A.2 (b).
A. Appendix

Figure A.2.: (a) Electron energy eigenvalues for a spherical CdSe quantum dot as function of the dot radius and (b) the corresponding radial wave functions for a dot radius of 3 nm.
A.3. Feedback scheme for controlled EM

![Flowchart]

Figure A.3.: Flowchart of the feedback scheme for the controlled electromigration process. When either the absolute conductance $G$ or the parameter $dIdV$ fall below a preset fraction of their reference value, the voltage $V$ is reduced by a factor $r_V$. If the measured conductance falls below the target value $G_{target}$, the process is terminated.
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