Master Thesis

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Hybrid devices based on carbon nanotubes

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Submitted on: 20/01/2016
Abstract

A reliable source of entangled states for use in quantum computing is highly sought after. One such source option is the Cooper pairs in a BCS superconductor. By fabricating a Cooper pair splitter using a central superconducting lead coupled to two quantum dots the hope is that the Cooper pairs can be split and continued entanglement measured.

This master thesis describes the fabrication steps and complications of fabricating a Cooper pair splitter using Vanadium as the central superconducting lead. Fabrication of the precise Cooper pair splitter geometry was successfully achieved. Unforeseen obstacles in a series resistance occurring in the normal contacts convoluted the data set however. The superconducting properties of the Vanadium was difficult to observe as well. This was believed to be a consequence of impurities mixing with the Vanadium during the fabrication process.

A correction for the series resistance in the normal contacts was achieved and characterization of the nanotubes showed promising results of features needed for entanglement detection. It is also believed that a change in the fabrication process of the Vanadium superconductor is possible. Cooper pair splitters using Vanadium is thus still of interest.

Resume

En pålidelig kilde til sammenfiltrede tilstande der skal bruges i en kvante computer er et meget eftersøgt emne. En sådan kilde er Cooper parene i en BCS superleder. Ved at fabrikere en Cooper par splitter med Vanadium som en central superledende kontakt koblet til to kvante prikker er håbet at Cooper parene kan blive delt og deres sammenfiltrering forsat målt.

Dette speciale beskriver fabrikations trinnene og komplikationerne ved at fabrikere en Cooper par splitter med Vanadium som central superledende kontakt. Fabrikationen af den præcise Cooper par splitter geometri blev succesfuldt udført. Uforudsete forhindringer i serie modstande der opstod i de normale kontakter komplicerede dog data sættet. De superledende egenskaber af Vanadium var også svære at observere. Dette menes at skyldte urenheder mixet med Vanadium under fabrikations processen.

En korrektion til serie modstander i de normale kontakter blev opnået og karakteriseringen af nanotuben viste lovende resultater for nødvendige egenskaber til brug i sammenfiltrerings eksperimenter. Det menes desuden at en ændring i fabrikations processen af Vanadium superlederen er muligt. Cooper par splitterer med Vanadium er således stadig af interesse.
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1. INTRODUCTION

In 1975 G. E. Moore, co-founder of Intel corporation, predicted that the number of components per integrated circuit would double every second year. This is the essence of the so-called Moores law\cite{1}. The rate of improvement has been steady until around 2012 when it started to drop off. It has been known for a long time that we will reach a point where we can’t shrink conventional transistors any more and the law will fail. Moore himself expects it happen soon.

"I see Moore’s law dying here in the next decade or so.” - G. E. Moore, 2015 \cite{2}

We are rapidly approaching a fundamental threshold were transistors physically can’t be made smaller. The physical obstacles we are facing are the speed of light and the atomic nature of materials. Transistors can’t be made smaller than a few atoms using conventional methods and data can’t be transmitted faster than the speed of light.

New promising candidates are needed if the development is to continue. One such candidate is the use of molecules as transistors which has had breakthroughs in recent years\cite{3, 4, 5, 6}. Another replacement candidate is Quantum computing. Quantum computers consists of sequences of qubits instead of the bits in a regular computer. Qubits can be represent a one or a zero just as a normal bit, however, it can also represent a superposition of the two states. A sequence of two qubits can thus be in a superposition of 4 states while a sequence of 3 can represent 8 states. A quantum computer can in general be in up to \(2^n\), \(n\) being the number of qubits, different states simultaneously. A regular computer can by comparison only be in one of those \(2^n\) states at a time. A quantum computer also enables the use of new complex algorithms that should be able to solve problems such as protein folding, quantum simulations and integer factorization faster than a normal computer\cite{7, 8}.

Quantum computing is full of possibilities, however, the need for a reliable source of entangled states is great. Cooper pairs are a possible of these entangled states. When cooling BCS superconductors below the critical temperature the electrons experience a slight attraction to each other and condense into pairs, Cooper pairs. The wave function of a Cooper pair
is
\[ |\psi_G\rangle \prod (u_k + v_k \epsilon_k^\dagger \epsilon_{-k}^\dagger) |\psi_0\rangle = u_k |0\rangle |0\rangle + v|k\uparrow\rangle |-k\downarrow\rangle. \] (1.1)

This is exactly an entangled state. The wavefunction demands that both of the states \(|k\uparrow\rangle\) and \(|-k\downarrow\rangle\) are occupied simultaneously. If the Cooper pairs can be split up they would represent an entangled state and they are thus a promising candidate for an entangled state source.

One theoretical way of splitting Cooper pairs is aptly named a Cooper pair splitter. A Cooper pair splitter forces the electrons to split up by letting them tunnel through quantum dots one electron at a time. By utilizing the mutual repulsion between electrons, a quantum dot can be fabricated to only allow one electron at a time. This single electron tunneling forces the Cooper pair to split up. By fabricating a quantum dot on each side of a superconductor, the Cooper pairs will have to split up and tunnel onto different quantum dots. Figure 1.1 shows a schematic of a Cooper pair splitter utilizing carbon nanotubes to create quantum dots.

Experiments have already been carried out measuring non-local signals in the two quantum dots. Cooper pair splitting devices have also been demonstrated in both nanowires[9, 10, 11] and carbon nanotubes[12, 13] . Though an increase in current has been measured, a proof that the electrons are still entangled is missing.

The proposal by Braunecker et al.[14] tries to address this question. By utilizing that spin-orbit interaction provides a spin filtering effect in carbon nanotubes suppressing the current for certain filter configurations. If a sufficiently bent nanotube is used as basis for the Cooper pair splitter the four fold degeneracy can be lifted and entanglement detected through a Bell-like inequality.

The Braunecker proposal requirese the following

- The quantum dot needs to exhibit four fold symmetry to be able to distinguish all the states.
- Superconductivity is necessary for the electrons to condense into entangled Cooper pairs. This is easily seen by identifying a superconducting gap in a bias spectroscopy plot.
- The critical magnetic field of the superconductor should be similar or higher than the spin-orbit magnetic field. Otherwise it will not be possible to alter the spin-orbit field without destroying the superconductivity.
- Spin-orbit interaction should dominate disorder
1. Introduction

Fig. 1.1: Schematic of a Cooper pair splitter device based on a bent carbon nanotube as presented in the Braunecker proposal[14]. Cooper pairs are split up as they are injection onto the quantum dot. Utilizing the difference in spin-orbit field of the two side of the nanotube, the spin-valley degeneracy is lifted when applying an external magnetic field. By measuring the current of all 16 combinations it is possible to deduce though a Bell inequality whether the electrons are still entangled.

- The spin bases must not be parallel and thus the spin-orbit magnetic field must not be parallel. This can be achieved by basing the device on a bent nanotube or using two segments at an angle.

- A specific pattern of non-local resonances should be observed.

All but the last requirement have already been demonstrated[15]. No spin entanglement has yet to be detected though but this thesis provides insight into the fabrication and measurement processes of carbon nanotube Cooper Pair splitters using Vanadium as the superconductor.

Outline of thesis

The problem statement behind this thesis was the following:

*This project will investigate carbon nanotube devices with superconducting contacts using nanofabrication and electron transport measurements at subkelvin temperatures.*
1. Introduction

Relevant theory will be reviewed in Chapter 2, while Chapter 3 will describe the fabrication process and measurement setup for the devices. An in depth step-by-step guide for the fabrication is available in appendix A. Finally Chapter 4 will present the analysis of and the acquired data.
2. THEORY

2.1 Carbon Nanotube

The following section provides a basic overview of the important aspects of carbon nanotubes that will be necessary to understand this thesis. The section has been influenced by Laird et al.[16] as well as Morten Canth Hels’ master thesis [15]. For a more in depth treatment see the former mentioned work by Laird et al.

2.1.1 Physical Structure of Carbon Nanotubes

A single walled carbon nanotube (SWCNT) can be described as a single sheet of graphene rolled into a cylinder, while a multi walled carbon nanotube can be seen as several of such sheets. In this thesis the focus will be on single walled carbon nanotubes and whenever carbon nanotubes (CNTs) are discussed will this refer to SWCNT.

CNTs consist of a hexagonal grid of carbon atoms as shown in Figure 2.1a. For analyzing CNTs they are thought of as a rolled-up strip with a chiral vector \( \mathbf{C} \) that connects lattice sites on opposite ends of the strip. The unit cell of graphene consists of 2 atoms with basis vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \), which when translated becomes a sheet of graphene. The chiral vector of the nanotube is described as

\[
\mathbf{C} = n\mathbf{a}_1 + m\mathbf{a}_2
\]  

(2.1)

with the chiral indices \( n \) and \( m \) being the coordinates of the graphene basis vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \).

This will in most cases produce a chiral structure, though 2 exceptions exist in armchair \( (n = m) \) and zig-zag \( (m = 0) \) structures (shown in Figure 2.1 b). Both the armchair and zig-zag structure are non-chiral and thus one half is a mirror image of the other.

A second way of describing the nanotube is by the diameter and the angle between the chiral vector and the graphene basis vector \( \mathbf{a}_1 \), the so called chiral angle \( \theta \).
2. Theory

The chiral angle is given by

\[ \theta = \tan^{-1} \left( \frac{\sqrt{3}m}{2n + m} \right) \]  \hspace{1cm} (2.2)

and becomes \( \theta = 0 \) for a zig-zag structure, \( \theta = 30^\circ \) for an armchair structure, and \( 0 < \theta < 30^\circ \) for a chiral structure. The diameter of a CNT can be described the following way

\[ D = \frac{\sqrt{3}a_{CC} \sqrt{n^2 + m^2 + nm}}{\pi} \] \hspace{1cm} (2.3)

with \( \sqrt{3}a_{CC} \) being the graphene lattice constant and \( a_{CC} = 0.142nm \) being the bond length between two neighbouring carbon atoms.

2.1.2 Electronic Structure of Carbon Nanotubes

To understand the CNT band structure we will start by looking at graphene. In graphene the most important feature are the Dirac cones located at the Dirac points \( \mathbf{K}, \mathbf{K}' \). These Dirac points are connected by reciprocal lattice vectors, which results in them having the same electron states and thus same energies. Dirac points at \( \mathbf{K} \) are time-reversal conjugates of Dirac points at \( \mathbf{K}' \). Close to the Fermi surface the dispersion relation is linear and given as

\[ E = \pm \hbar v_F |\kappa| \] \hspace{1cm} (2.4)

with \( E_F \), the Fermi energy, defined as zero energy and \( |\kappa| \) as the distance from the Dirac point. \( v_F \) is the Fermi velocity and is in the order of \( 8 \times 10^5 \) m/s.

Due to the much larger size of a nanotube compared to a graphene unit cell, the band structure can be approximated as a rolled up graphene sheet perturbed with a periodic boundary condition, the so-called zone-folding approximation. This boundary condition is

\[ \mathbf{k} \cdot \mathbf{C} = 2\pi p \] \hspace{1cm} (2.5)

with \( p \) being an integer. This restricts \( k_{\perp} \) in the nanotube, compared to it’s unrestricted state in graphene, to

\[ k_{\perp} = 2p/D. \] \hspace{1cm} (2.6)

The allowed k-values corresponds to the quantization lines in reciprocal space shown in Figure 2.2 a-b.

The bandgap of the nanotube depends on whether or not the lines intersect the Dirac points. If the quantization lines intersect the Dirac points
Fig. 2.1: The physical structure of a carbon nanotube is identical to a rolled up graphene sheet. (a) By rolling a sheet of graphene along the vector \( \mathbf{C} \) a nanotube is obtained. The chiral indices \((n,m)\) can be used to completely define the structure of the nanotube using the graphene basis vectors \((\mathbf{a}_1, \mathbf{a}_2)\). (b) The three classes of nanotubes: Zig-zag, Armchair and Chiral. Zig-zag arise when the chiral angle, \(\theta\), is 0, Armchair when \(\theta = 30^\circ\) and Chiral in all other cases. Adapted from \[16\].

the nanotube is metallic with a linear dispersion relation in the low energy regime (Figure 2.2 c). If the Dirac points do not lie on the quantization lines the nanotube is semiconducting and the dispersion relation becomes hyperbolic. In the hyperbolic case the conduction and valence bonds don’t meet at \(|\kappa_\parallel| = 0\) and a gap is created. This bandgap will have an energy of

\[
E_G = 2\hbar v_F |\Delta \kappa_\perp|
\]  

(2.7)

with \(|\kappa_\perp|\) being the separation between the quantization lines and Dirac points. In a semiconducting nanotube the bandgap is in the order of 700 meV/D[nm].

The dispersion relation for a quantized \(\kappa_\perp\) is then

\[
E(\kappa_\parallel) = \pm \sqrt{\hbar^2 v_F^2 \kappa_\parallel^2 + E_G^2/4}
\]  

(2.8)
2. Theory

Fig. 2.2: By imposing periodic boundary conditions on the rolled up graphene sheet $\kappa$ is constrained to quantized values. In the case of (a) the quantization lines intersect the Dirac points and the nanotube is metallic, compared to (b) where the nanotube is semiconducting. In (c,d) dispersion relations close to a Dirac point is shown for the former mentioned nanotubes. A bandgap appears in the semiconducting (b) nanotube while the metallic (a) nanotube shows no gap. Figure adapted from [16]

which gives the hyperbolic dispersion relation shown in Figure 2.2 d.

In a nanotube one can imagine the electrons circulating the nanotube two ways (clock- and counter clockwise). This is also evident when taking a closer look at the dispersion lines. The lowest energy states are the ones where the dispersion line is closest to $K$ and $K'$ points. It is also evident that a line that runs close to a $K$ point also runs close to a $K'$ point. We then classify the states as either $K$- or $K'$-states depending on the Dirac point they are closest to. It is then clear that $K$- and $K'$-states must be in the same energy band but since the points are time-reversed conjugates of each other they have to circulate in opposite directions. These points are also known as valley quantum numbers with a value of +1 for $K$-states and -1 for $K'$-states.

The $K$-states and $K'$-states are time-reversed pairs and when time-reversal symmetry is not broken these states are thus degenerate. When taken together with spin-degeneracy of the states the total degeneracy of nanotubes becomes four.

When using the “zone-folding approximation” it is assumed that no additional orbital overlap happens. In the case of the rolled up graphene sheet this is not the case as the curvature displaces the Dirac cones by a vector $\Delta \kappa^{cv}$ away from the $K$ and $K'$ points in reciprocal space. This vector is opposite for $K$ and $K'$. In a semiconducting nanotube the quantization of $\kappa_\perp$ has a much bigger impact than the displacement. However, in a metallic
nanotube this displacement of the Dirac cones introduces a bandgap of

\[ E_G^{cv} = 2 \hbar v_F |\Delta \kappa^c v_\perp| \]  

(2.9)

with \( \Delta \kappa^c v_\perp \) being the perpendicular component of \( \Delta \kappa^c v \) compared to the nanotube axis and the \( cv \) superscript denoting the curvature origin of the bandgap. The bandgap originating from this is always much smaller than the bandgap originating from the quantization of \( k_\perp \), and the nanotubes are thus called narrow-gap nanotubes. In the case of an armchair nanotube \( \kappa^c v_\perp = 0 \) since \( \Delta \kappa^c v \) is parallel to the quantization lines, and thus stays metallic.

The three different kind of nanotubes (semiconducting, narrow-gap and metallic) can be identified experimentally by measuring the current as a function of gate voltage given a constant source-drain voltage. Signature plots can be seen in Figure 2.3 a-c. As the energy levels are shifted up or down due to the gate voltage the fermi energy and gap are shifted relative to each other and if the fermi energy is shifted inside the gap, the result is a suppression of the current as is seen in the semiconducting case. In the case of a metallic nanotube there is no dependence on the gate voltage since there is no bandgap (or in the case of a very small bandgap \( E_G \ll k_B T \)). Finally there are the narrow-gap nanotubes where the bandgap is in the order of \( k_B T \) which results in a partial suppression of the current. By cooling down a narrow-gap nanotube the bandgap appears, as \( k_B T \) becomes smaller than \( E_G \) when the temperature is down to a few hundred milikelvin as is shown in Figure 2.3 d. Experimentally it has been shown that less than 1 % of nanotubes are metallic.

2.2 Quantum Dots

The following section has been influenced by ref [17] in addition to the previously mentioned works by Laird et al. and M. C. Hels.

2.2.1 Basic Carbon Nanotube Quantum Dot

Using the natural confinement of electrons to 1 dimension in nanotubes it is possible to fabricate quantum dots using tunnel barriers. When adding contact leads to a nanotube, Schottky barriers are induced between the lead and a semiconducting nanotube. By adding a source and drain lead onto a nanotube (shown in figure 2.4) one is thus able to confine the electrons to the region between the two leads. This is called a quantum dot. The barriers need to fulfill two requirements: The barrier has to be low enough to allow tunneling onto the dot, but at the same time the barrier has to be
2. Theory

Fig. 2.3: The bandstructure of a semiconducting nanotube is shown in (a), of a narrow-gap nanotube in (b) and of a metallic nanotube in (c). (d) Cooling a narrow-gap nanotube down to sub-kelvin temperatures reveals a small bandgap that is not visible at room temperature for the narrow-gap nanotube. Adapted from [16].

high enough to only allow a number of electrons that will be a good quantum number. By adding a plunger gate, a third electrode with no contact to the nanotube, it is furthermore possible to capacitively tune the energy levels in the quantum dot by either introducing a positive or negative voltage over the plunger gate. Figure 2.4 shows the basics of carbon nanotube devices. By measuring the current through the nanotube as a function of bias, gate voltage, magnetic field and so it is possible to extract the energy levels of electrons in the quantum dot.

Fig. 2.4: A basic nanotube device can be manufactured by adding a source and drain lead on the nanotube. This restricts the electrons to zero dimensions and a quantum dot is established. Using a plunger gate the energy levels of the quantum dot can be manipulated. Adapted from [16]
2.2.2 Quantum Dot Constant Interaction Model

In the following the constant interacting model[18] will be used to describe the quantum dot states. In the constant interacting model there are two important assumptions. The first assumption is that Coulomb interactions of an electron towards all other electrons, being on or off the the quantum dot, can be parametrized by a total capacitance, $C$. The second assumption is that the single-particle energy levels of electrons on the dot are independent of these interactions. Thus adding additional electrons to the quantum dot will not change the existing energy levels. The constant interaction model predicts the total energy of the quantum dot with $N$ electrons as

$$E(N) = \left(-\frac{|e|(N - N_0)}{2C} - \sum_i C_i V_i\right)^2 + \sum_{i=1}^{N} E_i.$$  \hspace{1cm} (2.10)

$N_0$ is the occupancy with no voltage applied to nearby gates ie. $V_i = 0$, $C_i$ are all the gate capacitances of nearby gates, and $E_i$ are the single-particle energy levels. The total capacitance $C$ is a sum of the capacitance over source, drain, and gate which is equal to $C = \sum_i C_i = C_s + C_d + C_g$.

The electrochemical potential of the quantum dot is defined as

$$\mu_{\text{dot}}(N) = E(N) - E(N - 1).$$ \hspace{1cm} (2.11)

If the potential of the dot is outside of the region between the source and drain potentials (Shown in Figure 2.5 a) no electrons can flow which results in Coulomb blockade. When the potential of the quantum dot lies in the region between the source and drain potential electrons can flow through as seen in Figure 2.5 b-c.

The addition energy when adding an electron to the quantum dot is given by

$$E_{\text{add}}(N) = \mu_{\text{dot}}(N + 1) - \mu_{\text{dot}}(N) = E(N + 1) - 2E(N) + E(N - 1) = E_C + \Delta E$$ \hspace{1cm} (2.12)

with $E_C = \frac{e^2}{C}$ being the charging energy. The two energies, charging energy $E_C$ and level spacing $\Delta E$, are important quantities for the quantum dot.

2.2.3 Transport in Quantum Dots

To describe transport in a quantum dot we need to establish a Hamiltonian for the quantum dot system. In this case a generalized Hamiltonian is given
Fig. 2.5: The potential landscape of a quantum dot experiencing Coulomb blockade. (a) The quantum is occupied by $N$ electrons resulting in a chemical potential of $\mu(N)$. To add the $N+1$ electron the chemical potential of the quantum dot would become $\mu(N+1)$, however, both of these states lies outside of the bias window, and thus a Coulomb blockade is in effect. In (b) the lowest unoccupied state lies within the bias window and an electron is able to tunnel onto the quantum dot. In (c) the highest occupied state lies within the bias window and it is able to tunnel to the lead. This is known as sequential tunneling. Adapted from [18].

\[
H = H_R + H_L + H_D + H_T
\]  \hspace{1cm} (2.13)

with $H_R$ and $H_L$ being Hamiltonians for the right and left contact, $H_D$ the Hamiltonian for the quantum dot and $H_T$ which is the tunneling Hamiltonian. Part of the Hamiltonian is a non-interacting part, more specifically $H_R$, $H_L$, and $H_D$ all describe the energy levels of the dot, right, and left contact. We combine these parts into a single non-interacting Hamiltonian, $H_0$. The tunneling part of the Hamiltonian is then split into two components

\[
H_T = H_{TR} + H_{TL}. \hspace{1cm} (2.14)
\]

where $H_{TR}$ is tunneling through the right contact, and $H_{TL}$ is tunneling through the left contact. In the case of first-order rate for transition between a contact and the quantum dot Fermi’s golden rule can be used with the tunneling Hamiltonian. The transition rate for an electron moving from
state $\alpha$ to state $\beta$ is

$$\Gamma_{\beta\alpha}^{(1)} = \frac{2\pi}{\hbar} |\langle\beta|H_T|\alpha\rangle|^2 \delta(E_\beta - E_\alpha).$$

(2.15)

This first order tunneling is called sequential tunneling, but to move electrons through a quantum dot two of the above processes are needed. The transport happens in steps as the electron tunnels from one contact onto the quantum dot and then in a subsequent step from the quantum dot onto the second contact. The different first order processes are shown in Figure 2.6.

Fig. 2.6: The varying first-order processes are shown. For these processes to be available a transition in the bias window has to be available. In (1)-(3) this is a two step process of sequential tunneling. In (4) the bias window has been increased to also include excited states. These can also be used for transport. Adopted from [19]

In the case of higher order tunneling we have to introduce a T-matrix. The T-matrix is given as [17]

$$T = H_T + H_T \frac{1}{E_i - H_0} T$$

(2.16)

with $E_i$ being the energy of the initial state. The second order rate is then given as

$$\Gamma_{\beta\alpha}^{(2)} = \frac{2\pi}{\hbar} |\langle\beta|H_T \frac{1}{E_i - H_0} H_T|\alpha\rangle|^2 \delta(E_\beta - E_\alpha).$$

(2.17)

The second order processes always transfer an electron from one contact onto the other (It is also possible for it to transfer it onto the dot and then back to the first contact, but this does not contribute to the current). In the case of an electron moving from the left contact to the right contact, two instances
can occur. The first instance would be an electron transferring from the left contact onto the quantum dot with an electron then transferring from the quantum dot to the right contact. In the second instance an electron is transferred from the dot to the right contact, followed by an electron from the left contact onto the quantum dot. The intermediate state has a higher energy than both the initial and the final step and is thus a virtual state. The transfer rate for moving an electron from the left contact to the right would then be

\[
\Gamma^{(2)}_{\beta\alpha} = \frac{2\pi}{\hbar} \left| \langle \beta | \left( H_{TR} - \frac{1}{E_\alpha - H_0} H_{TL} + H_{TL} - \frac{1}{E_\alpha - H_0} H_{TR} \right) | \alpha \rangle \right|^2 \delta(E_\beta - E_\alpha).
\]

(2.18)

This process is shown in Figure 2.7.

\begin{center}
\includegraphics[width=0.5\textwidth]{cotunneling.png}
\end{center}

\textbf{Fig. 2.7:} Second order processes are known as cotunneling. (a,b) In cotunneling events an electron is always transported from one lead to the other. This can be done using a virtual intermediate step with a higher energy than both the final and initial state. Adapted from [19].

The second order tunneling processes are called cotunneling. Cotunneling can furthermore be either elastic or inelastic. If they are elastic the final and initial energy state has the same energy. In inelastic cotunneling processes the final and initial electron states are different. The energy difference is provided by the process by e.g. the source-drain voltage.

\subsection*{2.2.4 Kondo physics}

The Kondo effect first described by J. Kondo in 1964 [20] arises from magnetic impurities in metals. As the temperature is decreased for a normal metal the resistance tends towards a residual resistance while superconducting metals experience a sharp drop to zero resistance at the critical temperature. If the metal have the aforementioned magnetic impurities, it will instead experience an increase in resistance once it reaches the Kondo temperature. The conduction electrons scatter at the magnetic impurities and experiences a spin-flip causing a spin singlet many-particle state with an energy of of \( k_B T_K \). This scattering is the cause of the increased resistance.
In quantum dots the Kondo effects differ from that of metals. In this case the important process is the transmission of an electron suffering a spin-flip and not spin-flip scattering. The Kondo effect in a quantum dot occurs if a single unpaired electron occupies a spin degenerate state. A quantum dot with an odd number of electrons will have this scenario as the occupied state with the highest energy will be occupied by one electron and be double degenerate. We can then imagine a cotunneling process happening with the unpaired electron on the dot tunneling to the contact, while an electron from the other contact with the opposite spin tunnels onto the dot. If the process happens from the left to the right contact the unpaired electron gains the energy $\epsilon_r - \mu_N$ while the electron from the left contact loses the energy $\epsilon_l - \mu_N$. If $\epsilon_r = \epsilon_l$ the energy of the system is conserved, however, the spin of the electron on the quantum dot will have been reversed. When summing over all processes of higher order as well, we get a sharp resonance of the tunneling density of states at the Fermi energy. This increased state at the Fermi energy enhances the current instead of suppressing it, as is seen from Kondo effects in metals. This enhancement of the current naturally increases the conductance and through Kondo resonances it is possible to achieve conductance of $2e^2/h$ for a double degenerate state instead of $e^2/h$ for a single level at zero bias. In the case of a carbon nanotube with fourfold degeneracy it is possible to achieve 4 times the normal rate at $4e^2/h$. As described, the Kondo effects involves cotunneling, so to observe any of the effects a large coupling to the contacts is needed.

**Fig. 2.8:** Kondo resonances appear from cotunneling events. An unpaired electron on the dot tunnels onto the lead while an electron with opposite spin tunnels onto the dot. The total spin of the quantum dot will then have changed with no change in energy. Adapted from [19].
2.3 Superconductivity and BCS Theory

For the following section provides a very brief introduction to superconductivity and BCS theory. The author has drawn upon the work done by references [21] and [22]. For an in depth look at the subject the work done by the mentioned references is referred to.

2.3.1 General Superconductivity

The concept of superconductivity has been known since 1911, when superconductivity was discovered by H. K. Onnes [23]. The phenomenon observed by Onnes was, that the electrical resistance of certain metals disappeared completely below a certain temperature. Since then more features of superconductors have been understood. The most important characteristics of superconductors are the following

- A superconductor will behave as if there is no electrical resistance. This phenomenon does not decay given no driving field. This has been observed for 2.5 years [22] but no change is expected in less than $10^{10}$ years[21].
- A superconductor can behave as a perfect diamagnet. This was discovered by Meissner and Ochsenfeld in 1933. They found that a superconductor in an applied magnetic field would create another magnetic field that precisely cancels the applied field. This led to the realization that a critical magnetic field could destroy superconductivity.
- An energy gap of $2\Delta$ is observed around the Fermi energy in the allowed energy levels. An electron thus need an energy difference, $\epsilon - \epsilon_F$, greater than $\Delta$ to tunnel onto a superconductor.

The first two points were described in 1935 by the brothers F. and H. London who proposed the following equations:

$$E = \frac{\partial}{\partial t}(\Lambda J_s)$$  \hspace{1cm} (2.19)

and

$$h = -c \text{ curl}(\Lambda J_s)$$  \hspace{1cm} (2.20)

where $\Lambda = \frac{m}{n_e c^2}$ is a phenomenological parameter.

The third point was described by J. Bardeen, L. N. Cooper and J. R. Schrieffer in 1957[24]. The BCS theory explained that superconductivity
was a result of electron-electron attractions making electrons bond together in Cooper pairs. The theory predicted that the minimum energy needed to break a Cooper pair and creating two quasi-particle excitations was

$$E_g(0) = 2\Delta(0) = 3.528k_BT_c. \tag{2.21}$$

### 2.3.2 BCS Theory

The basic idea proposed by L. N. Cooper in 1956 was that even a weak attraction, no matter how weak, can bind electrons together in pairs. With the Fermi sea being unstable against the formation of a Cooper pair this will continue until an equilibrium is established. The BCS groundstate given by Bardeen, Cooper and Schrieffer was

$$|\psi_G> = \prod_{k=k_1,...,k_M} (u_k + v_k c^*_k c_{-k}) |\psi_0> \tag{2.22}$$

where $|u_k|^2 + |v_k|^2 = 1$ and $|\psi_0>$ is the singlet wavefunction

$$|\psi_0> = \sum_{k>k_F} g_k c^*_k c_{-k} |F> \tag{2.23}$$

where $|F>$ is the Fermi sea with filled states up to $k_F$.

Using the pairing hamiltonian (given in ref [21] )

$$H = \sum_{k\sigma} \epsilon_k n_{k\sigma} + \sum_{k\ell} V_{kl} c^*_k c_{-k} c^*_l c_k \tag{2.24}$$

where $V_{kl}$ is the interaction potential, and by minimizing the potential value using

$$\delta <\psi_G|H - \mu N_{op}|\psi_G>= 0 \tag{2.25}$$

where $\mu$ is the chemical potential and $N_{op}$ is the particle-number operator, we can obtain

$$V_{kl} = \begin{cases} 
-V & \text{if } |\epsilon_k| \text{ and } |\epsilon_l| \leq h\omega_c \\
0 & \text{otherwise}
\end{cases} \tag{2.26}$$

where $\epsilon_k$ and $\epsilon_l$ are the single-particle energy relative to the Fermi energy.

Using this model, an equation for the energy gap can be obtained in

$$\Delta(0) = 2\hbar \omega_c e^{-1/N_0V} \tag{2.27}$$
Similarly we can obtain the critical temperature, which turns out to be

\[ k_B T_c = 1.13 \hbar \omega_c e^{-1/N_0 V} \]  

(2.28)

with \( N_0 \) being the density of electronic levels of a single spin population. Comparing this with the energy gap at \( T = 0 \) we get

\[ \frac{\Delta(0)}{k_B T_c} = \frac{2}{1.13} = 1.764. \]  

(2.29)

The gap is thus of the same order of energy as \( k_B T_c \). Most experimental values of the energy gap comply with this result as most values of \( 2\Delta \) falls in the range of \( 3.0 k_B T_c \) to \( 4.5 k_B T_c \).
3. FABRICATION AND MEASUREMENT SETUP

3.1 Fabrication

The fabrication of devices were done following the recipe demonstrated by Morten Canth Hels in his thesis [15]. The goal was to fabricate Cooper pair splitters using carbon nanotubes with a precise geometry such as the one shown in Figure 3.1. The desired geometry of a Cooper pair splitter consists of a superconducting lead in the center, with a normal lead on each side of the central superconducting lead. In addition to the leads, two side gates are positioned between the leads. This way two quantum dots are defined in the carbon nanotube. This geometry were successfully performed several times during the project, though not all generations used the same metals.

Fig. 3.1: A SEM image of the successful fabrication of a Cooper pair splitter geometry. This particular device was a part of generation 7 part 2.

A base chip with alignment marks was first produced using an Elionix ELS-7000 (acceleration voltage of 100kV) to expose the pattern in resist. Resist used for this step consisted of one layer of EL-6 and one layer of CSAR 4%. After developing the chip in O-xylene (60 sec), MIBK:IPA (30 sec) and IPA (30 sec), Tungsten and Platinum were then evaporated onto the sample using an AJA evaporation chamber to create the alignment marks. The base
chip was then left in 76°C NMP for 10 min to lift off the remaining resist.

The next step carbon nanotube catalyst was added to the chip. Two layers of A-6 resist were applied before exposing the catalyst pattern in a Raith eLine using an acceleration voltage of 20kV. The chip was then developed in MIBK:IPA (55 sec) and IPA(55 sec) and a catalyst consisting of iron nitrate (Fe(NO$_3$)$_3$) molybdenum acetate and alumina support particles [25] were deposited on the chip. The remaining resist was then removed during lift-off. The chip was ashed for 30 secs to remove any unwanted catalyst.

Carbon nanotubes were then grown using a Carbolite MTF 12/25/400 CVD oven. The nanotubes were grown at a temperature of 910°C. During the first 5 mins of warmup Argon was flowed through the oven, followed by Argon and Hydrogen untill the temperature reached the set value. This was followed by 10 mins of only Hydrogen flowing through the oven. Finally Hydrogen and Methane were flowed through the oven for 17 mins before the oven was turned off. During the cooldown Argon was flowed through. A more in depth description can be seen in Appendix A.

The chips were then imaged in the Raith eLine to minimize damage to the nanotubes\(^1\) (details concerning dose, voltage etc. can be found in appendix A). To further minimize exposure of the nanotubes the Raith eLine was focused, stigmated and aligned away from the nanotubes. A script was then used to do one imaging of each catalyst island.

After nanotube growth imaging, the chip was split into two parts, part 1 and part 2. Alignment marks and nanotube growth were thus the same for each generation, however, the following steps were done separately for each part.

Having now grown the nanotubes the next step becomes designing the desired devices. For this purposed DesignCAD 23 was used. The growth images were imported into the program and using the alignment marks it was possible to very precisely define the regions wanted for gates, leads etc.

During the first couple of generations the next step consisted of normal leads, side gates and bonding pads. However, a change in metal for the normal leads from Ti/Au to Pd/Au were done from gen 10 and onwards. Pd/Au easily peels off the chip and the normal contacts step was switched to the final stage in later generations.

From gen 10 and onwards superconducting leads, side gates and bonding pads were then made in the next step. EL-6 and A-4 resist were applied to the chip. The design was then imported to the Raith eLine and the design

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\(^1\) The Elionix ELS-7000 with an acceleration voltage of 100kV could potentially knock out carbon atoms from the nanotubes given the estimated minimum energy of 86keV [26] to do so.
was exposed (details concerning dose, voltage etc. can be found in appendix A). The chip was developed in MIBK:IPA (55 sec) and IPA (55 sec) and metal was evaporated onto the chip. A sticking layer (∼ 5 nm) of titanium was applied followed by a 60-70 nm layer of Vanadium (In the final generation this was changed to Ti/Al (3/15 nm) due to problems with the Vanadium). Finally lift off was performed. The evaporation was done in a thermal evaporator\(^2\) until generation 10. From generation 10 the evaporation was done using ebeam evaporation in an AJA evaporating chamber. This change was a consequence of a high current needed to evaporate the Vanadium in the thermal evaporator leading to high temperatures and problems during lift off.

The process was then repeated for normal contacts (or superconducting contacts for the first couple of generations). Two layers of resist were applied, one layer of EL-6 and one layer of A-4. The normal contacts design was exposed in the Raith eLine (details concerning dose, voltage etc. can be found in appendix A) followed by developing the chip in MIBK:IPA (55 sec) and IPA (55 sec). Until generation 10 a thin layer (∼ 5 nm) of Ti was evaporated followed by a 50 nm layer of Au. From generation 10 a thin layer (∼ 5 nm) of Palladium were evaporated followed by a 50 nm layer of Au. The evaporation in this step was done in the thermal evaporator. Finally lift off was performed. After all the processing steps were completed, the chips were bonded to chip carriers using aluminium wire. An in depth step by step recipe can be found in Appendix A.

### 3.2 Measurement Setup

All measurements in this project were performed using a Oxford Instruments Cryofree HelioxAC-V refrigerator. The HelioxAC-V refrigerator can obtain temperatures down to 300 mK. All experiments were performed at this temperature unless otherwise specified. No magnetic field was available.

The measurement setup is shown in Figure 3.2. The lock-in amplifiers used were of the model Stanford Research Systems SR830. Multimeters used were either Agilent 34401A through generation 10 part 1 or Keithley model 2614B from generation 10 part 2. The DAC used was a NI Daq . Voltage source for the gates were Keithley model 2400 through generation 10 part 1 and Keithley model 2614B from generation 10 part 2. Current amplifiers were of model Ithaco DL1211.

After the signal enters the current amplifier two outputs are available. The first output passes through a low-pass filter with a changeable time con-

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\(^2\) Edwards Auto 306 thermal evaporator
Fig. 3.2: Schematic of the nanotube devices and measurement setup. Current is applied through the central superconducting lead and measured two-terminally through the quantum dots. Spin orbit magnetic fields of the nanotube is shown to demonstrate the necessary difference required by the Braunecker proposal. Instruments used are specified in the text. Adapted with permission from [15].

For these experiments the time constant was configured to 100 ms. This output is then sent to the multimeter and the DC current is measured. The second signal does not pass through the low-pass filter and the unfiltered signal is then sent to the lock-in amplifier. The lock-in amplifier then measures the conductance. Differential conductance was obtained by numerically differentiation of the current.

All data acquisition was performed using the matlab-qd framework developed by Anders Jellinggaard3.

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3 The framework is continually upgraded and available at: https://github.com/qdev-dk/matlab-qd.
4. RESULTS AND DISCUSSION

4.1 CNT Characterization and Fabrication Success

Before further investigation of the nanotube, gate traces were performed at room temperature to check whether the fabrication and geometry of the device was successful. These traces were done at approximately $1 \times 10^{-3}$ mbar. Furthermore these gate traces identified whether a given nanotube was semiconducting, narrow-gap or metallic. During the project no metallic nanotubes were found, while a mix of semiconducting and narrow-gap nanotubes were obtained. Though the fabrication process was successful only a handful of devices had sufficiently good contact to both sides of the device and were cooled down. This was either due to non-optimal contact between the nanotube and contacts or failure in the geometry of the device and thus having only contact to one side.

Throughout the project a total of 6 generations, a new generation for each new base chip, were produced. Since each base chip was cleaved in two pieces a distinction was made between part 1 and 2 in each generation.

<table>
<thead>
<tr>
<th>Generation</th>
<th>Metal</th>
<th>Superconductor</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gen 7 part 2</td>
<td>Ti/Au (5/50 nm)</td>
<td>Ti/V (5/70 nm)</td>
<td>Low contact</td>
</tr>
<tr>
<td>Gen 8</td>
<td>Ti/Au (5/50 nm)</td>
<td>Ti/V (5/70 nm)</td>
<td>Low contact</td>
</tr>
<tr>
<td>Gen 9 part 1</td>
<td>Ti/Au (5/50 nm)</td>
<td>Ti/V (5/60 nm)</td>
<td>Lift off failure &amp; low contact</td>
</tr>
<tr>
<td>Gen 9 part 2</td>
<td>Ti/Au (5/50 nm)</td>
<td>Ti/V (5/60 nm)</td>
<td>Design failure &amp; low contact</td>
</tr>
<tr>
<td>Gen 10 part 1</td>
<td>Pd/Au (5/60 nm)</td>
<td>Ti/V (5/60 nm)</td>
<td>Ok contact</td>
</tr>
<tr>
<td>Gen 10 part 2</td>
<td>Pd/Au (5/60 nm)</td>
<td>Ti/V (5/60 nm)</td>
<td>Ok contact</td>
</tr>
<tr>
<td>Gen 11</td>
<td>Pd/Au (5/60 nm)</td>
<td>Ti/V (5/60 nm)</td>
<td>Fabrication failure</td>
</tr>
<tr>
<td>Gen 12 part 1</td>
<td>Pd/Au (5/60 nm)</td>
<td>Ti/Al (3/15 nm)</td>
<td>Ok contact</td>
</tr>
</tbody>
</table>

Tab. 4.1: Overview of the metals used during different generations and the status of the devices. Ti/Au was initially used for normal contacts, but was changed to Pd/Au to increase the contact from the normal leads to the nanotube. For the final device Aluminium was used as a superconductor instead of Vanadium due to problems fabrication problems with Vanadium.
Due to the geometry of the devices it was not possible to test for nanotube contact until a batch of devices were finalized. This meant that any problems arising during the processing were not discovered until the very end of the process. Thus optimization of the process was slow. During the first 2 generations (gen 7 part 2 and gen 8) the recipe had been altered slightly from the original found in Morten Canth Hels’ thesis [15]. Though the devices from gen 7 part 2 and 8 showed promise, the contact to the nanotubes were a bit lower than expected which was attributed to human errors during the process. Generation 9 showed the same pattern as the previous generation even though some of the tubes were serially connected due to a design failure and a decision was made to change the normal contact metals. Palladium was chosen as the new top contact material, due to it being known to provide a low ohmic contact resistance [27, 28]. Furthermore, gen 9 also experienced problems during lift off which was attributed to the high heat in the Edwards thermal chamber\(^1\) when evaporating vanadium. To prevent this in further generations the vanadium evaporation was moved to the AJA evaporation chamber. Devices from generation 10 part 1 + 2 were further examined in low temperature measurements. The conductance measured in gate traces in these experiments were lower than those done at room temperature by a factor of about 10. In addition no superconducting gap was observed making it necessary to examine the vanadium closer.

### 4.2 Superconductivity

Since no superconducting gap was observed in any of the previous samples several 4 probe arrangements were produced. These consisted of 4 bonding pads connected by a line of Vanadium with the desired width. The widths chosen were: 300 nm, 500 nm, 1 \(\mu\)m, and 5 \(\mu\)m. In previous devices a width of 300 nm had been used for the superconducting lead and superconducting behaviour had been seen in a strip with a width of 5 \(\mu\)m Vanadium. 500 nm and 1\(\mu\)m were deemed interesting widths to check what happened to the superconductivity as the samples were made smaller. When measuring the resistance through the 4 probe arrangements the following averages we obtained.

The resistance scales by 1/width and width multiplied by the resistance should thus be constant. This is what we see for the measurements done at 2.5K. All the samples have resistance of \(5−10 \times 10^3\Omega\). However, in the case of the 5\(\mu\)m strip the resistance doesn’t follow this for the 300 mK measurement. The resistance is one tenth of what it should be, had the temperature no

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\(^1\) Edwards Auto 306 thermal evaporator
4. Results and Discussion

<table>
<thead>
<tr>
<th>Width</th>
<th>R at 300 mK</th>
<th>R at 2.5K</th>
<th>width * R at 300 mK</th>
<th>width * R at 2.5K</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 nm</td>
<td>2.48 × 10^4 Ω</td>
<td>2.47 × 10^4 Ω</td>
<td>7.44 × 10^4 Ω</td>
<td>7.41 × 10^4 Ω</td>
</tr>
<tr>
<td>500 nm</td>
<td>1.44 × 10^4 Ω</td>
<td>1.44 × 10^4 Ω</td>
<td>7.20 × 10^3 Ω</td>
<td>7.20 × 10^3 Ω</td>
</tr>
<tr>
<td>1 μm</td>
<td>9.97 × 10^3 Ω</td>
<td>9.02 × 10^3 Ω</td>
<td>9.97 × 10^3 Ω</td>
<td>9.02 × 10^3 Ω</td>
</tr>
<tr>
<td>5 μm</td>
<td>1.11 × 10^3 Ω</td>
<td>9.59 × 10^2 Ω</td>
<td>5.55 × 10^2 Ω</td>
<td>4.80 × 10^3 Ω</td>
</tr>
</tbody>
</table>

Tab. 4.2: Resistance measurements of Vanadium strips was obtained. The results show that only the 5 μm wide Vanadium strip became superconducting as the samples were cooled down to sub-kelvin temperatures. Resistance scales as 1/width and width times resistance should thus be constant unless the sample is superconducting. The measured resistance are all of the same order of magnitude except the 5 μm strip at 300 mK. All measurements were performed using 4-probe arrangements except the 5 μm strip for which only 3 bonding pads were available.

influence on the result. When doing continuing sweeps of the 5 μm strips while heating the sample a clear increase in resistance is observed (Figure 4.1).

![Graph showing resistance increase](image.png)

Fig. 4.1: The resistance of the 5 μm strip is measured as the sample is heated. The sample clearly reaches a critical temperature at which the superconductivity is destroyed and the resistance sharply increases.

The 5 μm strip is concluded to be superconducting while the rest of the strips are not. Since superconducting Vanadium is observed it is highly unlikely that the Vanadium source is the problem. A more likely reason for the missing superconductivity is contamination of the Vanadium during the fabrication. One such contamination could be the resist used during the evaporation of Vanadium. If the temperature was too high and some of the resist melted and mixed with the vanadium this would bring impurities into play. This could also explain why the 5 μm strip is superconducting since the resist would contaminate from the sides leaving a band of pure Vanadium in the center of the strip. It should be possible to evaporate Vanadium without
the temperature in the evaporation chamber becoming as high as in this project, however, due to time limitations this was never examined.

### 4.3 Series Resistance

The following section will focus on devices from gen 10, and in particular device D3 from gen 10 part 2. Gate traces were done for the device at room temperature twice. The first gate trace was performed at a probe station while the second was performed in the cryo cooler before cooldown (shown in Figure 4.2). The trace in the HelioxAC-V refrigerator was done at a pressure of < $1 \times 10^{-3}$. The dip in conductance at respectively 0 and 7 indicates that the nanotube is a narrow-gap nanotube.

![Fig. 4.2](image)

*Fig. 4.2: Gate traces from device gen10 part 2 D3 was obtained at room temperature in the HelioxAC-V refrigerator before cooldown was started. The gate traces shows a dip in conductance around 0-10 backgate voltage indicating a narrow-gap nanotube.*

After cooldown to the base temperature of 300 mK the gate traces are much different though. As seen in Figure B.2 the traces show an almost constant conductance with dips around what was perceived to be the bandgap. However, another way to interpret this could be that of a series resistance capping the conductance except in the bandgap where the conductance naturally is much lower.

To correct for this one would have to subtract the series resistance. A simple way of doing this would be to assume that the series resistance can be described as

$$R_s = \frac{1}{G_{\text{max}}}$$  \hspace{1cm} (4.1)

where $R_s$ is the series resistance and $G_{\text{max}}$ is the maximum measure conductance. This, however, does not give a reasonable result due to the maximum value of the measured conductance being higher than the real conductance due to fluctuations. The conductance of a nanotube shouldn’t be higher than
4. Results and Discussion

Fig. 4.3: Gate traces performed at 300mK temperatures. The two top images (left image: left side of the device, right image: right side of the device) show the data in the entire range from [-20:20] with the bottom two images showing the same side of the devices but zoomed in around what is perceived to be the bandgap. The data can be understood two ways. One is of a constant conductance with dips in conductance. The other is that of a series resistance capping the conductance except in the bandgap where it naturally is lower.

\[ 2e^2/h \] so by limiting the \( G_{\text{max}} \) to 2 a slightly better result is had in

\[ G_{\text{max}} = \frac{1}{R_s + 1/2} \Rightarrow R_s = \frac{1}{G_{\text{max}}} - \frac{1}{2}. \] (4.2)

By subtracting \( R_s \) from the measured signal one gets

\[ G = \frac{1}{R_s + R_t} \Rightarrow R_t = \frac{1}{G} - R_s \Rightarrow G_t = \frac{1}{G - R_s} \] (4.3)

where \( G \) is the measured signal and \( G_t \) is the conductance of the nanotube.

When using this correction the data begin to resemble data from other nanotubes. A zoomed in picture of the data is shown in Figure 4.4.

The maximum measured conductance changes based on the bias voltage applied. This indicates that the resistance is biasdependent. Thus it is not possible to just get the series resistance for one bias voltage and then subtract it for all other data points. When doing bias spectroscopy the series resistance
4. Results and Discussion

Fig. 4.4: Applying the data correction to the previously obtained gate traces the picture looks completely different. It exhibits features similar to those usually obtained in carbon nanotube quantum dots compared to those of the unaltered data.

is then calculated and subtracted from each horizontal line. In Figure 4.5 bias spectroscopy plots of both the left and right side of device "gen10 part 2 D3" is shown. The top two plots are the data with no corrections while the two bottom plots have been subjected to the above mentioned data correction.

If indeed there is a series resistance the nanotube would experience a lower $V_{SD}$ than what was applied to the system. In that case one would expect to have to go to a higher bias to see an entire coulomb diamond, furthermore, if the resistance is bias dependent the coulomb diamond would be expected to be curved instead of straight. As the bias is increased and the series resistance lessened the nanotube would experience a higher $V_{SD}$ than just the increase in bias. This will in turn close the coulomb diamond faster and the curved line appear. This is also observed experimentally in Figure 4.6.

A strong case has been made for a series resistance to have appeared in the device. The series resistance affects both sides of the device and one would naively believe the resistance to be on the only section that both side share, the superconducting lead. The superconducting lead is made in one step and is thus one piece all the way to the bonding pad. This leaves the interface between the bonding pad and the bonding wire, the HelioxAC-V refrigerator, or a similar resistance in both normal leads as the most obvious causes. In the test of the vanadium strips no such resistance was observed. This excludes the HelioxAC-V refrigerator and the bonding pad/bonding wire interface as the same procedures were used there. However, when looking at Figure 4.3 we see that the conductance and thus the resistance is slightly different in the two sides.

In the normal leads an interface exists between the inner contact on the nanotube and the outer contact connecting it to the bonding pad. The
bonding pad and outer contact were made prior to the inner contact and an oxidising layer may have formed before the Pd/Au of the inner contacts were evaporated. To test whether the series resistance is in the normal leads and not in the superconducting lead, the voltage source is switched to the left normal lead. When measuring the resistance with the superconducting lead floated one measures twice the resistance during the system compared to when the superconducting lead is not floated (Data shown in appendix B). This further indicates that a series resistance exists in both the normal leads, possibly in the interface between the inner and outer contacts.

4.4 Characterization of Gen10 part2 D3

We now take a closer look at the characterization of device “Gen10 part2 D3”. As previously stated it is based on a narrowgap nanotube. Though the data correction described above helps on the clarity of the data, it is still only in the gap region much can be seen about the quantum dot. Figure 4.7 shows a zoomed in version of the lower left plot in Figure 4.5. The characteristic fourfold symmetry of a carbon nanotube quantum dot is observed. The left side of the device in general shows more coulomb diamonds than the right side, however, the shell structure of the quantum dot is clear only in a few
4. Results and Discussion

Fig. 4.6: If the series resistance decreases as the bias is increased the Coulomb diamonds should show curved sides instead of straight ones. This is exactly observed in the corrected data. As the bias is increased the quantum dots experiences a relatively higher bias increase than what is applied.

Fig. 4.7: A clear shell structure is observed in the left side of the corrected data. A fourfold nanotube structure is observed though switching during the measurement makes the interpretation more difficult.

Figure 4.8 shows two zoom ins of the right side of the device. The shell structure is much clearer on the right side, however, Kondo resonances dominate the picture. This is not ideal if the purpose is to produce Cooper pair splitters since the Kondo states are mixtures of the spin states and the electrons in the contacts. One of the requirements of the Braunecker proposal is well-resolved spin states, which can’t be achieved with the Kondo resonances. The level spacing between the shells is of the same order of magnitude as the ones reported by Morten Canth Hels in his thesis.

Another thing worth noticing is a possible gap in the conductance. When looking at Figure 4.5 a gap is observed in the uncorrected data set. The gap is also possible in the right side of the corrected data but is more difficult to observe in the left side. Though when zoomed in, a gap appears in the left places.
Fig. 4.8: Kondo resonances are observed in the corrected data set of the right side of the Cooper pair splitter device. The right image is a zoomed in version of the left showing clear shell structure though the individual states cannot be seen.

side too. Previous results obtained from the Vanadium strips suggest that the Vanadium should not become superconducting. In Figure 4.9 the top images depicts data where instead of sweeping the bias vertically, the backgate was swept and the sweep thus horizontally. The sweeps were performed in a range where no coulomb diamonds were observed. This eliminates that it could be an artefact of the measuring equipment behaving weird when sweeping across 0 bias. If the gap indeed is superconducting it should disappear when the temperature is increased. The bottom two images of Figure 4.9 depict this situation. A continuous bias sweep far away from any coulomb diamonds was performed while the sample was heated. The gap seems to reduce until it disappears at around 60 sweeps in both images. At the 60 sweep spot the temperature was around 3K while the sweeps were stopped at 5K. No magnetic field was available and consequently it wasn’t possible to determine whether a magnetic field could quench a possible superconducting state. One thing to note though is the fact that the gap didn’t go to zero. A critical temperature of around 3K is not unrealistic, however, due to the previous results from the vanadium strips, it is still not clear whether the gap is a superconducting gap.
Fig. 4.9: To exclude artefacts arising from sweeping across 0 in the bias window, horizontal sweeps of the sample was performed. Even though switching occurred during the measurement the gap was still visible. This is shown in the top two images. The bottom two images shows how the gap seemingly disappear as the sample is heated. 60 sweeps corresponds to about 3K while 100 sweeps corresponds to 5K.
5. CONCLUSION

In conclusion carbon nanotube devices with the desired geometry were produced successfully. Characterization of the devices, however, revealed that the metal used as a superconductor did not behave as expected. Even so, the devices did fulfill some of the requirements from the Braunecker proposal necessary for entanglement detection, namely:

- The fourfold symmetry of carbon nanotube quantum dots were visible making it possible to clearly identify states in the device. Though Kondo resonances did complicate the picture in some devices.

- Vanadium did show superconductivity when examined, however, only wider strips than the width used in the devices. By changing the fabrication process it should be doable, however, to produce Vanadium strips of the desired width.

The fabrication process worked well in general though. The difficulty of obtaining bent carbon nanotubes needed for the devices were seldom a problem and given the possibility of ashing and growing a second round of nanotubes the availability of nanotubes were good. The growth recipe from ref was thus successful.

One problem experienced in the fabrication process were that of a possible series resistance in the interface between two metals in the normal contacts. It is the opinion of the author that the evidence for this series resistance is comprehensive enough to conclude it’s existence. This series resistance convoluted the data and made the interpretation more difficult. A crude correction were presented and used with success.

Though the thesis did not advance the entanglement detection measurements it did provide useful insight into the fabrication of and obstacles of fabricating a Cooper pair splitter. Though promising results were had in ref [15], the requirements of the Braunecker proposal and entanglement detection remains unfulfilled and a successful devices using Vanadium as a superconductor is thus still of interest.
Appendices
Appendix A

FABRICATION

A.1 Fabrication overview

During the project a total of 6 different generations were fabricated. A generation consists of devices based on the same basechip and nanotube growth. Each basechip can be split into two parts thus allowing two different fabrication processes per generation. A basechip has enough bonding pads to bond a total of 48 Cooper pair splitter devices, or two times 24 if the basechip is split in two. The recipe that has been followed in this thesis was devised and optimized by Morten Canth Hels during his Master’s thesis. A few updates have been added during the authors work with the recipe.

The recipe can be divided up into 5 steps:

1. Creation of the basechip
2. Deposition of nanotube catalyst
3. Growth of nanotubes
4. 1st metal deposition, either normal or superconducting leads
5. 2nd metal deposition, either normal or superconducting leads

The specific metal combinations and thicknesses can be seen in Table 4.1.

A.1.1 Step 1: Creation of the basechip

- Cut out a 1.0x2.0 cm² SiO₂ chip.
- Clean the chip by sonicating it in acetone, flushing it with IPA and drying it with nitrogen.
- Bake the chip on a hotplate at 185°C for 4 min.
- Spin one layer of EL-6 resist at 4500 rpm for 1 min.
Appendix A. Fabrication

- Bake the chip on a hotplate at 185°C for 3 min.
- Spin one layer of CSAR4 resists at 4500 rpm for 1 min.
- Bake the chip on a hotplate at 185°C for 3 min.
- Expose alignment mark patterns and Large letters in the resist using an Elionix ELS-7000 with the following settings: Field size: 600 \( \mu \)m, Dots: 20000, Dose: 400 \( \mu \)C/cm\(^2\), Current: 10nA, Aperture: 120\( \mu \)m.
- Develop the chip at room temperature in O-xylene for 60s, MIBK:IPA for 60s followed by 30s in IPA.
- Ash the chip for 30s and evaporate Ti/Pt (5/60 nm) in AJA evaporation chamber.
- Lift-off in NMP at 76°C for 10 min. Sonicate for 1 min. Flush with transfer pipette.

A.1.2 Step 2: Deposition of nanotube catalyst

- Clean chip with acetone, followed by IPA and dry with nitrogen.
- Bake the chip on a hotplate at 185°C for 4 min.
- Spin one layer of A6 resist at 4500 rpm for 1 min
- Bake the chip on a hotplate at 185°C for 1 min.
- Spin a second layer of A6 resist at 4500 rpm for 1 min.
- Bake the chip on a hotplate at 185°C for 1 min.
- Expose catalyst pattern using a Raith Eline with the following parameters: Dose: 350 \( \mu \)C/cm\(^2\), area step size: 10 nm, dot dose: 0.1 pA, write field: 200 \( \mu \)m, acceleration voltage: 20kV, aperture: 30 \( \mu \)m. Note: In this step it is important to scan as little as possible to avoid having catalyst islands all over the chip. It is thus preferable to know the exact distance from the corner of a chip to the alignment mark.
- Develop in MIBK:IPA for 55s, followed by IPA for 55s. Dry with nitrogen.
- Stir catalyst solution at least 2 minutes.
- Apply 4 drops for a 1.0x2.0 chip using a transfer pipette.
Let the chip dry for 11 min under a lid to avoid contamination of stray drops of liquid.

Bake the chip on a hotplate at 185°C for 7 min.

Lift-off in 100 mL NMP for two hours at 76°C.

Spray the chip generously with acetone followed by IPA to remove unwanted catalyst. Dry with nitrogen.

A.1.3 Step 3: Growth of nanotubes

Before loading the chip into the oven a prebake step was performed to flush the oven of any contaminants. During the prebake step the gas flow was configured the following way:

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>$T_{set}$ (°C)</th>
<th>$T_{oven}$ (°C)</th>
<th>Ar</th>
<th>H$_2$</th>
<th>CH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>910</td>
<td>21</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
<td>910</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Once the oven has cooled to a couple of hundred degrees Celsius the process is continued.

- Ash the chip for 30s to remove any leftover resist.
- Load the chip into the oven.

The nanotubes were then grown using the following gas flows:

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>$T_{set}$ (°C)</th>
<th>$T_{oven}$ (°C)</th>
<th>Ar</th>
<th>H$_2$</th>
<th>CH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>910</td>
<td>200</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>910</td>
<td>350</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>910</td>
<td>910</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>910</td>
<td>910</td>
<td>-</td>
<td>0.1</td>
<td>0.65</td>
</tr>
<tr>
<td>57</td>
<td>0</td>
<td>910</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

- Take images of carbon nanotubes in SEM at an acceleration voltage of 1.5 kV. Use the following image properties: Size: 100 µm × 100 µm, resolution: 2000 points × 2000 points, point average: 1.

---

1 The Brooks controller in the lab displays the gas flow in percentages with the following conversion: gas flow = percentage × max flow. The maximum flow for the gasses used are: Ar: 2, H$_2$: 0.5, CH$_4$: 5 nL/min N$_2$. 

• If the concentration of nanotubes is too low the chip can be ashed and the growth step repeated.

• Design devices based on the SEM images. DesignCAD 23 was used for this purpose.

• Note: Do not ash or sonicate the chip from now on as that will destroy the nanotubes.

A.1.4 Step 4: 1st metal deposition

• Clean the chip with acetone, followed by IPA and dry with nitrogen.

• Bake the chip on a hotplate at 185°C for 4 min.

• Spin one layer of EL-6 resist at 4500 rpm for 1 min.

• Bake the chip on a hotplate at 185°C for 3 min.

• Spin one layer of A4 resist at 4500 rpm for 1 min.

• Bake the chip on a hotplate at 185°C for 3 min.

• Expose pattern for bonding pads, outer contacts, sidegate, and the superconducting contact in the resist using a Raith eLine. Settings for the inner contacts: Area step: 4nm, Dose: 390 µC/cm², Write field: 100 µm, Aperture: 30 µm, Acceleration voltage: 20 kV. Settings for outer contacts: Area step: 20 nm, Dose 390 µC/cm², Write field: 200 µm, Aperture: 120 µm, Acceleration voltage: 20 kV.

• Develop the chip at room temperature in MIBK:IPA for 55 sec followed by IPA for 55 sec. Dry with nitrogen.

• Load the chip in an evaporation chamber and evaporate the desired metal(s).

A.1.5 Step 5: 2nd metal deposition

Step 5 is almost identical to step 4, however, there is no need for exposure of the bonding pads and outer contacts in this step. It depends on the metal whether it is preferable to deposit the superconducting metal in the previous step or this. The metal that most easily peels off should be left for the final step.

• Clean the chip with acetone, followed by IPA and dry with nitrogen.
Appendix A. Fabrication

- Bake the chip on a hotplate at 185°C for 4 min.
- Spin one layer of EL-6 resist at 4500 rpm for 1 min.
- Bake the chip on a hotplate at 185°C for 3 min.
- Spin one layer of A4 resist at 4500 rpm for 1 min.
- Bake the chip on a hotplate at 185°C for 3 min.
- Expose pattern for the normal contacts in the resist using a Raith eLine.
  Settings for the contacts: Area step: 4nm, Dose: 390 µC/cm², Write field: 100 µm, Aperture: 30 µm, Acceleration voltage: 20 kV.
- Develop the chip at room temperature in MIBK:IPA for 55 sec followed by IPA for 55 sec. Dry with nitrogen.
- Load the chip in an evaporation chamber and evaporate the desired metal(s).
Appendix B

SUPPLEMENTAL DATA

Fig. B.1: By using one of the leads as the source contact and measuring the conductance through respectively the other normal contact (top images) and the superconducting contact (bottom images) the resistances can be compared. When the superconducting lead is floated the resistance is twice as high as when the superconducting contact was able to lead. This indicates that a series resistance is located in both of the normal contacts.
Fig. B.2: The full gate trace shown Figure 4.3 when the data correction has been applied.

Fig. B.3: The fourfold shell structure of a carbon nanotube quantum dot was observable several places in addition to the one shown in Figure 4.7.
BIBLIOGRAPHY


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