Electronic Transport in Ropes of Single Wall Carbon Nanotubes

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Chapter 1

Quo Vadis

'Since their discovery in 1991 [1], carbon nanotubes have attracted a great deal of attention ...'

A sentence like this opens most of the literature on carbon nanotubes. It sounds promising and at the same time decent enough. But it does not reveal the excitement the nanotubes caused, not only among scientists, but also in the general public. They contain such a wealth of most interesting characteristics that one does not know where to begin. Obviously, the carbon nanotubes are made from carbon, the most versatile element in the world. It forms brittle structures like graphite and durable material like diamond, not mentioned its innumerable compounds in chemistry and biology. The newer descendants of carbon, the buckminster fullerenes, occupied research in the 80’s and enriched the community with ideas of cages for atoms and frictionless ball bearings. And they supplied the solid state physics with an instructive example for a solid at the frontier between molecule and crystal.

The worthy successors are the long, hollow molecules of the carbon nanotubes. Their exceptional strength and their remarkable electronic properties do indeed attract a great deal of attention. Besides the basic interest of physics in these one dimensional systems, a vast number of applications has been proposed, ranging from ultrasmall probes in scanning probe microscopy [2] over artificial muscles [3] to hydrogen storage [4], from field emitters for flat panel displays [5] to nanoelectronics [6, 7]. As is often observed, the basic research trails the application since the question why it is working is felt less important as long as it is working. Most of the applications relying on the geometry of the nanotubes (SPM, hydrogen storage, field emission) have produced impressive results. But the picture is very different in case of the electronic applications. Though this field stimulated the most fantastic ideas about the use of carbon nanotubes, it is the field in which a detailed knowledge about the intrinsic properties and the interaction of the tubes is essential for any kind of progress. This work will expand the understanding of the electronic properties of the nanotubes in order to give impulses for application as well as basic research.

Chapter 2 will give a bottom-to-top review of the basic knowledge about
nanotubes as it emerged from research so far. It will cover the geometric and especially the electronic characteristics of the single nanotubes and will address the challenges encountered when dealing with complex arrangements of nanotubes. Supplied with this necessary background, chapter 3 will turn to the experimental characterization of such arrangements of tubes, called nanotube ropes. The findings will yield information on current transport in nanotube ropes and, even more important, they will show that the most important task in research in nanotube electronics is the study of the electronic interaction of the tubes. Exactly this point will be the topic of chapter 4. The measurements will supply valuable information on the coupling mechanism between and coherent transport in carbon nanotubes. Chapter 5 will move on to deepen the insight in the mechanisms having influence on current transport.
Chapter 2

Basics

First of all, it has to be clarified, what a carbon nanotube is, how it is constructed from carbon atoms, and what it looks like. The beauty and aesthetics of these hollow molecules goes along with a high rigidity and strength. But the main interest of this work is in the electronic characteristics of nanotubes and their interaction with one another. Thus, once a picture of the geometry of the nanotubes is drawn, the second section will move on to their electronic behavior. The band structure of the tubes will be studied thoroughly and conclusions will be drawn about current transport in a single tube. The fundamental implications of the reduced dimensionality of these systems will be addressed in the third section, before ensembles of tubes can be studied. These ensembles will be the focus of the last chapter, regarding both, their geometry as well as their electronics, before the main part of this investigation can begin.

2.1 Wrapping Up

The geometry of the nanotubes is that of a hollow cylinder. The carbon atoms, which the tubes consist of, form the surface of the cylinder and are arranged in a honeycomb crystalline lattice. This lattice is the same as found in the atomic planes of graphite. Graphite consists of planes of atoms stacked onto one another. This description of a crystal is commonly used when dealing with diffraction experiments and is not an appropriate view for most properties of the crystal, but in case of graphite this picture already captures most of the physics. While strong covalent bonds exist between atoms inside a plane, there is only van der Waals interaction between the planes, making graphite a structurally very anisotropic material. Its brittle consistence is the macroscopic evidence for the weak inter-plane interaction. Inside one plane, the carbon atoms are hybridized in the sp$^2$ configuration. Thus, they share three equal bonds with other carbon atoms in the plane and the remaining electron populates a $\pi$ orbital perpendicular to this plane. This electron is delocalized, similar to electrons delocalized in rings of benzene. One such atomic plane is called ’graphene’ and figure 2.1 shows its crystal structure. Graphite is obtained, when many of these
atomic planes are stacked onto one another.

The honeycomb lattice of the graphene planes is a triangular Bravais lattice with a two-atom basis. The nanotubes are formed by rolling up such an atomic sheet to a cylinder. The most comprehensive way to picture a nanotube is to make one by oneself. At the end of this work there are some sheets printed with a honeycomb lattice and the reader is welcome to remove them and build his or her own 'nanotubes'. To preserve the periodicity of the lattice, the roll-up may not be completely arbitrary. One has to match the atomic positions at the two edges of the sheet. This is fulfilled only if an atomic site is rolled onto another equivalent site of the lattice. Since the lattice is a Bravais lattice with a basis not all atomic positions are equivalent. (This can be seen e.g. in figure 2.1 where half of the atoms have a bond going strictly to the right, the other half has a bond going to the left.) The triangular Bravais lattice connects all equivalent positions by the lattice vectors \( \mathbf{R} = n_1 \cdot \mathbf{a}_1 + n_2 \cdot \mathbf{a}_2 \). Let us consider the vector \( \mathbf{C} = n \cdot \mathbf{a}_1 + m \cdot \mathbf{a}_2 \), as shown in figure 2.2.

If the sites connected by \( \mathbf{C} \) are positioned onto one another when rolling up the cylinder, the lattice matches and a nanotube is constructed successfully. The vector \( \mathbf{C} \) now runs around the circumference of the tube, which is hence called a \((n,m)\) tube. (One of the do-it-yourself sheets results in a \((10,10)\) tube, another in a \((13,6)\) tube.) The circumference is simply \( |\mathbf{C}| \) and the diameter of a \((n,m)\) tube is

\[
D = |\mathbf{C}|/\pi = a/\pi \cdot \sqrt{n^2 + m^2} \tag{2.1}
\]

\( (a = 2.46 \text{ Å}) \) [8]. The vector \( \mathbf{P} = \tilde{n} \cdot \mathbf{a}_1 + \tilde{m} \cdot \mathbf{a}_2 \) marks the new periodicity along the tube axis, with \( \tilde{n} = (n + 2m)/\text{lcd} \) and \( \tilde{m} = (−2n − m)/\text{lcd} \) and \( \text{lcd} \) being the largest common divisor of \((n + 2m)\) and \((−2n − m)\). For tubes build in this way, the term Single Wall carbon NanoTube or simply SWNT estab-
Figure 2.2: Graphene sheet with a lattice vector $\overrightarrow{C} = 5 \cdot \overrightarrow{a_1} + 2 \cdot \overrightarrow{a_2}$. When rolling up the sheet to a (5,2) nanotube, the atomic sites connected by $\overrightarrow{C}$ have to be matched. The shaded area will then be the cylinder surface and $\overrightarrow{C}$ will run around the circumference. The vector $\overrightarrow{P} = 3 \cdot \overrightarrow{a_1} - 4 \cdot \overrightarrow{a_2}$ is perpendicular to $\overrightarrow{C}$ and marks the periodicity of the nanotube along its axis.

lished. Some examples of tubes with different roll-up vector are depicted in figure 2.3. Now, every choice of $n$ and $m$ results in a nanotube with somewhat different appearance, but not all types of tubes are really unique. E.g. the (13,6) and (6,13) tubes are just mirror images. Moreover, the threefold symmetry of the lattice further degenerates the choices for $n$ and $m$, making for example the tubes (10,10), (-10,-10), (10,-20), (-10,20), (20,-10), and (-20,10) indistinguishable. Figure 2.4 depicts the choices for $(n,m)$ which are sufficient to reproduce all tubes possible. Some combinations result in tubes of special symmetry. The $(n,0)$ tubes are called 'zig-zag' tubes since their circumference runs along a zig-zag chain of bonds as shown in figure 2.3. The bonds following the circumference of the $(n,n)$ tubes form an 'armchair' (an example for the imagination of physicists), as can be seen best at one of the do-it-yourself models. The remaining tubes are called helical or chiral. These symmetries will become very important in the next section, when talking about the electronic structure of the tubes.

To get an impression what the size of the nanotubes is, let’s put some numbers. A typical tube of the (10,10) type (an 'armchair' tube) has a diameter
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Figure 2.3: Several examples for tubes with different roll-up vectors [9]. The diameters of the tubes, according to formula 2.1, is 0.68 nm, 0.7 nm, and 1.04 nm, respectively. Note the zig-zag like chain of bonds running around the circumference of the (9,0) tube and the 'armchair' like chain in the case of the (5,5) tube.

Of course, such a tube is not visible by bare eye, and a bundle of 100 of them is necessary to be spotted with the best optical microscope. Using scanning tunneling microscopy [10, 11, 12] the crystalline structure of the tubes was verified. Despite their small diameter, their length can be micrometers [6], which makes nanotubes the (geometrically) most anisotropic molecules in the world. E.g. the do-it-yourself model (appendix A) of the (10,10) tube has a diameter of 4.5 cm, so in a consistent scale it should extend over 50 m from end to end.

Concerning the ends of the nanotube, these are the points where the symmetry, or better the periodicity, of these macromolecules is broken. Sometimes the tubes are found to terminate in an open end, quite like rolled-up paper sheets serving as the simplest models for nanotubes, but usually they are closed by hemispherical end caps [13]. Figure 2.5 shows the end of a nanotube with a cap being one half of a spherical fullerene (a 'bucky ball') of the appropriate size.
2.1. WRAPPING UP

Figure 2.4: Any nanotube possible can be constructed by connecting the origin (large gray circle) with one of the marked lattice sites by a vector $\mathbf{C}$, which serves as roll-up vector for the tube. The use of any unmarked lattice site results (due to the symmetry) in a nanotube which can also be constructed by using one of the marked sites.

(cf. figure 2.3). The end caps, which are curved in two dimensions, are formed by inserting pentagons in the usual hexagonal structure of the graphene sheet.

Until now, the only restriction posed on constructing nanotubes has been the conservation of the lattice periodicity of the graphene honeycomb lattice. But the roll-up process itself already changes the graphene structure since the atomic sheet is no longer planar. It is clear that there has to be a limit for the curvature of the sheet the bonds between the carbon atoms are able to follow. And indeed the smallest tube found to date has a diameter of 0.5 nm, which corresponds to a (6,0) tube [14]. On the other hand, the largest tubes with diameters of 20 nm or more are expected to collapse due to interactions with other tubes or a substrate (figure 2.6). But between these extremes all possible structures are found when producing nanotubes.

Of course, the tubes are not produced by rolling up atomic sheets of carbon atoms, but they grow under certain conditions in a self-assembly process (for a review, see [13]). The material for the growth is usually supplied by an arc discharge between graphite electrodes or by evaporizing material from a block of graphite with a laser beam. Chemical vapor deposition of carbon is another process in development. The carbon material deposits on an anode
Figure 2.5: Model of the end of a (10,10) tube [9]. Like in fullerenes, the hemispherical end cap is formed by inserting pentagons into the usual array of hexagons.

or on the walls of the process chamber and the nanotubes grow starting at a carbon pentagon or part of an end cap, which are discussed to act as nucleation centers. In most processes, some metallic catalysts like Ni or Co are added to the graphite to help producing large (i.e. long) nanotubes rather than the short, more or less spherical fullerenes. According to the growth conditions, the produced nanotube material, the 'soot', contains various forms of nanotubes together with fullerenes, graphite and amorphous carbon. The most prominent process to produce large quantities of single-wall carbon nanotubes is a laser ablation technique developed at Rice University [15]. It produces nanotubes with diameters close to 1.35 nm, the diameter of the (10,10) tube. Though first investigation pointed to most of the tubes being indeed of the (10,10) type [15], newer results showed that no special chirality (a single (n,m) type) is preferred [16]. To date, no technique is known to produce a specific type of nanotube, though it would clearly be very valuable for research and future applications.

Once the nanotubes are separated from the by-products of the process, the investigation can begin. It turned out, that the tubes are very rigid and stable structures. When placed on a surface and manipulated with a tool like an atomic force microscope, they can sometimes be moved, but it proved very difficult to cut them into parts [18]. They showed very high bending stiffness with a Young modulus of several TPa [19, 20]. Their sound velocity, which is a measure for the elasticity modulus and hence for their rigidity, is around $1.5 \cdot 10^4$ m/s [21] (compare this to $Y \approx 0.2$ TPa and $c = 5 \cdot 10^3$ m/s for steel). The nanotubes were observed to follow the surface corrugation of the substrate.
2.2. HOW DO ELECTRONS FEEL IN HERE?

The relation between nanotubes and graphene regarding the geometry was already pointed out in the last section. This relation holds for the electrical properties, too. In graphene, three of the four valence electrons of carbon are hybridized in sp² orbitals forming covalent σ bonds to neighboring atoms, and the one remaining electron populates a p orbital. The half filled p orbital forms a valence bond with one bonding π and one antibonding π* orbital with the neighboring atoms. The bonding π orbital is filled, while the antibonding π* orbital is empty. Since all atoms contribute an electron in a p orbital, the electrons in the π orbital are delocalized over the entire atomic plane. This
situation is very similar to the delocalized electrons in conjugate double bonds, e.g. in benzene. But in contrast to benzene, where the electrons are restricted to the limited geometry of the benzene ring, in graphene the electrons can move in the plane with momentum. This leads to the band structure of graphene.

The band structure is usually presented in the first Brillouin zone of the reciprocal lattice which is depicted in figure 2.7 for graphene. The Bravais lattice of graphene is a triangular lattice with lattice constant $a = 2.46\,\text{Å}$. The reciprocal lattice is thus triangular, too, with a lattice constant $b = 4\pi/\sqrt{3}a$ and the first Brillouin zone has the shape of a hexagon. Figure 2.8 shows the band structure along several directions in the Brillouin zone. The lower lying valence bands formed by the $\sigma$ bonds (as well as the antibonding $\sigma^*$ bands) and the bonding and antibonding $\pi$ and $\pi^*$ bands can be seen, the $\pi$ and $\pi^*$ bands being emphasized. As was stated above, the bonding $\pi$ orbital is filled and the antibonding $\pi^*$ orbital is empty, thus the Fermi level is located between these bands. The $\pi$ and $\pi^*$ bands touch at the K points, that is in the corners of the Brillouin zone, and the Fermi level is fixed by this. Since the bands only touch the Fermi level (and one another) at single points of the Brillouin zone, the density of states vanishes at the Fermi level and graphene is a zero gap semiconductor. (In graphite, the weak interaction between the graphene planes results in a small overlap of the $\pi$ and $\pi^*$ bands, hence a small but finite density of states at the Fermi level is populated with electrons and holes, which makes graphite a semimetal [22, 23].) Since electronic transport is dominated by the electronic states near the Fermi level, the K points are the most interesting ones in the Brillouin zone.

Figure 2.9 shows the electronic bands near the Fermi level, i.e. parts of the $\pi$ and $\pi^*$ bands. The bands touch at the corners of the Brillouin zone and form...
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The σ and σ* bands are derived from the sp² hybrid orbitals forming the in-plane bonds. The π and π* bands (emphasized) result from the delocalized p orbitals. Since every carbon atom supplies one electron in its p orbital, the bonding π band is completely filled, while the antibonding π* band is completely empty. These bands touch each other at the K point, that is in the corners of the Brillouin zone, and thus the Fermi level is pinned there, making graphene a zero gap semiconductor.

Figure 2.8: Band structure of graphene along several lines in the Brillouin zone [24]. The σ and σ* bands are derived from the sp² hybrid orbitals forming the in-plane bonds. The π and π* bands (emphasized) result from the delocalized p orbitals. Since every carbon atom supplies one electron in its p orbital, the bonding π band is completely filled, while the antibonding π* band is completely empty. These bands touch each other at the K point, that is in the corners of the Brillouin zone, and thus the Fermi level is pinned there, making graphene a zero gap semiconductor.

'cones' above and below the Fermi level. They can be described by

\[ E(k) = E_F \pm \hbar \cdot v_F \cdot |k - k_F| \]

where \( k_F \) is the momentum at a K point and \( v_F = |\varphi(k)| = |h^{-1} \cdot dE/dk| \approx 10^6 \text{m/s} \). This description holds for a range of several hundred meV around the Fermi level [25]. The states at the K points can be visualized very easily. In figure 2.10 the six momenta belonging to the K points are retransferred into the real lattice. They correspond to a motion along the 'zig-zag' directions in the graphene lattice. This is reasonable, as the zig-zag directions offer the most
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Figure 2.9: Three dimensional plot of the graphene band structure near $E_F$. The cones represent the $\pi$ and $\pi^*$ bands touching in the corners of the Brillouin zone.

Figure 2.10: The momenta of the K points in the reciprocal lattice (right hand side) correspond to a motion along the 'zig-zag' directions in the graphene sheet (left hand side).

direct path for current transport if transport is imagined as moving an electron from bond to bond.

Now, what are the similarities and differences between the electronic structure of graphene and the one of nanotubes? Geometrically, a nanotube is constructed from graphene by rolling up the sheet of atoms to a cylinder, matching the lattice at the ends of the sheet. So, the (n,m) nanotube is periodic along
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Figure 2.11: A graphene sheet as to be rolled up to form a (3,3) tube. In the real lattice (left hand side), the vectors $P$ and $C$ mark the periodicity of the tube along and perpendicular to its axis. The tube surface is shaded. In the reciprocal lattice (right hand side), the dashed lines cutting through the Brillouin zone mark the momenta which are allowed states in the nanotube according to quantization condition 2.2.

its circumference with $C = n \cdot a_1 + m \cdot a_2$. This is a first class example for periodic boundary conditions. All electronic states of the tube have to match this periodicity around the circumference and thus their momentum $k$ has to fulfill

$$k \cdot C = 2\pi \cdot i,$$

with $i$ as an integer [8]. This is the quantization condition for the momentum parallel to $C$, around the circumference, while the momentum along the tube axis (i.e. parallel to $P$) is not affected. In figure 2.11 the situation is visualized. The dashed lines mark the momenta which satisfy the quantization condition and are thus allowed states in this special nanotube. The only degree of freedom for the electronic momentum left is along the tube axis. The momentum around the circumference is quantized. Thus, each of the bands of graphene ($\sigma$, $\sigma^*$, $\pi$ and $\pi^*$) splits into a number of one dimensional subbands (labeled by $i$), depicted in figure 2.12. The subbands are called one dimensional, although the belonging wave functions extend over the cylinder circumference and most of the subbands ($i \neq 0$) even possess angular momentum. This is in analogy to the electronic wave functions of atoms, where the states are called zero dimensional while they have an extent in three directions.

One puzzling fact about figure 2.12 has to be addressed, that is the unusual presentation of the band scheme. The bands in this diagram extend over different ranges along the momentum axis. That is, since the quantization of the graphene band structure in the first Brillouin zone was done solely according to the periodic boundary condition along the circumference. As soon as the quantization lines reach the boundary of the first Brillouin zone of the graphene plane, the subbands end in this figure. But now, one has a new, one dimensional crystal with a new periodicity along the tube axis. The periodicity along
Figure 2.12: When the graphene sheet is rolled up to a nanotube, every band of the graphene band structure (figure 2.8) splits into several subbands labeled by the subband index $i$, according to quantization condition 2.2. The momentum $k$ is directed along the nanotube axis. The emphasized lines in the figure are the subbands of the $\pi$ and $\pi^*$ bands of graphene.
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Figure 2.13: Band structure of a (3,3) nanotube. This is derived by splitting the band structure of graphene (figure 2.8) into subbands according to quantization condition 2.2 (figure 2.12), and subsequently transferring all subbands into the first Brillouin zone of the nanotube \((-\pi/a < k < \pi/a)\). Again, the \(\pi\) and \(\pi^*\) derived subbands are emphasized. Two of these subbands meet at the Fermi level.
the axis is $|P|$, thus all subbands have to be transferred into the first Brillouin zone of the tube between $-\pi/|P| < k < \pi/|P|$. This is done in figure 2.13 for the (3,3) tube, the example considered so far. As in all the (n,n) tubes, the period along the tube axis is $|P| = a$, and these parts of the subbands which reach beyond the new Brillouin zone boundaries of $\pm \pi/a$ are retransferred.

Now, what can be learned from the band structure of the nanotubes when they are derived in this way? In graphene, the states at the corners of the Brillouin zone were the most interesting ones regarding electronic transport. At these K points the $\pi$ and $\pi^*$ bands meet at the Fermi level. Are these states allowed in a (n,m) nanotube, that is, do they fulfill the quantization condition? The band structure of the (3,3) tube depicted in figure 2.13 supplies an example, where the K points are included in the quantization condition (for $i = 0$ and $i = \pm 3$) and thus the appropriate subbands derived from the $\pi$ and $\pi^*$ bands meet at the Fermi level. In contrast to graphene, where the bands meet at the boundary of the Brillouin zone (more precisely, at the corners), the meeting points are now inside the Brillouin zone of the tube at $\pm 2/3 \pi/a$. As was discussed in the last paragraph, this happens due to the new periodicity of the tube.

When evaluating the condition at the K points, one finds that if $n - m = 3 \cdot i$ (i integer), the K points are allowed states in a (n,m) tube [8]. That means, if n-m is not an integer multiple of 3, there are no states at the Fermi level allowed and the filled $\pi$ and empty $\pi^*$ subbands are separated by a finite energy gap. Thus, these tubes are semiconductors, e.g. a (13,6) tube has a gap of about 600 meV. On the other hand, when n-m is an integer multiple of 3, the K points are allowed states and at least one pair of the $\pi$ and $\pi^*$ subbands meets at the Fermi level. Again, it is a good approximation to describe the bands by a linear dispersion around $E_F$ [25]

$$E(k) = E_F \pm \hbar \cdot v_F(k - k_F),$$

but now the states are one dimensional (note that $k$ and $k_F$ are now scalars). A linear dispersion relation in one dimension leads to a finite density of states and hence the tubes with $n - m = 3i$ are metallic. Sorting all possible tubes into these categories, one third of the tubes is found to be metallic, i.e. fulfill $n - m = 3i$, while two thirds of the tubes are semiconducting.

Figure 2.14 shows how the quantization condition results in semiconducting and metallic tubes when applied to the graphene band structure. If the quantization lines include the K points, the tube is metallic (i.e. there are allowed states at the Fermi level), while if the quantization misses these points, an energy gap between the subbands results. As can be seen, the closer the quantization is to the K points, the smaller the energy gap will be. When the diameter of the tube is increased, the interval between quantization lines for different subbands i shrinks and the lines draw closer to the K points, so the gap decreases. Using the quantization condition 2.2, one can compute how close (or how far) the K points are missed by the subbands. For a metallic tube, this distance is zero, at least for one subband-K point combination. For
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Figure 2.14: Three dimensional plot of the graphene band structure near $E_F$, together with the quantization condition marked by dashed lines in the Brillouin zone. The resulting subbands in the $\pi$ and $\pi^*$ bands (cones) are marked by the dotted lines. The upper figure shows a situation, where the K points are included in one of the quantization lines ($i=0$ and $i=\pm 3$), hence the belonging subbands are touching (or crossing) at the Fermi level and the tube is metallic. In the lower figure, the quantization lines miss the K points and a finite energy gap between the subbands results.
Figure 2.15: Construction of a (2,4) tube from a graphene sheet. The quantization lines in the reciprocal lattice are spaced by \( \Delta k = 2\pi/|C| \) and miss the K points by at least \( \delta k = 1/3 \cdot \Delta k \).

The semiconducting tubes the minimum distance between a subband and a K point turns out to be

\[
\delta k = \frac{1}{3} \cdot \frac{2\pi}{|C|} = \frac{1}{3} \cdot \Delta k,
\]

where \( \Delta k \) is the separation of the quantization lines in the reciprocal space (cf. figure 2.15). Due to the linear dispersion relation around the K points, the energy gap for the semiconducting tubes turns out to be

\[
E_{\text{gap}} = 2\hbar v_F \delta k = \frac{2}{3} \hbar v_F \frac{2\pi}{|C|} = \frac{4}{3} \frac{\hbar v_F}{D}.
\]

The gap energy scales inversely with the diameter D of the tube. Figure 2.16 visualizes the dependence of the gap energy on the tube diameter. These are the main features in the band structure of nanotubes, summarized in the statement that, depending on the roll-up vector \((n,m)\), the tubes can be metallic \((n-m=3i)\) or semiconducting \((n-m \neq 3i)\). But there are two add-ons to be made.

The first add-on concerns the value and the multiplicity of the Fermi points in the metallic nanotubes. It seems to be, there should be six Fermi points according to the six K points of the graphene Brillouin zone, but this is not the case. Each K point belongs to three Brillouin zones so only \(6 \times 1/3 = 2\) K points belong to the first Brillouin zone. This becomes clear, if another unit cell is chosen for the first Brillouin zone as in figure 2.17. Unambiguously, this unit cell contains only two K points and the quantization results in two Fermi points for the nanotube. Figure 2.18 shows a band structure calculation for a (10,10) tube, in which the subbands resulting from the quantization of the graphene band structure, as well as the Fermi points at \( \pm 2/3 \pi/a \) can be seen.
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Figure 2.16: Gap energies for tubes of different diameters. One third of the tubes is metallic (the ones fulfilling \( n-m = 3i \)), hence they have zero energy gap. The gaps of the other two thirds of the tubes decrease with increasing diameter according to equation 2.3.

But the value \( k_F = \pm 2/3 \pi/a \) does not apply to all metallic nanotubes. While armchair tubes have this Fermi momentum, tubes with a different chirality have a different Fermi momentum. Although the Fermi points of all of the metallic nanotubes result from the same K points of the same graphene band structure, the Fermi momentum of the nanotube is just the projection of the graphene Fermi momentum along the actual tube axis. Figure 2.19 shows how this makes the tube’s Fermi momentum depend on its chirality. Thus, some Fermi mismatch between different metallic tubes is created [26].

The second add-on concerns the curvature of the graphene sheet, when it is rolled up to form the tube. So far, the quantization condition was applied to a perfect, i.e. planar graphene sheet. When the sheet is rolled up, the bending of the bonds leads to a mixing of the \( \sigma \) and \( \pi \) orbitals [27]. The consequence is, that transport along and perpendicular to the curvature (i.e. along the circumference and along the tube axis) becomes different and the dispersion relation of the bands change. The important result is a shift of the band crossing of the \( \pi \) and \( \pi^* \) bands away from the K points [28]. Figure 2.20 shows the new positions of the band crossings together with the quantization conditions for different tubes. The semiconducting tubes are not significantly affected by this, since the quantization lines are far from the K points anyway. The armchair tubes are unaffected as their quantization still contains the shifted band crossings, so they remain metallic. But the quantization in the non-armchair tubes \((n – m = 3i, i \neq 0)\), while still including the K points, now slightly miss the band crossings. So they become semiconducting, too, but their gap of some 10 meV is considerably smaller than the gap of the semiconducting tubes with \( n-m \neq 3i \).
Figure 2.17: Reciprocal lattice of graphene with a conventional choice for the Brillouin zone (left hand side) and an alternative choice (right hand side).

(The shift of the band crossings is always much smaller than the separation between the quantization lines, so there is no possibility for a semiconducting tube to become metallic by this process.)

This situation can also be considered from a less theoretical point of view. The metallic states in graphene, the K points, correspond to a motion along the zig-zag chains (cf. figure 2.10). In general, all these directions are somehow bent around the tube circumference, when the graphene sheet is rolled up. So all these states are no longer identical with the unperturbed states of graphene. But in the armchair nanotubes, one of these zig-zag directions runs along the tube axis and is thus not curved during the roll-up. The movement along this direction keeps its metallic character and the armchair tubes stay metallic [30].

Using these informations one can distinguish between three types of nanotubes when talking about their electronic properties:

- the semiconducting ones with a gap of several 100 meV due to the one dimensional quantization \(n - m \neq 3i\),

- the small gap semiconducting ones with a gap of some 10 meV due to the curvature of the graphene sheet \(n - m = 3i, i \neq 0\), and

- the metallic armchair tubes \(n = m\).

Figure 2.21 is an extension of figure 2.16 which now includes the small gap tubes. Both kinds of gaps decrease with increasing diameter \(D\), the quantization gaps \(\sim 1/D\), the curvature gaps even \(\sim 1/D^2\). It is not clear whether these small gap tubes can be observed, since further interactions and corrections to the band structure (e.g. electron-phonon coupling) could dominate over the intrinsic gap or restore the metallic character. In any case, these gaps could only be detected at low temperatures while they have no significance at room temperature.
2.3 One Way Only

As was shown in the previous section, the motion of the electrons in the nanotubes is severely restricted, first to the atomic plane of graphene and second to the limited region of the cylinder circumference. They may only move 'freely' along the tube axis, populating several one dimensional electronic bands. Now, this regime of transport, though not easy to realize, is well known, for example from one dimensional wave guides in semiconductor heterostructures. But still, there are some differences. In most of the well-established one dimensional systems, several electronic bands cross the Fermi energy and thus contribute to the electronic behavior. Consequently, these systems should be labeled quasi-one dimensional, since the interaction between bands disturbs the one dimensional character and eventually leads to two dimensional behavior. On the other hand, in the nanotubes only two subbands, derived from the \( \pi \) and \( \pi^* \) bands, cross the Fermi energy. The wave function of the electrons is evenly spread over the

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**Figure 2.18**: Calculated band structure of a (10,10) nanotube [29]. Note two of the subbands crossing the Fermi level at \( k = \pm 2/3 \pi/a \).

In conclusion, the electronic properties of nanotubes, even more than their physical appearance, depend dramatically on their roll-up vector \((n,m)\).
Figure 2.19: Fermi wave vectors $k_F$ for two different metallic nanotubes. Although they result from the same K point momenta of graphene, the projection along the actual tube axis results in different Fermi momenta for tubes of different chirality.

whole cylinder surface while they are moving along the tube axis. This is a picture completely different from what is typically used for describing an electron. The electron is no longer a small particle moving randomly over the cylinder surface, but it 'lives' on the circumference of the tube as a whole.

Here again, the electronic structure of the tube is closely related to its geometry, since it is clear that everything that disturbs the geometry of the tube immediately disturbs its electronic properties [31]. Every defect, every bent or twist reflects in the electronics, since the electron 'samples' the tube as a whole on its way along the axis. This close relation weakens, when the tube diameter increases. For the big tubes ($\geq 10$ nm diameter) that many subbands are allowed, that for finite temperatures and finite excitations (which are necessary for measurement) the bands start to mix and interact so that we end up with a two dimensional behavior of the electrons. In these big tubes, the electrons can move again over the surface like small particles. Therefore defects and imperfections of the tube affect the electrons only locally [32]. So the tubes cover the whole regime from true one dimensional behavior to two dimensional electronic motion.

The most obvious difference between electronic motion in one and two (or three) dimensions is the fact, that in one dimension, all electrons move in the same direction. They can move faster or slower, they can reverse their momentum, but they can not deviate from this direction (the tube axis, in case of the nanotubes). This has fundamental consequences for current transport in nanotubes.

The prominent consequence is, that current transport in one dimensional
Figure 2.20: When the graphene sheet is rolled up to form a cylinder, the points where the $\pi$ and $\pi^*$ bands of graphene meet at the Fermi level (x) shift away from the K points (+). The energy gap of the semiconducting tubes (left) is only slightly affected by this, the (n,n) armchair tubes (right) still include the band crossings and thus remain metallic. The non-armchair tubes (center), which include the K points in their quantization condition, and thus were predicted to be metallic, now miss the band crossings slightly and thus acquire a small energy gap.

Figure 2.11: The momentum conservation, together with energy conservation, greatly affects the possibilities of momentum transfer, the 'phase space' for scattering. This way, the one dimensional character changes almost all the interactions known from three dimensional systems. The most dramatic example is the electron-electron scattering. Strictly spoken, it is forbidden for free electrons (i.e. electrons with a free electron like dispersion relation) in one dimension due to energy and momentum conservation. Interestingly, the linear dispersion relation in the nanotubes yet allows electron-electron scattering.
Figure 2.21: Energy gaps for nanotubes of different diameters [30]. The left hand side figure is comparable to figure 2.16 while the right hand side figure is a detail for small energies. The large energy gaps due to the quantization condition scale \( \sim 1/D \), while the small energy gaps due to the curvature of the graphene sheet scale as \( \sim 1/D^2 \) (D is the diameter of the tube).

These somewhat puzzling effects lead to the conclusion, that whenever one starts considering interactions in one dimensional systems, one has to carefully check what implications the energy and momentum conservation laws have.

Another phenomenon is the prediction of Luttinger liquid behavior in nanotubes [34] (and one dimensional systems in general [35]). Electrons which can only move in one dimension, i.e. forward and backward, can not pass each other due to the Pauli exclusion principle. They are lined up like pearls on a string and consequently behave very different compared to non-interacting electrons like the ones in a Fermi gas or even the weakly interacting ones in a Fermi liquid. Current transport should be affected by this since all electrons (the whole string) have to be moved in order to carry a current. Finding Luttinger liquid behavior in nanotubes would be the proof, that indeed the picture of a small electron moving between huge atoms, as taught by classical physics, is not appropriate. But unfortunately, the signs for Luttinger liquid behavior are somewhat poor, i.e. a power law of resistance on temperature [36]. So, while some experiments point to such an effect in nanotubes [37, 38], its existence is still under discussion.

The one dimensional nature of the system is not restricted to the electronic structure. The lattice vibrations, the phonons, become one dimensional too. Thus the phonon density of states for the acoustic phonons is independent of energy (this is simply a consequence of their linear dispersion relation). Now, the phonon density of states determines the heat capacity of the lattice, which becomes linear in temperature for the one dimensional systems in contrast to its \( T^3 \) law in three dimensions. Together with the much more rigorous restrictions energy and momentum conservation pose for scattering in one dimension, the phonon density of states changes the temperature dependence of the metallic resistance. Where a \( T^5 \) law dominates in the Grüneisen range in three dimensions, a linear temperature dependence of resistance is encountered in nanotubes even at low temperatures [39]. For the one dimensional structures, the mathematics is often much easier than in three dimensions, but sometimes the implications are hard to believe. Not only the temperature dependence of
the scattering rate, and hence the resistance, is affected by the dimensionality, but also the absolute value. Due to the strongly reduced phase space for scattering in one dimension, the scattering probability is greatly reduced and mean free paths between scattering events with phonons of micrometers even at room temperature are predicted [40, 41].

The nanotubes contain a true wealth of most interesting physical effects, which are currently examined thoroughly by the scientific community. What helps in this issue is the robustness of their characteristics. While most of the formerly used model systems (like semiconductor heterostructures [42]) are only one dimensional at lowest temperatures, the nanotubes are unaffected by temperature. (Of course, there are thermal excitations and lattice vibrations, but the electronic structure itself is not changed crucially by the temperature.) In addition, they have a long term stability and are not prone to degradation like some of the artificial structures as chains of atoms on a substrate surface (probably the most one dimensional system imaginable, but with a profound lack of stability). But what makes the nanotubes that interesting not only to physicists, is that there are so many different tubes and their possible combinations make almost every fantastic idea about their use at least imaginable.

2.4 The Nanotube Family

The focus of the last sections has been on the single wall carbon nanotubes and has offered insight into their geometry, their electronics and the reasons which make them that interesting to physics. Equipped with this basic knowledge, this section turns to the more complex structures which are usually found as the outcome of the production processes.

This outcome, the 'soot', consists of various amounts of amorphous carbon, remnants of the metal catalysts, small crystalline particles of graphite, and different fullerenes (bucky balls) together with the wanted nanotubes [13]. The nanotubes are separated from the undesired fractions by solving the soot, usually in solvents like dichlorethane, sonication and filtering. Subsequent Transmission Electron Microscope (TEM) studies show that these 'tubes' are not simply single wall nanotubes (SWNT, the ones known from the previous sections), but belong to the next higher level of self-organization of the nanotubes. One possibility for the single tubes is to bundle together forming what is called a rope of SWNTs. As the scheme in figure 2.22 illustrates, the tubes in a rope are aligned parallel to each other, hold in place by the van der Waals interaction with the other tubes. The cross section shows a regular, triangular, close packed lattice provided that the diameters of the tubes are about the same (figure 2.23). If the process parameters during growth of the tubes allow for very different diameters, the tubes can arrange in ropes too (with the cross section of the rope no longer being regular), or they can grow inside each other to form multi wall carbon nanotubes (MWNT), looking alike the scheme in figure 2.22. The projections of figure 2.24 show such MWNTs 'from above'. The separate walls of the concentric single tubes can be seen clearly.
Figure 2.22: Schematics of a rope of SWNTs aligned parallel to each other by self-organization (left hand side). If the tube diameters are similar, the rope cross section shows a regular triangular lattice. If the tube diameters vary too much, the tubes grow inside one another, forming multi wall nanotubes (MWNTs, right hand side). The graphene sheet forming the tubes is indicated by the shading.

These two classes of self-organization of nanotubes mark the starting point for all investigations. From here, one can return to the single wall tubes by continuing the process of solvation and sonication on the ropes of SWNTs. When the van der Waals forces between the tubes are eventually overcome, the ropes will disperse to single tubes again. Of course, the MWNTs cannot be taken apart in this way without destroying the single tubes. On the other hand, instead of dispersing the material to single tubes, one can treat the material to form even higher levels of organization. The purified soot can be pressed to a thin sheet of more or less aligned tubes, a kind of 'paper' made of nanotube fibers, which is often called 'bucky paper' [43].

Now, what are the properties of these new structures? Are they very different from what is known from the SWNTs? Regarding the geometry, ropes of SWNTs as well as MWNTs come in very different sizes. The diameters range from several nanometers up to 50 nm which corresponds, in case of ropes, to a bundle containing from a couple up to several hundreds of tubes. Big MWNTs can easily have a dozen of concentric shells [13]. Both types are usually many micrometers long. Judging from the TEM images, the distance between the tubes in a rope and between the shells of a MWNT is 3.4 Å [16, 1]. This is the same distance as is found in graphite for the distance between the graphene sheets. So obviously, the van der Waals interaction effective in graphite is also responsible for stabilizing the complex tube arrangements. As we know from graphite, the graphene sheets can glide along one another without the single planes being destroyed. And indeed, one can extract single tubes from a bundle by dragging with a sharp tip of a STM or AFM [2, 44]. But even if the bonding forces between tubes are weak, i.e. van der Waals forces like in graphite, the mere presence of neighboring or inserted tubes changes the stiffness of the system. In figure 2.6 it is seen that the tubes can be flattened when interacting with the substrate. Figure 2.25 shows that the insertion of additional tubes in MWNTs reduces this effect and a similar stiffening is to be expected for ropes of SWNTs.
2.4. THE NANOTUBE FAMILY

Figure 2.23: Transmission electron micrograph of a rope of SWNTs, showing the cross section of the rope. Note the very regular lattice in which the tubes are arranged [9].

The geometric arrangement of the tubes led to the conclusion, that weak van der Waals forces are mediating the interaction between the tubes. What does this mean for the electrons in the tubes? In the model system graphite, one finds a small overlap of the $\pi$ and $\pi^*$ bands near the Fermi level as a result of the interaction between the neighboring graphene planes [22]. This overlap changes the zero gap semiconductor graphene into semimetallic graphite, with a small conductivity between the planes. The first guess would thus be to expect a weak interaction leading to small conductivity between the tubes. But the situation in case of the tubes is different from graphite in a point very important to electronic behavior: Neither the ropes nor the MWNTs are periodic three dimensional crystals!

An individual SWNT is a periodic one dimensional crystal with period $|P|$. Thus the electronic transport in the tube can be described by a band structure with one dimensional subbands and the tube can be identified to be metallic or semiconducting depending on its roll-up vector [8]. But if different tubes with different roll-up vectors are arranged in a bundle, there will be no periodicity in the rope cross section. Even if the tubes are arranged in a regular, triangular lattice like the one shown in figure 2.23, every lattice site is occupied by another kind of tube. (The tube diameter alone is not a suitable criterion for distinguishing the tubes from one another. E.g., compare the diameters of the (10,10) and the (11,9) tube according to formula 2.1. So even if the tube diameters are very similar, thereby enabling a regular lattice over the cross section of the rope, there is no way to find a rope made from only one kind of tube.) Moreover, one does not find a periodicity of the rope along its axis, since every tube contributes its own period $|P|$ and the arrangement of all tubes together
is no longer periodic.

The same arguments are valid for the MWNTs. There are tubes with different diameters (and thus unambiguously different roll-up vectors) and with different periods inserted into each other. Even if a very large MWNT with many shells is considered and one states that this slightly bend stack of graphene sheets is much alike graphite, there is no correlation between the sheets. While in the three dimensional crystal of graphite the sheets are stacked in a regular ABAB sequence [23], the different roll-up vectors of the MWNT tubes corrupt any order. So the MWNTs possess as much periodicity in their structure as the ropes: none. But the periodicity is the basic condition for describing electronic transport through the system as a whole. Since ropes and MWNTs lack
2.4. THE NANOTUBE FAMILY

Figure 2.25: The insertion of additional tubes into a SWNT increases the rigidity of the system and thus reduces the deformations of the tube due to interactions, for example with the surface [17].

this prerequisite, they can not be treated as a unit when talking about their electronic properties.

This does not mean that there is no electronic structure or electronic transport at all. The last sections showed that the single tubes, of which the more complex systems consist, are metallic, at least some of them, that they offer electronic modes (subbands) for transport, that they have a very low electron-phonon interaction due to their one dimensional character which improves the electronic transport, in one word, they can be excellent conductors. Now, what is the proper way to describe the electronics of the ropes and the MWNTs? Since they lack the periodicity required for an all over band structure, they have to be treated as a couple of individual, one dimensional and parallel aligned electronic systems. But that does not mean, that they lack any interaction. One can easily imagine that an electron can change from one tube to another, either to a neighboring one in a rope or to a adjacent shell in a MWNT. That electrons can indeed be transferred from one tube to another was proven by drawing a current through a junction of two crossed tubes [45]. The question is how easily the electron can change between tubes, i.e. how strong the electronic coupling really is. But apart from what mechanism mediates the coupling, the fact that one deals with a disordered arrangement of metallic and semiconducting tubes, is not in favor of any electronic interaction.

Several investigations indeed point to a weak coupling [46], confirming the picture of essentially independent tubes in these systems. For example, a behavior typical for Luttinger liquid was observed in ropes of SWNTs [37]. Since this is a purely one dimensional effect, the interaction obviously does not disturb the electronic structure of the single tubes. Different magnetoresistance measurements in ropes as well as in MWNTs provided no sign of a three dimensional motion of the electrons, that is no indication for a strong coupling between adjacent tubes [39, 47]. So the picture that emerges is that of several, independent, one dimensional tubes running along a common axis, either
parallel or inside each other, with only being barely aware of the other tubes.

Somewhat more practical, once an electron is inside a tube, it stays there. This is the basic conclusion about electronic transport in complex arrangements of nanotubes. Most of the designs (some people would say fantasies) about possible nanoelectronics are based on this statement. Imagine a MWNT consisting of two concentric tubes, the inner one metallic, the outer one semiconducting. This would be the smallest wire ever seen, the insulation readily included. Two more shells would make it a coax cable. A thousand of these in a bundle would easily fit in the channel of a state-of-the-art MOSFET. By dragging nanotubes over the surface of a substrate one could assemble electric circuits of every desired geometry. Custom tailored nanoelectronics could be constructed by interconnecting metallic tubes quite like copper wires. But these ideas pose very different demands on the tubes. On one hand, the electronic properties of the single tubes should not be disturbed by the presence of other tubes, best realized, if there is no interaction between the tubes, but on the other hand, we would like to bring metallic tubes into electrical contact, and this clearly requires a coupling of the tubes. What is desperately needed for to put these ideas onto a firm ground, is a detailed knowledge about the interaction between nanotubes.
Chapter 3

First Steps

The previous chapter has presented the carbon nanotubes and has given insight into the reasons which make nanotubes thus fascinating objects. But as has become clear, there are several open questions about their electronic and structural characteristics. With this chapter, this investigation will focus on the electronic transport in nanotube samples. The method of choice here are multi terminal measurements at ropes of single wall nanotubes. The first section will deal with the fabrication of electric contacts to nanotubes and the general technique for performing electrical measurements at these samples. A qualitative discussion of four terminal measurements at ropes (section 3.2) will be followed by a quantitative analysis revealing the dominant mechanisms creating resistance in the nanotubes (section 3.3). From the discussions, conclusions will be drawn about how to fabricate electric contacts to nanotubes, the topic of section 3.4.

3.1 How To Make Contact

In order to gain insight into the electronic characteristics of nanotubes, a great deal of different methods has been applied to the tubes. There are for example scanning tunneling spectroscopy [11, 12], Raman scattering [48], thermoelectric [49] and microwave measurements [15], Electron Energy Loss Spectroscopy (EELS) [50] and, of course, multi terminal electrical measurements. Most of these methods are studying large samples, i.e. mats of nanotubes or ‘bucky paper’, and thus provide information on the composition and averaged properties of the sample, like the occurrence of semiconducting and metallic tubes via the observable energy gaps. But some of the methods are suited to study single tubes and their electronic behavior. Especially the Scanning Tunneling Spectroscopy (STS) on single wall carbon nanotubes in a very impressive manner confirmed the semiconducting and metallic band structures of the different tubes and linked them to the geometry, i.e. the roll-up vector of the tubes (figure 3.1).

Multi terminal electric measurements, too, were used to study single tubes,
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Figure 3.1: Scheme for scanning tunneling spectroscopy (STS) at a nanotube. The tube is dispersed onto a gold substrate. The local density of states of the nanotube at the position of the tip is obtained by measuring the differential resistance of the sample in a two terminal configuration. In addition, a topographic image of the sample can be obtained from which the roll-up vector of the tube can be determined [11, 12].

representing the most direct method for probing the electrical transport in the tubes. They offer various advantages over other methods, namely they are sensitive to single and small numbers of tubes (in contrast to the averaging methods of Raman, EELS and microwave studies), they probe the electronic transport properties directly (rather than only related properties like the thermoelectric power), and they account for the non-local nature of current transport (instead of measuring the local properties of a tube at a given position like in STS). Of course, none of these methods alone, not even the multi terminal transport measurements can claim to capture the full physics of the tubes. Only the combination of all methods can form a consistent picture of the nanotube transport characteristics.

The first step in making electrical measurements on a sample is to attach electric contacts to it. This can be done in very different manners, and the most simple way is to put the nanotube, or the rope or the multi wall tube, onto a conducting substrate, preferably gold (figure 3.1). This noble metal is chosen very often as material for electric contacts, since it can be cleaned very well and does not degrade or oxidize at the surface afterwards. Moreover, it is a very good conductor. Once the tube is placed on this conducting surface, the second electrode, which is inherently needed for an electric measurement, is placed on top of the tube. This second electrode is the tip of a STM, which enables local measurements of the electronic structure of the tube at the position of the tip, especially spectroscopic measurements of the electronic density of states. So, this method complements excellently the transport measurements which probe the non-local characteristics of the tubes.

The non-local measurements require another kind of contact geometry, i.e. two or more separate electrodes along the tube. These are necessary in order to
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**Figure 3.2**: Part of a tube lying on an insulating substrate with two metal contacts attached to it. The metal contacts can be deposited first and the tube is dispersed onto them (bottom contact), or the tube is dispersed first and the metal is deposited afterwards (top contact).

draw a current through the length of the tube. The most wide-spread method for applying several contacts to nanotubes (or ropes) is to put a nanotube onto an insulating substrate and to subsequently deposit metal contacts onto the nanotube. Or to put the tube over predefined metal contacts on an insulating substrate. Figure 3.2 shows examples for both methods. Since several contacts have to be attached along the length of the rope, the contacts have to be rather small, i.e. of the nanometer scale.

The contacts are usually made from classic metals, since their properties are well known and they do not show any undesired effects like classical or quantum mechanical size effects. A very prominent choice is gold for the aforementioned reasons, but also metals like titanium have shown to make a good electric contact to nanotubes [51]. Beside the classical metals, nanotubes themselves have been proposed to serve as contacts, but the fabrication of such a geometry is very difficult (cf. section 3.4). In this investigation, electrical measurements on nanotube samples have been made according to the following recipe: The ropes were dispersed onto an insulating substrate, located with a Scanning Electron Microscope (SEM) and several metal contacts were attached to the ropes. Afterwards, the samples were mounted in a continuous flow $^4$He cryostat and the measurements were taken using lock-in technique.

Regarding this procedure, several points have to be taken into account:

1. Choice of the substrate. There are a lot of insulating materials, which are robust enough to serve as substrate for all kinds of electric measurements. But silicon offers itself for quite a lot of reasons. The surface of silicon already forms a native insulating oxide with the ambient oxygen. By thermal oxidation at high temperatures in an oxygen atmosphere, the quality of the oxide, especially its insulating properties, can be optimized and the thickness can be determined exactly. Moreover, the bulk of the silicon substrate retains its properties. A very popular choice is to use highly (degenerate) doped silicon with a thermally oxidized surface and this done in this work, too. The doped silicon under the insulating top layer remains metallic even at lowest temperatures and can thus serve as a back gate for a possible control of the carrier density in the nanotubes. Last but not least, silicon is inexpensive.
Figure 3.3: Schematic of a rope consisting of metallic and semiconducting tubes. The rope cross section is a regular triangular lattice (cf. 2.23) with lattice constant 1.7 nm, but the tubes are arranged in a random distribution on the lattice sites. Ropes with a typical diameter of 20 nm contain about 100 tubes, 1/3 of them being metallic. The ropes are dispersed onto a silicon substrate covered by a 100 nm thick thermal oxide.

2. Deposition of nanotube ropes. The nanotubes were dispersed in dichloroethane, the solution was homogenized by sonication for a short period, and then a drop of the solution was put onto the substrate. While the solvent evaporated, the tubes laid down at random positions on the surface of the substrate.

3. Location of nanotube ropes. Before attaching any contacts to a rope, the ropes have to be located on the surface, which is conveniently done with an Atomic Force Microscope (AFM) or a SEM. The ropes of SWNTs used in this work were produced in a laser ablation technique and consist of tubes with diameters close to 1.35 nm, this is the diameter of the (10,10) armchair tube. The tubes in the rope form a regular triangular lattice with a lattice constant of 1.7 nm and the complete ropes have diameters of the order of 20 nm (figure 3.3). Thus, they are visible in SEM images and this tool was used to locate the ropes. The position of the ropes was recorded in coordinates relative to a fixed point on the substrate. A number of alignment marks was prepared on the substrate before deposition of the ropes in order to serve as such reference marks.

4. Fabrication of contacts. Once the positions of the tubes was known, several metal contacts were attached to them. This was done by electron-beam lithography. In short, an electron sensitive resist was spread over the sample, the resist was exposed in the desired areas (where the contacts should be) with the electron beam of a SEM, and the sample was put in a developer liquid, which only dissolved the exposed areas of the resist. Now the contact areas were free of any resist, while the rest of the sample was still covered. An addi-
3.1. HOW TO MAKE CONTACT

A sputter treatment (see section 4.1) was introduced at this stage. Then, 5 nm titanium and 100 nm gold were deposited uniformly over the sample and the unexposed resist was dissolved in acetone, which removed not only the resist, but also lifted off the metal, which lay on top of it. Only the metal that stuck directly to the surface (in the exposed and developed areas of the contacts) stayed on the sample. In this way the metal contacts (as well as the alignment marks previously mentioned) were fabricated. With the use of electron-beam lithography, contacts with a width of 200 nm were fabricated, which enabled attachment of several contacts to an individual nanotube rope with a length of only several micrometers. (Do not get confused, a single molecule with a length of a few micrometers is a really huge molecule, but as soon as one tries to attach electric contacts to a sample with a length of a few micrometers, it becomes a very tiny sample.)

Above it has been stated, that the contacts can lie above the tube or rope as well as below the tube or rope (cf. figure 3.2). These types of contacts are named top and bottom contacts. In order to make bottom contacts to a rope instead of top contacts as described above, the contacts are simply made before deposition of the nanotube ropes. (The predefined alignment marks can also serve as bottom contacts as they are made from a suited material, namely gold.) If a nanotube lays down onto such a pre fabricated contact, the bottom contact is already done. But due to the random deposition of the ropes onto the surface, these bottom contacts are made by chance, in contrast to the intentionally attached top contacts. In order to obtain a higher yield of bottom contacts the tubes should be deposited intentionally onto them (but no procedure is known for that so far) or they have to be moved onto the contacts after deposition. This second suggestion contains some risk, since the tube can be damaged when being manipulated, e.g. with an AFM tip. Due to the intimate relation between geometry and electronic in case of the nanotubes, the structural damage would affect the electronic properties, which is not necessarily welcome. So, most of the contacts made in this work are top contacts made after the deposition of the tubes, but also bottom contacts were used.

In order to load the microscopic rope with its attached contacts to a macroscopic measurement environment, the metal contacts have to be enlarged until they reach handable sizes. Figure 3.4 shows several SEM micrographs with different magnification following this process. The electrical contacts attached to the rope gradually widen when running away from the tube, until eventually they are that wide, that macroscopic wires (with a diameter of 25 μm) could be welded to them. These wires run to bond pads on a standard device for micro electronic measurements, a chip holder or chip carrier. The measurement electronics is designed to accommodate these chip carriers with whatever sample is mounted. This gives a maximum flexibility in measurements, since the samples are exchanged with the whole chip carrier. This concludes the preparation of the nanotube samples.

The following paragraphs will deal with the measurement setup and will present the relevant techniques. In this investigation, both two and four terri-
Figure 3.4: SEM micrographs showing different magnifications of a completed nanotube sample. The nanotube rope can be seen in the first picture, where it makes contact to a top, a bottom and two more top contacts (from left to right). The crosses, arranged in a regular array, are the alignment marks, which are used to locate the tube and, if the tube runs across them, can be used as bottom contacts. The remaining top contacts were fabricated in a second lithography step. They widen gradually while running away from the tube (second and third picture), until they become large enough, that wires can be attached to them (fourth picture). The sample is mounted into a standard chip carrier and the wires are attached to its bond pads (last picture).

nal measurements were taken at the samples using standard lock-in technique according to figure 3.5. Using the preresistor $R_0$, the reference signal of the lock-in serves as a current source, connected to the sample via two of its contacts. The voltage drop at these contacts (two terminal, figure 3.5 a) or at two other contacts (four terminal, figure 3.5 b) is detected by the lock-in. The two terminal (2t) or the four terminal (4t) resistance is then computed by dividing the voltage drop by the generated current. Usually, the preresistor $R_0$ is chosen to be much larger than the total (two terminal) resistance of the sample. Thus, the current generated is simply $U/R_0$ to a reasonable accuracy. In this case, $R_{2t} = U_{2t}/I = R_0 \cdot U_{2t}/U$ and $R_{4t} = U_{4t}/I = R_0 \cdot U_{4t}/U$. If the sample resistance is not much smaller than the preresistor, but comparable to or even bigger than $R_0$, which will often be the case in this work, the current has to be computed by the exact formula $I = (U-U_{2t})/R_0 = U/(R_0 + R_{2t})$. Now, one finds $R_{2t} = U_{2t}/I = R_0 \cdot U_{2t}/(U-U_{2t})$ and $R_{4t} = U_{4t}/I = (R_0 + R_{2t}) \cdot U_{4t}/U$. Thus, in order to compute the four terminal resistance, the two terminal resistance has to be known already. If it is not known, it has to be measured in advance of the 4t measurement. (If, for some reason, it is known that $R_{2t} \ll R_0$, the
current can be computed via the simpler formula, putting up with some inaccuracy, and the 2t measurement is obsolete.) In this configuration, the 2t and 4t resistances can be measured as a function of several parameters, e.g. the temperature, an applied magnetic field, or an external gate voltage (using the degenerately doped bulk silicon under the insulating surface as a back gate).

When the values $U_{2t}/I$ and $U_{4t}/I$ have been named 2t and 4t resistance in the last paragraph, it has been assumed tacitly, that the measurements are done in a linear response or ohmic regime. That means, one expects the voltage drop to be doubled if the current is doubled and vice versa. If this is not the case, the measured resistances depend on the magnitude of the measurement current, i.e. $R_{2t}(I)$ and $R_{4t}(I)$. From such a non-ohmic behavior one can often draw as much conclusions as from the temperature dependence of the resistances. Thus it would be desirable to measure this non-ohmic behavior and figure 3.6 shows, how this is done. An additional dc voltage source is applied in series to the usual ac lock-in voltage. The generated current now consists of a dc and an ac part. Thus the voltage drop at the sample contains both a dc and an ac part. But the lock-in only measures the ac part, neglecting any dc signals. The advantage is, that now quantities called 'differential resistances' can be computed by $U_{2t,ac}/I_{ac}$ and $U_{4t,ac}/I_{ac}$, which are functions of the applied dc current $I_{dc}$. For small ac signals, these quantities are close to the derivatives of the current-voltage characteristics of the sample. Figure 3.7 visualizes the method at a model I-U characteristic. This method can thus measure the non-ohmic behavior of the sample resistances. Compared to a pure dc measurement, which yields $U_{dc}/I_{dc}$ instead of $dU/dI \approx U_{ac}/I_{ac}$, the direct measurement of the differential resistance is much more sensitive to a change in sample behavior.

The non-ohmic behavior of the sample resistance imposes strong implica-
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Figure 3.6: Configurations for measuring the differential resistance of a nanotube sample. A dc voltage $U_{dc}$ is superimposed onto the reference voltage of the lock-in. The total sample current $I_{ac} + I_{dc}$ creates a mixed ac/dc voltage drop at the sample, from which only the ac part $U_{2t,ac}$ or $U_{4t,ac}$ is detected by the lock-in. The differential resistance of the sample at a given value of $I_{dc}$ is computed by $U_{2t,ac}/I_{ac}$ or $U_{4t,ac}/I_{ac}$, respectively.

tions on the measurement process. In order to obtain the proper linear response and differential resistance of the sample the measurement current $I_{ac}$ (and the voltage drop $U_{ac}$) may not exceed some limiting values. For example, in the model I-U characteristic of figure 3.7 these limits are given by $I_{no}$ and $U_{no}$ for the linear response regime. In case of the nanotubes, a voltage drop of some meV can already change the resistance of the sample, especially when interference effects are involved in transport (chapters 4 and 5). When sample resistances of several MΩ are to be measured, currents in the nA range can already distort the resistance. This gives a rule of thumb what currents and voltage drops have to be used in nanotube measurements.

One point that turned out during the measurements is that the samples are extremely sensitive to discharges of static electricity. A static charge can easily produce a potential of some 100 to 1000 V and the discharge via a sample resistance of a MΩ then causes current pulses in the mA range. These current pulses were found to destroy the samples. Thus, extreme care has to be taken in the handling of the samples. All equipment has to be grounded to avoid the build-up of any static charge, especially the person performing the experiments. When changing the electrical connections to the sample, for example when switching from a two to a four terminal measurement, all sample contacts have to be grounded simultaneously. A critical point in this case is the mounting of the sample into the otherwise grounded equipment. Before the chip carrier is inserted, it is not grounded and may thus carry static charge by itself. In order to avoid the destruction of the sample already when inserting it into the electronic equipment, all bond pads of the chip carrier and thus all contacts to the nanotube sample are shorted. These shorts may not be removed until the chip carrier with the sample has been safely mounted.
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The multi terminal measurements, which were discussed in the previous section, are used to characterize ropes of single wall carbon nanotubes. Figure 3.8 shows a SEM micrograph of a rope with a number of metal electrodes attached to it. This sample is somewhat special as it has, due to its position on the surface, several contacts being partly of the top and partly of the bottom type, as is
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Figure 3.8: SEM micrograph of the sample belonging to the measurements of figure 3.9 showing a top view, and a schematic cross section along the rope axis. The contacts 1, 2, 6, and 8 are bottom contacts (the alignment marks (crosses) deposited first serve as contacts), while the contacts 3, 4, 5, and 7 are top contacts, deposited after the tube was dispersed onto the surface and spotted with the SEM.

Figure 3.9 shows the temperature dependence of the four terminal resistance of this rope in this configuration. As can be seen, the resistance decreases monotonically on lowering the temperature, a behavior well known for metallic systems and reported sometimes for nanotubes [39, 15]. (The reason why this behavior is not routinely found in nanotubes is the strong influence of the
3.2. WHEN CURRENT FLOWS

Figure 3.9: Four terminal measurements at a rope of SWNTs. The electric configuration was according to figure 3.8. The sample was cooled in a cryogenic $^4$He gas flow.

contacts onto the nanotubes and their resistance, as will become clear in the following discussion and section 3.4.) This monotonic decrease of resistance is a clear sign that indeed metallic tubes are contained in the rope and do carry the current. But the temperature dependence supplies much more than just the fact that the system is metallic. One can identify two major features in the measurement, that is a linear decrease of the resistance down to lowest temperatures and a finite residual resistance. In order to understand these features, the next paragraphs will discuss the possible scattering mechanisms in nanotubes which are creating resistance.

First, there is scattering at static defects in the tube. Such defects may be lattice imperfections like impurities or crystal defects, but also deformations of the tube are a kind of lattice 'imperfection' and thus have to be regarded as defects. In addition, the finite length of the tube supply another kind of defect, namely the ends of the tube, which act as backscatterers for the electrons. Whatever the nature of such a defect will be, an electron scattered at such a defect will transfer some of its momentum to the scatter center. This momentum transfer is the microscopic origin of the observed macroscopic resistance. Thus, scattering at defects is always effective in creating resistance. In metallic systems, this scattering process leads to a temperature independent contribution to resistance, which scales with the defect density. The mean free path (mfp) $L_0$ between scattering events is given by the density of the defects along the tube axis and the resistance of a segment of length L is proportional
Another scattering process creating resistance is the scattering of electrons at lattice vibrations or phonons. In this process the electron emits (or absorbs) a phonon and thereby transfers some of its momentum to the phonon. In classical three-dimensional metals this leads to a temperature dependent contribution to resistance, which is linear at high temperatures and follows a \( \sim T^5 \) power law at low temperatures (Grüneisen range) due to small angle scattering at acoustic phonons [52]. In case of the metallic nanotubes, one finds a very different behavior due to two different reasons. One is the reduced dimensionality of the system, the other is the occurrence of two bands of opposite dispersion crossing at the Fermi level. What are possible electron-phonon scattering events in nanotubes? Figure 3.10 shows the band structure of a metallic nanotube near the Fermi level. The bands crossing at the two Fermi points \( \pm k_F \) have linear dispersion \( E(k) = E_F \pm \hbar v_F (k - k_F) \). Thus, there are only two types of electrons near the Fermi level, namely electrons moving to the right with velocity \( v_F \) (bands 1 and 2') and electrons moving to the left with velocity \(- v_F \) (bands 2 and 1'). In order to create resistance, a scatter process has to change an electron from right moving to left moving (or vice versa, depending on the direction of the current). Since optical phonons are frozen out at low temperatures, only acoustic phonons with a linear dispersion relation \( E_{ph} = \hbar \cdot c_{ph} \cdot k \) are available for scattering processes. Process A scatters an electron from one Fermi point to the other, i.e. it requires a momentum transfer of at least \( 2 \cdot k_F \). Therefore, the acoustic phonon needed for this process has to have at least an energy of \( E_{ph, min} = 2 \cdot \hbar \cdot c_{ph} \cdot k_F \approx 100 \text{meV} \). Such phonons are neither activated at low temperatures, nor can an electron emit such a phonon since all possible final states are occupied. Thus the process is frozen out, i.e. damped exponentially, quite like scattering at optical phonons. This results from the reduced dimensionality of the system, leaving no freedom for scattering at low energy acoustic phonons like in small angle scattering known from systems of higher dimension.

But there is another process that can not be frozen out at lowest temperatures and which remains fully effective in creating resistance. In process B, shown in the detail on the right hand side of figure 3.10, an electron is scattered from band 1 to band 2 near one Fermi point. This involves just a small momentum transfer, but due to the opposite dispersion of the bands, the velocity of the electron is fully inverted. This means that this process is extremely effective in creating resistance. Moreover, it can not be frozen out, since the bands 1 and 2 cross at the Fermi level. Consider the situation as depicted in figure 3.10: A right-moving electron in band 1 with momentum \( k_F + \delta k \) and excess energy \( \epsilon = \hbar \cdot v_F \cdot \delta k \) is scattered by a phonon with momentum \( k_{ph} \) and energy \( E_{ph} = \hbar \cdot c_{ph} \cdot k_{ph} \) into a left-moving state. Since the phonon velocity is much smaller than the Fermi velocity \( (v_F \approx 10^6 \text{m/s}, c_{ph} \approx 10^4 \text{m/s}) \) the energy transfer \( E_{ph} \) to the phonon is much smaller than the excess energy \( \epsilon \) of the electron. Thus, the final state for the electron in band 2 has almost the same excess energy \( \epsilon \) and momentum \( k_F - \delta k \). The phonon momentum is thus approximately \( k_{ph} \approx 2 \cdot \delta k \) and the energy transfer \( E_{ph} \approx 2 \cdot \hbar \cdot c_{ph} \cdot \epsilon \ll \epsilon \). The
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Figure 3.10: Backscattering of an electron by a phonon in a metallic nanotube. The left hand side picture shows the band structure near the Fermi energy with the subbands 1 and 2 (1' and 2', respectively) crossing at ±k_F. For the intraband electron-phonon scattering (process A, 1 → 1'), a minimum momentum transfer of 2 · k_F is necessary and the process is frozen out at temperatures below E_{ph,min} = 2hc_{ph}k_F. The right hand picture shows a detail of the band structure around the right Fermi point +k_F. The interband scattering (process B, 1 → 2) does not have an activation energy and is thus effective even at low temperatures. This process can be responsible for the linear temperature dependence of the resistance of the metallic nanotubes.

The scattering rate for this process will depend on the appropriate transfer matrix element |M|^2 assumed to be independent of the energy transfer and the density of the available initial and final states.

\[
\frac{1}{\tau} \sim |M|^2 \int_{-\infty}^{+\infty} d\epsilon \rho_i(\epsilon) \cdot \rho_f(\epsilon - E_{ph}) \cdot f(\epsilon) \cdot (1 - f(\epsilon - E_{ph}))
\]

Here, \( f(\epsilon) = (1 + exp(\epsilon/k_BT))^{-1} \) is the Fermi distribution for the electrons and \( \rho_i = \rho_f = 4/(2\pi hv_F) \) are the densities of states for the initial and final states in bands 1 and 2. These densities of states are simply constant for one dimensional subbands with linear dispersion. The transfer matrix element itself creates some new selection rules resulting from the coupling of the electronic wave function to the lattice distortion caused by the phonon. It was shown [40], that only transverse acoustic phonons and twistons, a special kind of transverse acoustic phonon in nanotubes [21], can scatter electrons from band 1 to band 2 (process B), while longitudinal acoustic phonons can only mediate intraband scattering, that is backscattering from one Fermi point to the other without changing the band index (process A). The latter process was already shown to require a minimum momentum transfer of 2k_F and is thus frozen out at low temperatures. This leaves only the scattering at transverse acoustic phonons.
Figure 3.11: Example for an electron-electron scattering process in a metallic nanotube. The band structure is a detail around one of the Fermi points. An applied voltage $U$ results in a splitting of the Fermi level (occupied states are shaded). The surplus right moving electrons carry the current. Two right moving electrons in band 1 can scatter into left moving states in band 2, which creates a resistance, while the total momentum of the electronic system is conserved. The scattering rate is linear in temperature and thus can be responsible, too, for the observed temperature dependence of the resistance [28].

and twistons (process B) to be considered.

$$\frac{1}{\tau} \approx \int_{-\infty}^{+\infty} d\epsilon f(\epsilon) \cdot (1 - f(\epsilon - 2c_{ph}/v_F\epsilon))$$

$$\approx \int_{-\infty}^{+\infty} d\epsilon f(\epsilon) \cdot (1 - f(\epsilon))$$

$$= \int_{-\infty}^{+\infty} d\epsilon \frac{1}{\cosh^2(\epsilon/k_BT)}$$

$$= k_BT$$

The approximation * in the formula above cannot be made, if a finite activation energy for the scattering has to be raised. In this case an exponential behavior would result for the scattering rate. But with two bands crossing at the Fermi energy, an activation energy is not necessary and the scattering rate is thus proportional to the temperature. Effectively, one can say, the phonon scattering in the nanotubes (determined by process B) is always in the high temperature limit. This is, since an electron with excess energy $\epsilon = k_BT$ always possesses the energy $E_{ph} \ll k_BT$ necessary to be backscattered completely. The temperature dependence of this process matches with the observed behavior of the resistance. Thus, electron-phonon interaction is one possible process responsible for creating resistance in nanotubes.
A third mechanism is electron-electron scattering. This is somewhat unexpected, since the total momentum of the electronic system is conserved in such a process. No momentum is transferred to the lattice and thus no resistance is created in normal metals. But again, the unusual band structure in metallic nanotubes produces another difference to 'normal' metals. Figure 3.11 shows a detail of the band structure of a nanotube around one of the Fermi points. When a voltage $U$ is applied to the tube, the Fermi level splits into two separate levels for the left and right moving electrons respectively and a current flows in the tube, carried by the surplus right moving states. (The occupied states are marked by shading.) This opens phase space for the electron-electron scattering process shown. While energy and momentum are conserved, the two right moving electrons change to left moving states. An analysis in a tight binding calculation [28] showed that the scattering rate of this process is linear in temperature, too. Thus, electron-electron scattering can just as well be responsible for causing the observed temperature dependence of the resistance as electron-phonon scattering.

These three scattering processes state the mechanisms creating resistance in nanotubes. Their temperature dependencies match the observations and thus explain indeed the behavior of the resistance. But the extent to which these three processes influence the current transport can only be determined by a quantitative analysis of the theoretical and experimental scattering rates.

3.3 Inside The Tube

Now that the features in the resistance measurements are explained qualitatively, a quantitative discussion will try to expand the understanding of electric transport in nanotube ropes. This section will focus on the temperature dependence of the 4t resistance in figure 3.9. As the last section stated, scattering at static defects as well as scattering at acoustic phonons and at other electrons are responsible in creating the 4t resistance. These processes act independent from each other, thus their contributions are simply added. In a one dimensional system with a limited number of modes $M$ contributing to current transport ($M=2$ for metallic nanotubes), the resistance is given by the resistance quantum for each mode, $h/2e^2$, divided by the number of modes $M$ which act as parallel channels for current transport. The scattering enters the resistance of a sample of length $L$ by the average number of scattering events. Defining a mean free path $L_{mfp}$ between scattering events, this number is given by $L/L_{mfp}$. Thus, each scattering event causes a resistance contribution $R = h/2e^2 \cdot 1/M \cdot L/L_{mfp} = h/4e^2 \cdot L/L_{mfp}$ in each tube (neglecting any interference effects, [33]) and the 4t resistance of a rope can be described by

$$R_{4t}(T) = R_0 + \frac{dR}{dT} \cdot T = \frac{h}{4e^2} \cdot \frac{L}{L_0} \cdot \frac{1}{N} + \frac{h}{4e^2} \cdot \frac{L}{L_{el-ph}} \cdot \frac{1}{N} + \frac{h}{4e^2} \cdot \frac{L}{L_{el-el}} \cdot \frac{1}{N}. \quad (3.1)$$

In case of the defect scattering the mfp between the static scattering centers $L_0$ is temperature independent. In case of the electron-phonon and electron-
electron scattering the mfps between scattering events, $L_{\text{el-ph}}$ and $L_{\text{el-el}}$, supply the temperature dependent part of the resistance.

Formula 3.1 accounts for the fact that a number $N$ of tubes in the rope are in direct contact with the metal electrodes and participate in current transport. These tubes would conduct in parallel, thus the resistances scale inversely with this number of tubes. In case of the measurement of figure 3.9, bottom contacts were used as current source and drain, thus the current will be flowing predominantly in metallic tubes at the bottom of the tube. A sketch of a rope lying on a bottom contact is given in figure 3.12. As can be seen, for a rope consisting of a random mixture of metallic and semiconducting tubes (ratio 1/3 to 2/3) only a couple of metallic tubes is in direct contact to the metal electrodes. Thus, the number $N$ of tubes involved in current transport can be expected to be rather small.

A fit to the 4t resistance of figure 3.9 according to equation 3.1 yields

$$R_{4t}(T) = 764(\pm 4)\Omega + 2.66(\pm 0.02)\Omega/K \cdot T,$$

and from figure 3.8 one obtains $L = 1.1(\pm 0.2)\mu m$. With these values, the scattering mfp can be determined to be $N \cdot L_0 = 9.3(\pm 1.7)\mu m$ for the defect scattering. The two contributions from the electron-phonon and electron-electron scattering can not be distinguished at this stage due to their identical temperature dependence. Thus a combined scattering length $L_{\text{el-xx}} = L_{\text{el-ph}} \cdot L_{\text{el-el}}/(L_{\text{el-ph}} + L_{\text{el-el}})$ for scattering at some other particle has to be defined. This yields a value of $N \cdot L_{\text{el-xx}} = 10.7(\pm 1.9)\mu m$ (at 250 K) (or equivalently, $d\rho_{\text{exp}}/dT \cdot 1/N = 2.4(\pm 0.4) \cdot 10^6 \Omega/(K \cdot m)$). The scattering lengths for defect and two-particle scattering turn out to be comparable at room temperature. But what are the absolute values of these lengths?

There are numerous theoretical investigations about the electron-phonon
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coupling in nanotubes and graphene, predicting the temperature dependence of the resistance \( d\rho_{el-ph}/dT \) to be around \( 2 \cdot 10^7 \Omega/(K \cdot m) \) [53, 40, 54], while experimental work points to a much weaker coupling, being only about \( 5 \cdot 10^6 \Omega/(K \cdot m) \) [41]. For the electron-electron scattering recent work supplies an upper bound for the contribution of \( d\rho_{el-el}/dT \approx 0.2 - 0.5 \cdot 10^6 \Omega/(K \cdot m) \). This enormous difference between the scattering mechanisms allows to distinguish them. The experimental value for the temperature dependence is at least (for \( N=1 \)) of the order \( 2.4 \cdot 10^6 \Omega/(K \cdot m) \), much larger than what electron-electron scattering can yield. On the other hand, the electron-phonon interaction can easily account for the absolute value of the resistance, suggesting that several tubes contribute in parallel. Thus, obviously, the electron-phonon interaction dominates the temperature dependence of the resistance, explaining both the observed linear power law and the magnitude of the resistance.

So far, the argumentation showed that the resistance of the nanotubes is dominated by scattering at defects and electron-phonon scattering. The remaining task is to determine the number of tubes involved in transport and thus the exact scattering lengths for the two processes. Comparing the theoretical predictions for the electron-phonon coupling with the experimental observation, one is led to the conclusion that \( N=2-8 \) tubes conduct in parallel in the rope. A larger number of tubes is extremely unlikely, given the weak interaction between the tubes and the typical geometry of the rope. With this estimate, the mean free path \( L_0 \) for the scattering at defects becomes \( L_0 \approx 1 - 4 \mu m \), being much larger than what is encountered in 'normal' metals. Thus, the nanotubes show a very low intrinsic defect density. It is noteworthy, that these values for \( L_0 \) are comparable to the distance between the metal electrodes attached to the rope (figure 3.8). This suggests that the deformations of the tubes by the contacts do indeed pose the main scattering centers in the tubes, rather than impurities or crystal defects. The intrinsic mean free path in an undisturbed nanotube could be even larger, but is limited by the contact separation. This would mean that the tubes are nearly perfect crystals with intrinsic defect densities well below one defect per micrometer. The 'defects' are only caused when contacts are attached to the tubes (or ropes).

There are two ways to tackle the task of refining the quantitative values. The first one starts with the theoretical calculations for the electron-phonon scattering rate. Comparing the prediction of \( d\rho_{theo}/dT \approx 2 \cdot 10^7 \Omega/(k \cdot m) \) [53] to an experimental value of \( d\rho_{exp}/dT \cdot 1/N = 2.4(\pm 0.4) \cdot 10^6 \Omega/(K \cdot m) \), implies a number of \( N=8 \) tubes to participate in transport. This would correspond to a mfp \( L_0 \approx 1 \mu m \), which is the distance between some metal contacts, unimportant if top or bottom contact. But is this likely? The measurement

\[ \text{Actually, the electron-electron scattering rate scales with the interaction strength of the electrons. In the tight-binding calculation of ref. [28] the on-site interaction } u \text{ is compared to the hopping integral } t \text{ determining the transport and yields } d\rho_{el-el}/dT = 0.2 - 0.5 \cdot 10^6 \Omega/(K \cdot m) \cdot (u/t)^2 \text{. An upper bound for } u/t \text{ can be obtained from the charge gap opening at low temperatures in interacting systems. This gap is at least of the order } t e^{-10 t/u} \text{ for a (10,10) tube. In the measurements of figure 3.9 no such gap is observed down to at least 10 K, corresponding to a gap energy of 1 meV at most. Given the value } t \approx 2.7 eV [11] \text{ one finds an upper bound for } u/t \leq 1 - 1.5. \]
configuration used the contacts 1 and 8 as current source and drain, and the contacts 3 and 4 as voltage probes. Thus the current is injected via bottom contacts, that means into tubes in the bottom of the rope, which are in direct contact with these electrodes. Additional bottom contacts along the rope have to be expected to strongly affect the current carrying tubes, i.e. to act as scattering centers. In contrast to this, the top contacts, where the metal is evaporated on top of the rope, some 20 nm apart from the bottom of the rope, are not expected to greatly affect current transport in the bottom tubes. (The load of the electrode is buffered by the tubes in the upper part of the rope.) A mean free path of the order of the distance between bottom contacts would be more realistic. Moreover, the number of metallic tubes at the bottom of a typical rope (for an example, see figure 3.3), is rather small, i.e. four or five tubes.

In addition, due to the weak coupling between the tubes, the current will favor paths with as few inter-tube transistions as possible. Single tubes bridging all the way between source and drain would carry almost all the current. This further reduces the number of tubes expected to be involved substantially in transport, namely the one bridging all or at least most of the distance. Thus, considering the geometry and composition of the rope, a very small number N of tubes contributing is very likely.

With this realization, one can go the other way around. The current transport in the bottom tubes is strongly affected by the bottom contacts only. The top contacts are too far from the bottom tubes in order to distort them considerably. The lateral distance between the bottom contacts nearest to the voltage probes, i.e. contacts 2 and 6, is determined to be \( L_0 \approx 5 \, \mu m \) (cf. figure 3.8). With this, one obtains \( N = 2 \), consistent with the expectation of only a small number of tubes carrying the current. Returning this number to the electron-phonon scattering, an experimental value of \( d\rho_{exp}/dT = 4.8(\pm 0.8) \times 10^6 \Omega/(K \cdot m) \) is found, very close to the experimental observations of Hertel and Moos [41]. This scenario explains the data found in the four terminal measurement consistently.

The main results, that can be drawn from the experimental findings are:

- The scattering length for the electron-phonon interaction is of the order of several micrometers, even at room temperature. From the arguments of above a length of \( L_{el-ph} = 5.3(\pm 1) \, \mu m \) at 250 K follows.

- Only a small number of tubes is carrying the current in the nanotube ropes.

- The tubes are almost perfect crystals.

- The attached contacts themselves act as backscattering centers.

- The simultaneous use of top and bottom contacts resulted in non-invasive voltage probes for the 4t measurement.

Further investigations are clearly necessary to study the discrepancy between the theoretical predictions for phonon scattering and the experimental results.
Figure 3.13: Schematic of a SWNT running over several bottom contacts. The tube is strongly distorted and the electronic structure is altered at the bending points (black dots). In extreme cases, these distorted regions can form tunnel barriers inside the tube.

This will allow further insight into the connection of electronic and mechanical properties of the nanotubes.

3.4 To Better Roads

One of the results of the last section was that the metal electrodes attached to the nanotubes disturb the electric transport. Spoken in plain terms, the contacts themselves create most of the resistance they measure. This effect is well known from electrical transport measurements conducted at nanotubes [31, 37]. When the tubes are forced to bend over a bottom contact, especially if it is a single nanotube, the distortions are often so severe that the unbend parts of the tube between the contacts are almost isolated from the contacts (figure 3.13, [31]). For such nearly isolated systems Coulomb blockade is known to dominate transport if the sample dimensions are small enough. Now, the nanotubes are indeed very small objects with diameters of the order of a nanometer and with lengths of micrometers. The capacitance of the nanotube is thus of the order of $10^{-18} F$, and a voltage of several meV has to be applied for to add even a single electron to the tube. Such a charging effect, arising if the sample is not properly attached to the contacts, makes a determination of the intrinsic transport properties nearly impossible.

Contact resistances which arise when simply applying a metal electrode to the tube are not easily avoided. But the deformations of the tube at the contacts can be reduced by sinking the contacts into the substrate surface. This was successfully done by Yao et al. [55]. They contacted a single tube and promptly showed that it is able to carry a current up to $20 \mu A$. The conclusion from that is that the electron-phonon coupling is very weak, as was found in the last section too, since otherwise a current of this magnitude would heat up the lattice to its melting point in no time.

In order to make an electric contact which does not interfere with the electronic properties of the nanotubes, even greater efforts were undertaken. A very impressive achievement was made by de Heer et al. by dipping the nanotube into a liquid metal (figure 3.14 a). They observed conductance quantization in the nanotubes which is only visible if there is almost no backscattering in the sample and no contact resistances other than the one due to the change
Figure 3.14: a) Scheme for two terminal measurements at nanotubes attached to a metal tip. The second contact is made by dipping the tubes in a liquid metal (mercury). This 'soft' contact makes it possible to measure the conductance quantization in nanotubes [57]. b) Scheme for four terminal measurements at nanotube ropes using multi wall tubes as voltage probes. A sharp metal tip is pressed in a mat of nanotubes and a rope sticking to it is pulled out halfway. The multi wall nanotubes are gently pressed to the rope [15].

of transport dimensionality. This means they were able to make a 'soft', ideal contact to the tube. But the use of a liquid metal in order to contact the tube is not feasible in all situations like, for example, a four terminal measurement.

Another approach to make non-invasive contacts is to use other nanotubes as current and voltage probes. First steps in this direction were made by Thess et al. in using MWNTs as voltage probes (figure 3.14 b). From a theoretical point of view it is often desirable to use a system very similar to the sample when probing the sample properties. In the case of the nanotubes this can avoid problems arising at the metal-tube interface of the contacts (change of dimensionality [see above], mismatch between the Fermi momentum of the metal and the tube [56], charging of the tube due to a difference in work function [11]). Still, the tubes are deformed when other tubes, which are e.g. used as voltage probes, are crossing them. This could be avoided by attaching the probe tube in parallel to the sample tube. Thus, a clever contact geometry will remove much of the problems.

But the use of nanotube contacts in studying nanotubes requires a detailed knowledge about how nanotubes do interact with each other. The important question is, how good the contact between nanotubes is. In section 3.3 it was found that only a couple of tubes do conduct in a nanotube rope, though several dozen metallic tubes are present. This finding suggests that the electric contact is rather poor even between metallic tubes. So, can a good contact be established when simply placing metallic tubes near each other? A first approach to this question was made by Fuhrer et al. [45], who investigated
the contact between crossed metallic nanotubes and found a reasonable electric resistance of the order of 100 kΩ. But the deformation of the tubes at the crossing still played a significant role.

The electric coupling between nanotubes is of vital importance for both, the basic research in intrinsic nanotube characteristics as well as the interconnection of tubes on the way to a possible application in nanoelectronics. Thus, the next chapter will be concerned with this coupling between tubes aligned parallel to each other in nanotube ropes. The main interest will be in the mechanism mediating the interaction, but additional information will emerge about the transport inside the tubes.
Chapter 4

Connections

The last chapter has been concerned with the electronic characteristics of ropes of single wall carbon nanotubes. It has turned out that electronic transport in ropes of tubes is realized via transport in single, essentially independent tubes in the rope. But the question remained if and how the tubes are interacting electronically. This will be the topic this chapter. The problem arising is that the coupling is very weak, which leads to a small inter-tube conductivity. Meanwhile the conductivity inside a tube is very large. The consequence is that an electric current injected into a tube stays in the tube rather than changing to another one. Thus, one has to force the current to transfer from one tube to another in order to investigate this interaction. The most straight-forward way to do so is current transport between single tubes attached to each other. But the mechanical distortions of such a geometry can easily affect the measurement and alter the intrinsic process.

Another way to tackle the problem is to deteriorate the conductivity inside the nanotube. This will eventually lift the discrepancy between intra-tube and inter-tube transport and coupling between tubes will receive more and more importance. The following sections will describe the solution found for the investigation of inter-tube coupling in ropes of nanotubes. This will involve a sputter treatment of the ropes introducing defects into the top tubes (section 4.1). It turns out that localization in the damaged areas increases the resistance in the damaged tubes when the sample is cooled (section 4.2). When current transport is blocked in the damaged tubes by localization the current switches to undamaged, unblocked tubes in the rope (section 4.3). This change of current path will eventually allow to study the inter-tube coupling (section 4.4).

4.1 Holes In The Road

The preparation of the ropes for this part of the investigation runs almost exactly as was described in section 3.1. The ropes are dispersed on a silicon/silicon dioxide substrate, located with a SEM and the contact areas for several top contacts are defined lithographically. But before depositing any metal contact onto
the rope, a sputter treatment is performed. At this stage the sample is totally
covered by a 200 nm thick resist layer and only the contact areas, where the
metal contacts will be after deposition, are uncovered. The sputter treatment
is done by exposing the sample to an Ar\textsuperscript{+} ion beam of 500 eV energy. When
impinging on the uncovered regions of the rope, the ions will cause defects in
the otherwise almost defect-free nanotubes in the top part of the rope. The
ions knock carbon atoms from their lattice sites and these can displace other
atoms themselves. So defects are produced in a cascade of scattering events.
These defects will alter the electric conductivity in the damaged parts of the
tubes.

The extent of the sputter damage depends on the number and the energy
of the ions impinging during the treatment. The samples were exposed for 20
seconds to beam of Ar\textsuperscript{+} ions with an energy of 500 eV. With the typical particle
density of the beam of 1.5 \cdot 10^{15}/m^2s one obtains a density of 3 \cdot 10^{16}ions/m^2
hitting the nanotube rope. The sputter cascade produced by each ion was
simulated with a Monte Carlo calculation for ion bombardment [58]. It turned
out that the cascade of every ion causes eight to nine carbon defects in the
material. The defects are located down to a depth of 6 nm inside the rope
(figure 4.1) determined by the density of the target material and the energy
of the ions. The low density of the material is very important for this rather
high penetration depth. The hollow construction of the nanotubes results in a
density of only 1kg/l for the close packed ropes. When the defects are located
inside a depth of 6 nm, this means that only the tubes in the top part of the
rope are damaged during the treatment. But most of the tubes, the ones in the
bottom part of the rope, remain undamaged. Figure 4.2 illustrates the situation.
The sputter depth of 6 nm corresponds to four to five layers of damaged tubes
counted from the top. Due to the statistic nature of the sputter damage, the
tubes in the next layer may be damaged too, even if with a much lower density.
This makes the estimate to be 6 – 7.5 nm. (One has to remember here that
current transport in nanotubes is one dimensional. The electrons sample the
tube circumference as a whole when moving along the tube and thus notice any
defect; they cannot run around them. Thus the tubes are always damaged as
a whole as soon as there is a defect somewhere on the circumference.)

Given the above results, one finds a defect density of 4 \cdot 10^{25}/m^3 corre-
sponding to a ratio of about one defect per 1000 atoms. A (10,10) tube, a
typical example in the ropes, has a number of 40 atoms per unit cell of length
a, that is an atomic density of 1.6 \cdot 10^{11}atoms/m. The mean distance between
scatterers is thus $L_{\text{defect}} \approx 6\text{nm}$. This defect density is low enough to preserve
the nanotubes as entities. i.e. they are not completely destroyed during the
sputtering. On the other hand, this defect density is high enough to expect a
strong influence on the electric conductivity of the damaged tubes. In the sput-
tered rope, one now finds four types of nanotubes: damaged and undamaged
metallic and semiconducting ones.

Once the sputter treatment was completed, the metal electrodes were de-
posited on the rope. It is important to note that the ropes were only damaged
4.1. HOLES IN THE ROAD

Figure 4.1: Distribution of damage introduced by sputtering. The data were obtained by a Monte Carlo simulation for ion bombardment [58]. Every impinging ion causes an average number of 8.6 defects in the tubes. The damaged region extends about 6 nm deep into the rope. This results in the four to five top layers of tubes in the rope being damaged (scheme of the cross section of the rope on the right hand side).

in the areas which were exposed lithographically and where the contacts are deposited. The segments of the rope between the contacts were left completely undamaged as they were covered by the resist during the sputtering. Figure 4.2 accounts for this in that the tubes in the top part of the rope are only shaded (damaged) underneath the electrode. The sputtered regions thus have a length along the rope axis corresponding to the width of the contacts, i.e. about 200 nm. The damage extends 6-7.5 nm deep inside the rope and the defects in a tube have a mean distance of $L_{\text{defect}} \approx 6 \text{ nm}$ (the similarity of the numbers is incidental).

What is the effect of this sputter treatment onto the electronic transport? Now there are four types of nanotubes in the sputtered ropes: damaged and undamaged metallic and semiconducting ones. The semiconducting tubes have an energy gap of about 500 meV and are thus insulating at low temperatures and give only a negligible contribution to the conductance at room temperature. The undamaged metallic ones are very good conductors (section 3.3) but they are not in direct contact to the metal electrodes and thus do not carry any significant current. The tubes neighboring the contacts, which do carry the current in these samples, are the damaged metallic tubes. The resistance determined in a four terminal measurement would thus be the one of the damaged metallic tubes in the top of the rope. Typically the 4t resistance of sputtered samples are of the order of 100 kΩ at room temperature, much larger than what was
found for transport in undamaged tubes in figure 3.9. Obviously, this increase in resistance is caused by the introduction of the defects into the current carrying tubes. But the rope and the tubes between the contacts are composed of very different parts. Figure 4.3 shows the sequence of damaged and undamaged areas in a current carrying top tube of the rope. In the model network these areas are represented by resistances $R_d$ and $R_u$. The resistance in the undamaged areas $R_u$ is very small compared to the damage induced resistance $R_d$ and can thus be neglected. A 4t measurement thus yields $R_4t \approx R_d = h/4e^2 \cdot L/L_0$. Here, $L$ is not the distance between the voltage probes, but the length of the damaged region in the tube, that is $L \approx 200 \text{ nm}$. $L_0$ is the mean free path between scatterers and turns out to be $L_0 \approx 5 \text{ – } 10 \text{ nm}$ using the typical 4t resistances. This is in very good agreement with the defect density calculated by the simulation of the sputter damage.

In conclusion, by a sputter treatment defects were introduced into segments of the nanotube ropes before deposition of the electrodes. By numerical Monte Carlo simulations the defect density was found to be one defect per 1000 atoms corresponding to a mfp of $L_{\text{defect}} \approx 6 \text{ nm}$. Only the tubes in the top part of the rope (down to a depth of $\approx 6 \text{ nm}$) were damaged, and only over a length of $\approx 200 \text{ nm}$ underneath the contacts. The defect density is confirmed by the measurement of the 4t resistance which is greatly increased by backscattering at the defects.
4.2 It’s Getting Tough

While the last section stated that the sputter damage introduced into the top tubes of the rope increased the measured resistance considerably, the current obviously still flows in these top tubes in which it is injected by the contacts. Still no coupling to other tubes is observed. So the next step is to further deteriorate the current transport in the top tubes.

Figure 4.4 shows the 4t resistance of a damaged sample as a function of temperature. At high temperatures the resistance is indeed much bigger than
Figure 4.4: Four terminal resistance of a sputtered sample as a function of temperature. Note that the resistance is always much higher than for an unsputtered sample (figure 3.9) due to scattering at the introduced defects. The resistance increase with decreasing temperature is caused by localization in the damaged areas. The steep decrease at lowest temperatures will be discussed in section 4.3.

what is found in undamaged ropes (figure 3.9). And upon cooling the sample the resistance increases even further. In the case of the undamaged rope the resistance decreased with decreasing temperature since scattering at phonons were reduced. Here, where the current flows in damaged tubes, the resistance increases when cooling the sample. (The steep decrease at lowest temperatures will be the topic of the next section and is postponed.) This increase of resistance with decreasing temperature is not understandable in classic transport theory by some backscattering process. There is no scattering process known to be more effective when the sample is cooled. Scattering at static defects is not affected by temperature at all. And the rates for electron-phonon and electron-electron scattering are reduced when lowering the temperature due to the decreasing phase space for these processes. In order to describe this strange behavior another process called localization is necessary.

In the last section it was sufficient to consider incoherent scattering at static defects in order to describe the resistance in the damaged tubes. The important word here is ‘incoherent’. In the classic transport theory the electron moves in a conductor and suffers collisions or scattering events with different partners. Resistance is created by momentum transfer from the current carrying electron to the scattering partner, may this be a phonon, another electron, or a static
4.2. IT’S GETTING TOUGH

defect. In this picture the single scattering events are independent from one another. The wave nature of the electrons and the belonging interference effects are neglected. But the quantum mechanics contributed a new definition of resistance: An electron that returns during its motion to its origin does not contribute to conductance. Any process returning an electron to its origin is thus generating resistance. The usual mechanisms for backscattering fit to this definition as well as the phenomenon of localization where coherent superposition of backscattering leads to an additional increase in resistance.

Consider an electron moving in a conductor which contains a lot of static defects as in figure 4.5. The electron is scattered often and there is some possibility that it returns to its origin, that is that the scattering creates resistance. But the quantum theory revealed, that the probability for an electron to return to its origin is higher than what is expected from classic transport theory. In order to create resistance the electron starts at A and returns via some path Γ to A. This path can be passed in either direction and each one contributes to resistance. The classic theory simply counts the closed paths returning the electron to its origin in order to determine the resistance. The quantum theory however considers also the interference of these paths. The total probability for an electron to return to A via the paths ±Γ is determined by the absolute square of the sum over the probability amplitudes $a_{±Γ}$.

$$A_Γ = |a_{+Γ} + a_{-Γ}|^2 = |a_{+Γ}|^2 + |a_{-Γ}|^2 + a_{+Γ} \cdot a^*_{-Γ} + a^*_{+Γ} \cdot a_{-Γ}$$

Since the path $−Γ$ is simply the time-reversed counterpart of $Γ$, the probability amplitudes $a_{+Γ}$ and $a_{-Γ}$ are identical. Thus the total probability for returning to A is $A_Γ = 4 \cdot |a_{+Γ}|^2$ including the interference terms and only $A_Γ = 2 \cdot |a_{+Γ}|^2$ neglecting them. In classic transport theory the interference terms are not taken into account since the scattering events are considered independent from one another, i.e. the electron is scattered incoherently. But if the electrons are moving coherently along the path $Γ$, the reflection probability $A_Γ$ is doubled by the interference.

When is current transport coherent? The term coherent does not refer to a single electron but to the ensemble of all electrons studied. If all electrons which start with the same initial conditions are moving through the conductor in the same manner, finding the same probabilities for being reflected or being transmitted, then current transport is called coherent. In the example of figure 4.5, where the electrons move through a disordered conductor with static defects, every electron starting at the same position with the same initial velocity will suffer the same scatterings and transport is thus coherent. In this case the interference terms contribute to the resistance. But if the electrons should suffer any unpredictable scattering events along their path every electron would move in a different way through the conductor and the coherence (of the ensemble of electrons) is lost. In this case of unpredictable scattering events affecting the transport, the interference terms can indeed be neglected. Examples for such incoherent (i.e. unpredictable) processes are electron-electron and electron-phonon scattering. In both processes the moment at which the scattering occurs is not fixed. Both processes are thus called 'phase-breaking' or
CHAPTER 4. CONNECTIONS

Figure 4.5: Part of a disordered conductor with static scattering centers (x). Closed paths like $+\Gamma$ and $-\Gamma$ return an electron starting at A to its origin and give rise to resistance. If the electron does not suffer an incoherent scattering event like electron-electron or electron-phonon scattering while travelling $\pm \Gamma$, the contributions of the time-reversed paths interfere constructively and the resistance contribution is doubled. In contrast to closed paths like $\Gamma$, paths like the ones connecting B to C give rise to conductance.

If the dominant scattering process in a sample is incoherent scattering (e.g. phonon scattering at high temperatures in 'normal' metals), there is no possibility for an electron to be backscattered coherently. For a backscattered electron the paths $\pm \Gamma$ superimpose incoherently and the resistance can be described classically. But if there is coherent scattering during the dephasing time $\tau_\Phi$ the paths interfere and the full quantum mechanical result is valid, i.e. the resistance is increased by coherent backscattering.

In order to describe the coherence effects mathematically one defines a 'dephasing' time $\tau_\Phi$, being the mean time between incoherent scattering events (e.g. electron-electron or electron-phonon scattering). During this time interval the electrons move coherently. Thus, this time is sometimes called 'coherence' time. When this time has elapsed, an incoherent scattering event ends the coherent motion of the electrons. During this time interval the electrons cover a distance called the 'coherence' length. The meaning of this length is the average distance an electron can travel coherently before being scattered incoherently. In order to observe a strong implication of coherent backscattering onto the resistance, the electrons have to be scattered very often coherently during the time $\tau_\Phi$. Only then many backscatter paths $\Gamma$ result in such a diffusive motion which can interfere coherently. For diffusive motion, the 'coherence' length covered during the 'coherence' time is given by

$$L_\Phi = \sqrt{D \cdot \tau_\Phi} \quad (4.1)$$

with D being the diffusion constant. In case of one dimensional transport in a metallic system, the diffusion constant is determined by the Fermi velocity
and the mean time between coherent scatterings $\tau_0$ as $D = v_F^2 \cdot \tau_0$. The above formulas are only correct for diffusive motion, i.e. for $\tau_0 \ll \tau_\Phi$. The strength of the localization (and other interference effects) is determined by the ratio of the coherence length $L_\Phi$ to the mfp between coherent scattering events $L_0 = v_F \tau_0$, i.e. the number of scattering events which can interfere coherently. The longer the 'coherence' length, the longer the electrons can move coherently, the more coherent scattering events can take place, the more backscattering paths $\Gamma$ occur which can interfere, the higher is the resistance observed.

Once more, the effect coherence has on the resistance is that all paths $\Gamma$ returning an electron to its origin double their contribution to resistance if their length is smaller than the coherence length $L_\Phi$. When the occurrence of incoherent scattering events is reduced (for example by lowering the temperature) the dephasing time $\tau_\Phi$ and the coherence length $L_\Phi$ increase and more paths are contributing interference terms to the resistance. This process, called localization, leads to an exponential increase in resistance when the coherence length is increased. This localization effect is very pronounced in samples with a low dimensional current transport. In three dimensions the number of paths like $\Gamma$ returning an electron to its origin and thereby creating resistance is by far outnumbered by paths contributing to the conductance of the sample. But the relative number of backscattering or localizing paths increases when the dimension of current transport is reduced to two and especially down to one dimension. In the latter case there are only two possibilities for the outcome of a scattering event, namely backscattering or forward scattering. And every backscattering process immediately yields a localization path $\Gamma$. Thus, localization behavior is expected to be much more pronounced in one dimensional systems than in any higher dimensional transport.

Including the interference effects, the resistance in the damaged metallic tube being a one dimensional system can be described in the following way [33]. The total length $L \approx 200nm$ of a damaged part, which dominates the resistance, is divided into a number $L/L_\Phi$ of coherent segments in series. Each segment contributes the usual resistance quantum $h/2e^2$ amplified by a factor describing the localization. This factor depends exponentially on the ratio of the coherence length $L_\Phi$ to the so called localization length $M \cdot L_0$. Here, $M$ is the number of modes in the system (for a metallic nanotube $M=2$) and $L_0$ is the mfp between coherent scattering events (defect scattering). The resistance is then computed by

$$R_d = \frac{L}{L_\Phi} \cdot \frac{h}{2e^2} \cdot \frac{1}{2} \cdot \left( e^{\frac{2L_\Phi}{ML_0}} - 1 \right). \quad (4.2)$$

When the coherence length grows with decreasing temperature, the resistance of the damaged tube is increased exponentially by the localization. But when the coherence length becomes much smaller than $L_0$, the distance between defects, the transport becomes incoherent and the localization correction has to vanish. This is indeed the case and can be seen when expanding formula 4.2 for small
The first term is the usual resistance formula for incoherent transport which was used in sections 3.3 and 4.1. In both cases the coherent and incoherent scattering lengths were comparable and thus transport was essentially incoherent. The next term describes what is sometimes called 'weak' localization, observed in systems where the coherence length is comparable to the localization length \( M \cdot L_0 \), for example two dimensional electron gases [59] and sometimes even metals [60]. The higher order terms which lead eventually back to formula 4.2 are only rarely observed. Just highly disordered systems with little incoherent scattering are possible candidates. Metals would be promising with a mean distance between defects of some nm and coherence lengths (at low temperatures) of some \( \mu m \) [61], but due to their high electron density they always possess an enormous number \( M \) of conducting channels preventing them from all but weak localization. The case of the nanotubes is very different. They have very low scattering rates for incoherent processes like electron-phonon scattering (section 3.3) and thus offer high coherence lengths. Moreover they only possess \( M=2 \) conducting channels. Usually the tubes are almost defect-free, but the disorder necessary for localization can be generated by introducing defects in a sputter treatment. In the present situation, the mfp between defects is very small, being of the order of \( L_0 \approx 5 – 10 \) nm. The nanotubes can thus easily reach the regime of 'strong' localization where \( L_\Phi \gg M \cdot L_0 \).

The resistance in the damaged nanotubes can indeed be described by localization as shown in figure 4.6. The fit to the experimental data is acquired by evaluating formula 4.2 with reasonable assumptions for the length of the damaged region \( L = 200 \) nm, the mfp between scatterers \( L_0 = 10 \) nm and the temperature dependence of the coherence length\(^3\). This latter quantity is determined by the temperature dependence of the phase-breaking scattering process. For example, if one would assume electron-phonon scattering to be dominant in phase-breaking, the linear temperature dependence of its scattering rate would transfer to the coherence time \( 1/\tau_\Phi \sim T \) and would yield a coherence length \( L_\Phi = \sqrt{D \cdot \tau_\Phi} \sim T^{-1/2} \). The exact parameters are in anticipation of the results of the next section. With these assumptions, one major feature of the resistance of the damaged sample is understood. The localization in the damaged parts of the top tubes increases the resistance upon cooling the sample. But the second feature in the behavior of the resistance, the steep decrease at lowest temperatures, is not covered by this explanation. The next section will correlate this

\(^3\)In order to be correct, one would have to consider two times the half of a damaged segment between the voltage probes (cf. figure 4.3), that is

\[
R_d = 2 \cdot \frac{L/2}{L_\Phi} \cdot \frac{h}{2e^2} \cdot \frac{1}{2} \left( e^{\frac{2\pi L_\Phi}{2e^2 L} - 1} \right).
\]

At this point, this makes no difference to the value of \( R_d \), since the interest here is in the behavior at higher temperatures. It will though become important in the next section, when the phase coherence length at lowest temperatures eventually becomes comparable to \( L \). For the sake of simplicity, this subtlety will be taken care of later.
4.3 The Passing Lane

So far the last section was only concerned with current transport taking place in a damaged surface tube close to the electrodes. The resistance of this surface tube is increased by the introduction of defects during a sputter treatment, raising the sample 4t resistance from some kΩ to some 100 kΩ at room temperature. The resistance increases strongly when the sample is cooled. It was shown that this is caused by localization in the damaged areas of the tube (coherent backscattering), when the coherence length increases with decreasing temperature. But the experimental results can only partly be explained by this (figure 4.6). At low temperatures around 20 K a steep decrease in resistance is observed in the sputtered samples. This decrease will now be shown to be caused by the presence of undamaged tubes in the rope. The idea is that these
undamaged tubes take over the current transport at lowest temperatures.

The undamaged tubes in the rope offer parallel channels for current transport. These parallel tubes in the bulk usually do not carry any significant current. First, they are not in direct contact to a metal electrode. Second, they are only weakly coupled to the surface tube which carries the current. But when current transport in the surface tube is hindered by localization, the current will switch to an undamaged tube in the bulk of the rope, which offers a low resistive channel for transport. The fact that the tubes are only weakly coupled can be taken into account by a high coupling resistance connecting the tubes. This high coupling resistance will suppress any current transfer between the tubes as long as the single tubes are low resistive, i.e. undamaged. However, when transport is blocked in the current carrying surface tube, this coupling resistance allows the current to switch to an undamaged and thus unblocked tube in the bulk. The 4t measurement would then detect only the low resistance of the undamaged bulk tube carrying the current at lowest temperatures.

This idea will now be developed, so that one becomes able to analyze the experimental data quantitatively. Figure 4.7 shows a model network of resistances which accounts for the situation. It is an extension of figure 4.3 where a second metallic, undamaged tube in parallel to the damaged tube is added. This seems a drastic simplification of the actual geometry of the rope consisting of about 100 tubes. Nonetheless it is a realistic point of view since most of the tubes will not enter the picture for several reasons. First of all, the semiconducting tubes in the rope are insulating at these low temperatures, anyway. Second, the model confines to a single damaged metallic surface tube to carry the current at high temperatures, since it was already shown that only a small number of tubes, presumably only one or two, are involved in usual current transport (section 3.3). Third, when transport is blocked in the surface tube, the current switches to the closest undamaged metallic tube in the rope, since this tube out of all undamaged tubes is expected to have the smallest of the generally large coupling resistances. The damaged tubes nearby the surface tube are blocked by localization too and will thus not take over the current. The model of figure 4.7 will thus cover all relevant aspects of the actual geometry.

What are the different resistances in figure 4.7? Like in figure 4.3 the damaged tube is described by a series of resistances $R_d$ caused by localization according to formula 4.2. The small resistances of the undamaged areas inbetween the contacts can be neglected compared to $R_d$. The coupling between the surface and the bulk tube is modelled by resistances $R_t$ placed underneath the contacts, i.e. connected to the localization areas of the damaged tube. The reason is that the current will only leave the surface tube via the coupling resistance if transport gets blocked (for example by localization). In the areas between the contacts, where the surface tube and the bulk tube are both undamaged, a transfer is not a favorable alternative for current transport. The segments of the undamaged tube are represented by resistances $R_u$ being of the order of some $k\Omega$. In principle, these resistances are different since they depend on the length of the segment and on temperature. But it will turn out, that the
Figure 4.7: Extension of the model depicted in figure 4.3. In addition to the damaged metallic tube in direct contact to the electrodes, the model system now comprises also a weakly coupled undamaged metallic tube in the bulk of the rope. The interaction is described by coupling resistances $R_t$. These are connected to the surface tube only in the damaged segments, because only there changing the tube via a huge coupling resistance $R_t$ is possible. In the undamaged segments between the contacts transport inside the tube via $R_u$ is favored. The resistances $R_u$ are in principle different for each segment, but they are always much smaller than the $R_d$ and the $R_t$ resistances and it turns out that their exact values are unimportant for the results of the simulations. The contact resistances $R_c$ are only observable in a 2t measurement, but are excluded from the 4t resistance.
actual values of these resistances are not important since they are connected via the high coupling resistances $R_t$. Last but not least, contact resistances $R_c$ are introduced into the leads. This takes care of the possibility that the metal electrodes could be not ideally connected even to the surface tube\(^5\). These contact resistances will not show up in a 4t measurement but will contribute to the 2t resistance of the sample.

In order to reproduce the measurements quantitatively one has to assess the values of the different resistances in the model. The resistances of the undamaged tube segments $R_u$ are taken to be some kΩ in the simulation. Their actual value and temperature dependence is unimportant as long as they are much smaller than the coupling resistances $R_t$ to which they are connected. These coupling resistances are assumed to be temperature independent. (A justification for this is given in the next section. At least, it is already clear at this point, that the coupling cannot freeze out at lowest temperatures, since the sample would then be insulating in contrast to the observations.) The resistances in the damaged tube, $R_d$, are described by formula 4.2. The length of the damaged areas is determined by the contact width of the specific sample. The average distance between the defects can be estimated according to sections 4.1 and 4.2 to be $L_0 = 5 - 10 \, \text{nm}$. The coherence length, especially its temperature dependence is given by the dominant dephasing scattering process. Since the resistance is created in a strongly disordered part of the tube, the motion of the electrons is diffusive and thus the coherence length is given by $L_\Phi = \sqrt{D \cdot \tau_\Phi}$ as already described in section 4.2.

Figure 4.8 compares experimental data of three sputtered samples to fits according to the model. The agreement is mostly excellent. The simple model already describes the situation very well. The 4t measurement shows the increase in resistance due to localization in the damaged tubes when the sample is cooled from high temperatures. When the resistance in the damaged tube $R_d$ becomes comparable to the coupling resistance $R_t$, the undamaged bulk tube participates in current transport. Eventually, the localization blocks the surface tube completely at lowest temperatures and the 4t measurement only detects the low resistance $R_u$ of the undamaged bulk tube carrying all the current. Meanwhile, the 2t measurement shows the increase in resistance due to localization, too. But instead of a steep decrease like in the 4t measurement, the 2t resistance saturates at low temperatures. This is since both channels, the surface and the bulk tube, are high resistive in the 2t configuration. The surface tube due to localization, the bulk tube due to the coupling resistances involved when the current switches its path. When all current flows via the undamaged bulk tube at lowest temperatures, the 4t measurement gives $R_u$ (central segment only), while the 2t resistance is $R_c + R_t + 3 \cdot R_u + R_t + R_c \approx 2 \cdot R_t + 2 \cdot R_c$.

\(^5\)An inevitable contact resistance is already given by the change of dimensionality of transport at the metal nanotube-interface. In addition, impurities can be present at the interface resulting from the sample preparation. These can be residues of the solvent used when dispersing the nanotubes onto the substrate or of the resist used in electron-beam lithography. Additional 'contact' resistances can arise from the deformation of the tubes when the metal electrodes are deposited onto the ropes.
Figure 4.8: Several examples for electric measurements at sputtered ropes. The 4t and the belonging 2t measurements of three samples are shown on the left and right hand side, respectively. The symbols denote the experimental data, the solid line is a fit according to the model described in the text and depicted in figure 4.7. The parameter set used for the simulation is denoted in the 2t graph. The agreement is mostly excellent, the most prominent deviation being the occurrence of additional contact resistance $R_c$ in the 2t resistance of sample c). These were not included ab initio into the simulation, since their occurrence is not a common feature of the preparation (cf. samples a) and b)).

It has been stated above that the 4t resistance maximum is always located around 20 K. The position of the maximum is related to the switching of the current from the damaged to the undamaged tube. The condition $R_d \approx R_t$ gives a rough estimate for the position of the maximum. Due to the exponential dependence of $R_d$ on temperature this condition is preferably fulfilled at around...
20 K, where the localization turns out to increase $R_d$ very fast. This is the reason why the maximum lies always around this temperature. But the behavior of the localization depends very sensitive, i.e. exponentially on the actual defect density in the sample. Thus slight variations in $L_0$ alter the resistance $R_d$ considerably, thereby corroborating any strict correlation between the position of the $4t$ resistance maximum in temperature and the coupling resistance.

There are some deviations of the model data from the experimental results. In the $2t$ measurement of figure 4.8 c) the experimental resistance exceeds the fit by far. This is probably due to a large and temperature dependent contact resistance $R_c$ in this case. Though the model takes the possibility of such additional contact resistances into account (cf. figure 4.7), these were not included in the simulations of figure 4.8. In the case of sample c) such contact resistances are present, but they are absent in samples a) and b). Such additional contact resistances were sometimes observed in the $2t$ measurements, but the quality of the $4t$ simulations is not affected by the presence (or absence) of these, since they are connected in series to the sample and thus are excluded from the $4t$ resistance. Another type of deviation encountered sometimes is seen in the $4t$ measurement of figure 4.8 b). This measurement shows that the total resistance at lowest temperatures is not always given by the resistance $R_u$ of the undamaged tube. This happens when the localization is not strong enough to block the transport in the damaged tube sufficiently. A slight correction to the model will resolve this discrepancy.

When the models of figures 4.3 and 4.7 were proposed, the two resistances $R_d/2$ between each pair of contacts were combined to a single one neglecting the resistance of the undamaged tube segment inbetween. This was done for the sake of clearness. This procedure is correct only if the two resistances can be treated incoherently, that is as long as the coherence length is much smaller than the length of each segment, $L_\Phi \ll L/2$. Once the coherence length becomes comparable to $L/2$, one has to compute the resistance of each segment separately and subsequently add them. Thus, in formula 4.2 describing the resistance $R_d$ one has to add two times the resistance of a segment of length $L/2$ instead of computing the resistance of only one segment of length $L$.

$$R_d = 2 \cdot \frac{L/2}{L_\Phi} \cdot \frac{h}{2e^2} \cdot \frac{1}{2} \cdot \left( e^{\frac{2L_\Phi}{\hbar v_0}} - 1 \right) \text{ for } L_\Phi < L/2.$$  

At first, this does not seem to be more than a cosmetic correction. But at the stage when $L_\Phi \geq L/2$, the above formula has to be reconsidered. When the coherence length exceeds the length of the damaged segment $L/2$, the whole area will be one coherent segment. Thus, the coherence length $L_\Phi$ has to be replaced by $L/2$.

$$R_{d,max} = 2 \cdot \frac{h}{2e^2} \cdot \frac{1}{2} \cdot \left( e^{\frac{2L/2}{\hbar v_0}} - 1 \right) \text{ for } L_\Phi \geq L/2.$$  

Thus, at lowest temperatures the resistance of the damaged segment saturates once the coherence length exceeds half the segment length. If this resistance $R_{d,max}$ is much larger than $R_t$, the coupling resistance, the blocking of the
4.3. THE PASSING LANE

Figure 4.9: Several examples for 4t measurements at sputtered ropes with high coupling resistances. The symbols denote the measurement, the solid line the simulation according to the model system. The resistance $R_d$ did not become large enough to block the transport in the damaged tube sufficiently. Therefore the current did not switch completely to the undamaged tube and the 4t resistance did not drop to its limiting value $R_u$. The simulations are made according to the corrected model which takes the finite extent of the damaged areas into account when computing the resistance $R_d$ due to localization.

In total, measurements at 13 samples were taken and simulated according to the model. Especially the non-monotonic behavior of the 4t resistance was reproduced in a very satisfactory manner. The evaluation of the simulations yields numerical values for the parameters used in the fits. These are the coupling resistance $R_t$, the mfp between scatterers $L_0$ and the temperature dependence of the coherence length $L_\Phi(T)$. The latter quantities enter the simulation via the resistance $R_d$ of the damaged tube segments. (The resistances of the undamaged tube $R_u$, since always connected via the much larger coupling resistances $R_t$, do not affect any numerical value of any other parameter. On
the one hand, this is positive for the reliability of the obtained values, on the other hand, no statement can be made about $R_u$ except for its existence.) For the temperature dependence of the coherence length a power law behavior $L_\Phi = A \cdot T^{-\alpha}$ is assumed. Due to formula 4.1 this corresponds to a behavior of the coherence time $\tau_\Phi \sim T^{-2\alpha}$. Such a dependence of $\tau_\Phi$ on temperature is expected if a single phase-breaking scattering process limits the coherence time. The observed value of $\alpha$ will then give information on this process, since every scattering shows a characteristic temperature dependence. A problem with this description will only arise if several phase-breaking scattering mechanisms have comparable influence on the coherence time, which will cause deviations from a simple power law.

Now that the simple model from figure 4.7 has proven to be able to describe the situation in the sputtered samples, one can advance to a detailed analysis of the parameters found in the simulation. It turns out that the most reliable parameter involved in the simulation is the coupling resistance $R_t$. The height of the 4t resistance maximum is solely determined by $R_t$. A qualitative way to understand this is to remember that the resistance maximum is connected to the switching of the current to the undamaged tube. The switching occurs when the temperature dependent resistance in the damaged tube $R_d$ is comparable to the coupling resistance $R_t$. At this temperature, all resistances $R_d$ can be replaced by the value $R_t$ (the $R_{u,s}$ are neglected anyway) and the total 4t resistance of this network depends only on $R_t$, namely it is $R_{4t}(T_{\text{max}}) = R_t/3.41$. (The numerical factor is only understood in a quantitative treatment.) Thus, the coupling resistance is readily obtained from the 4t measurement. For the samples studied in this investigation the values ranged from 2 MΩ up to 500 MΩ. The explanation of these values in terms of a coupling mechanism will be the topic of the next section. The enormous range the values span will be linked to the geometry of the rope.

The other parameters enter the simulation via $R_d$ according to formula 4.2. All experimental data could be reproduced using values of $L_0 = 5 - 10$ nm, which connects excellently to the predictions of the sputter simulation and the measured room temperature resistances (section 4.1). The absolute values of the coherence length are of the order of several 100 nm at low temperatures as is seen in figure 4.10. Combining this with the diffusion constant $D$ (determined by $L_0$) one finds from formula 4.1 a coherence time of the order of several picoseconds at low temperatures. (In a ballistic motion of the electrons this would correspond to a mean free path of several micrometers between phase-breaking scattering events.) Altogether, the power law ansatz for the coherence length works very well.

But the exponent in this assumed power law behavior varied between $\alpha = 0.25 - 0.7$. This is somewhat unexpected, since all samples were prepared in the same manner. The statistic nature of the sputter damage ($L_0 = 5 - 10$ nm) is the only known difference so far. Thus, one would expect to find the same phase-breaking scattering process in all samples and thus a narrow distribution of $\alpha$ around the value corresponding to this phase-breaking mechanism.
The observation of a span of values suggests that more than one mechanism is involved in phase-breaking. What scattering mechanisms are available for limiting the coherence length in the damaged nanotubes?

From the last chapter we know that electron-phonon and electron-electron scattering are predicted to occur in undamaged nanotubes, with the electron-phonon scattering being dominant. Both processes are phase-breaking due to the fact that the outcome of such a scattering is not predictable. The scattering rates for both processes are linear in temperature and the electron-phonon scattering time was found to be of the order of picoseconds at room temperature. The scattering time for the electron-electron process are even larger. Thus, in order to contribute to phase-breaking as is found in the damaged tubes (picoseconds at low temperatures) these processes would have to be dramatically enhanced by the presence of the defects. It is well known that this is indeed the case, at least for the electron-electron scattering [62, 63, 60]. The diffusive motion of the electrons extends the interaction time between the electrons and increases the scattering rate. But usually not only the absolute value of the scattering rate is changed but also the temperature dependence. Unfortunately, there do not exist any predictions about the behavior of electron-phonon or electron-electron scattering in disordered nanotubes. Thus, no decision can be made by the value of $\alpha$ whether these processes are substantially involved in phase-breaking or not.

Figure 4.10: Dependence of $L_\Phi(T)$ as inferred from the simulations for all 13 samples. The symbols are guides to the eye for a dependence $\sim T^{-0.33}$ (circles) and $\sim T^{-0.5}$ (diamonds).
There are several other scattering mechanisms which can be responsible for limiting the coherence length (and time). These are Nyquist scattering and Thouless ‘scattering’. Both processes are not creating resistance by themselves, since there is no momentum transfer from the electronic system to some scattering partner. Thus, they cannot be observed in the resistance of the undamaged tubes and were not mentioned in section 3.2, consequently. But both processes are phase-breaking and therefore affect the localization being an interference effect.

The Nyquist scattering describes the scattering of an electron at the field-fluctuations of the other, surrounding electrons. Due to the statistic nature of these fluctuations such a scattering is different for each electron, thus the electronic ensemble loses its coherence. For one dimensional systems the scattering time $\tau_N$ is predicted to follow a power law on temperature $\tau_N \sim T^{-2/3}$ [64]. Since the scattering rate depends on the degree of disorder in the sample it is difficult to assess an exact value to the scattering time, but at least there is a distinct statement about the temperature dependence.

The Thouless phase-breaking process is not exactly a scattering process. But it limits the coherence due to the thermal smearing of the electrons. The thermal energy $k_B T$ poses an inevitable uncertainty for the energy of the electrons in the ensemble. Speaking in the terms of section 4.2, the starting conditions for the electrons moving through the conductor are not exactly identical. Thus, each electron will sample the defect distribution with a somewhat different energy and the longer the paths $\Gamma$ become, the larger will be the differences in electronic motion for electrons with different energy. This effect is described by assessing a finite ‘lifetime’ for the coherence due to thermal smearing. This is done by using the uncertainty relation, which gives a Thouless time $\tau_{Th} = \hbar/k_B T$ limiting the coherence of the electronic ensemble. At low temperatures of about 1 K this corresponds to a scattering time of several picoseconds, being already of the correct order in case of the nanotubes. If Thouless ‘dephasing’ is indeed dominant in phase-breaking, it would thus yield a temperature dependence $L_{Th} \sim T^{-1/2}$ for the coherence length.

In figure 4.10 two lines are marked as guide to the eye for two different exponents, namely $\alpha = 0.33$ (corresponding to Nyquist scattering) and $\alpha = 0.5$ (Thouless scattering, el-el and el-ph scattering). Both processes could be involved in limiting the coherence judging from this plot. But as can be seen in formula 4.1, the coherence length is not the proper quantity to be compared to the phase-breaking mechanisms. Due to the diffusive motion, the coherence length does explicitly depend on the disorder by the diffusion constant $D = v_F^2 \tau_0 = v_F L_0$. Thus, it is necessary to switch over to the coherence time when comparing different samples. Still, this time can depend itself on the extent of the sputter damage (disorder-enhanced el-xx scattering, Nyquist scattering), but it is in any case the better choice. Figure 4.11 depicts the results of the simulation for the temperature dependence of the coherence time $\tau_0(T)$ for the different samples. Again, the guides to the eye suggest that both processes are involved. (Besides, disorder-enhanced electron-electron and
4.3. THE PASSING LANE

Figure 4.11: Dependence of \( \tau_\Phi(T) = 1/v_F L_\Phi^2(T)/L_0 \) (cf. formula 4.1) for the 13 samples. Again, the symbols are guides to the eye representing \( \tau_\Phi \sim T^{-0.66} \) (circles) and \( \tau_\Phi \sim T^{-1} \) (diamonds). The heavy grey lines indicate the electron-phonon scattering time for an undamaged tube and an estimate for the Thouless dephasing time \( \tau_{Th} = \hbar/k_B T \).

electron-phonon scattering were never excluded from the picture, but lacking any assumptions at least on their temperature dependence they are excluded from the discussion.) Due to the dependence of the Nyquist scattering on the disorder, it is possible that for different samples with a different degree of disorder the balance between Thouless and Nyquist scattering can be in favor to the one or the other. This explains, why no distinct power law identifying one dominant phase-breaking mechanism has been found. But the statistics the experiments offer so far are not sufficient to justify further statements. The next chapter will present first measurements on the energy dependence of the coherence length and new hints on the contribution of different phase-breaking mechanisms will arise there. Before continuation of this discussion, the analysis of the coupling mechanism between nmotubes will be presented in section 4.4.

Summarizing the informations gained in this section:

- Sputtered samples show a pronounced four terminal resistance maximum in the temperature dependence around 20 K.

- The maximum in the 4t measurement is caused by the interplay of damaged and undamaged tubes in the rope and can be described in a simple resistance network model. The value of the maximum is determined by the coupling resistance \( R_t \).
• The coupling resistance $R_t$ is temperature independent. The values found range from 2MΩ to 500 MΩ.

• The resistance $R_d$ in the damaged tube is caused by strong localization. The temperature dependence of $R_d$ determines position and shape of the resistance maximum. The exponential dependence of the resistance on temperature pins the resistance maximum to the observed temperatures around 20 K.

• The defect density found in the simulations $L_0 = 5 - 10 \text{ nm}$ agrees very well with the sputter simulations and the room temperature resistances.

• The temperature dependence of the coherence length shows a mixing of different phase breaking processes, suggesting the dominant ones being Nyquist scattering and Thouless dephasing (thermal smearing).

• The coherence time in the damaged nanotubes is of the order of picoseconds at low temperatures, close to the limiting value of the Thouless time.

4.4 How To Change The Lane

This section will turn to the interpretation of the obtained coupling resistances $R_t$ in order to identify the coupling mechanism between nanotubes. The values found for the 13 samples under consideration are depicted in table 4.1. As can be seen, the values cover a large range between 2 and almost 500 MΩ. These values resulted from the simulations of the 4t measurements in a very simple manner being determined solely by the height of the resistance maximum. The coupling resistance was assumed to be temperature independent and the simulations were successful using this assumption. This implies that the coupling mechanism is temperature independent (at least, it may not freeze out at lowest temperatures) and has to cover two magnitudes of coupling strength for the given sample geometry.

This coupling is not mediated by an overall three dimensional band structure of the rope, as was already stated in section 2.4. The reason for that is the lack of three dimensional crystalline periodicity in the ropes. Thus, single particle mechanisms for the inter-tube coupling between individual nanotubes have to be identified. Hopping processes are discussed as candidates for inter-tube transport [65]. In this framework current transport is described by electrons hopping via some intermediate states (e.g. via other nanotubes) between the initial and final state (tube). If one considers this case using the data from table 4.1, the resistance for a single transfer (one hop) would have to be associated with the lowest value found up to date in our analysis, that is 2 MΩ. The highest value of 500 MΩ would then need 250 transfers in series, which is barely imaginable with only 100 tubes in the rope. Moreover, most hopping processes are thermally activated and thus the coupling between tubes would eventually freeze out, leaving the rope insulating at lowest temperatures, in contrast to the
4.4. HOW TO CHANGE THE LANE

<table>
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<tr>
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</thead>
<tbody>
<tr>
<td>2.04 ± 0.07</td>
<td>15 ± 0.7</td>
<td>40 ± 2</td>
<td>95 ± 3</td>
<td>139 ± 7</td>
</tr>
<tr>
<td>4.8 ± 0.7</td>
<td>15.5 ± 1</td>
<td>71 ± 3</td>
<td>109 ± 0.5</td>
<td>483 ± 27</td>
</tr>
<tr>
<td>6.1 ± 0.7</td>
<td>20.5 ± 0.5</td>
<td>75 ± 2</td>
<td></td>
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</table>

Table 4.1: Coupling resistances $R_t$ for 13 samples inferred from the 4t measurements.

experiment. Hence, hopping processes cannot be responsible for the observed values of $R_t$.

A good explanation for the data is electron tunneling between the involved tubes. In this process a small range of distances of the tubes spans a large range of resistances due to the exponential dependence of the tunnel current on distance. In addition, this process is temperature independent and allowed at lowest temperatures. In order to describe the tunnel process linking the damaged surface to the undamaged bulk tube via the distance $d$, one can refer to the coupling of one dimensional wave guides [66, 67]. There one finds for the tunnel current between the two waveguides

$$I_t = e \int_{-\infty}^{+\infty} dE D(E) v_\perp(E) f(E + eU)(1 - f(E)) T(E)$$

$$\approx e \int_{E_F}^{E_F + eU} dE D(E) v_\perp(E) T(E)$$

for small temperatures. $D(E)$ is the density of states and $v_\perp$ the velocity perpendicular to the tunnel barrier. The transmission probability $T(E)$ depends on the height $\Phi$ and the thickness of the tunnel barrier $d$ (the distance between the tubes) and is independent on the energy as long as $eU \ll \Phi$. When current transport in the damaged tube is blocked by defect scattering, the velocity $v_\perp$ can be approximated by $v_F$. The density of states in the nanotube is constant due to the linear dispersion relation. Thus one obtains

$$I_t = e \cdot \frac{4}{2\pi \hbar v_F} \cdot v_F \cdot T \cdot eU \quad \Rightarrow \quad R_t = \frac{\hbar}{4e^2} \cdot \frac{1}{T(\Phi, d)}.$$ 

In tunnel processes the transmission through a barrier is determined by the overlap of the wave functions which extend with an exponential damping $e^{-\kappa x}$ into the barrier region. $\kappa$ is linked to the barrier height $\Phi$ via the dispersion relation. For the nanotubes the dispersion is linear in a large range around the Fermi energy, i.e. $E = E_F \pm \hbar v_F (k - k_F)$, and yields $\kappa = \Phi / (\hbar v_F)$. The total transmission through a barrier of thickness $d$ is then given by $T = e^{-2\kappa d}$. Thus, the result for the theoretical description of the coupling resistance is

$$R_t = \frac{\hbar}{4e^2} \cdot \frac{1}{T} = \frac{\hbar}{4e^2} \cdot e^{2\kappa d}. \quad (4.3)$$

The coupling resistance depends on the distance between the tubes and the height of the barrier which have to be tunneled. Now, what are the values to
be chosen for \( d \) and \( \Phi \). The barrier height depends on the material the barrier consists of. As a first guess one would suggest the work function of the material (\( \approx 4.5 \, eV \), [68]) to pose the barrier height. But the tubes are embedded into a rope of other nanotubes. These tubes are tunneled by the electron, most of them being semiconducting. Like for tunneling through other insulators, the barrier height should be given by the conduction band edge of the insulator. All nanotubes share the same graphene origin and thus the work functions are expected to be equal [45] and the Fermi energy in the metallic tubes aligns midgap the semiconducting energy gap. The barrier height thus should be half the energy gap and with an average gap of 500 meV in the semiconducting tubes in the rope (average diameter 1.35 nm [15], energy gap according to [8, 11]) one finds \( \Phi = E_{\text{gap}}/2 \approx 250 \, \text{meV} \). Using \( v_F = 10^6 \, \text{m/s} \) [32] results in a penetration depth of \( 1/2\kappa \approx 1.25 \, \text{nm} \), comparable to the electronic correlation lengths found for ropes of random composition in a tight-binding computation [26]. (Random composition refers to the random roll-up vector of the nanotubes, not to their geometric arrangement in the rope.)

The distances \( d \) between the tubes which are possible are given by the regular triangular lattice the tubes are arranged in (figure 4.2). The lattice constant is 1.7 nm, and thus the distances \( d \) can only take discrete values \( d = 1.7 \, \text{nm} \cdot \sqrt{i^2 + j^2}, \) with \( i \) and \( j \) being integers. This discretization of the distances and the belonging coupling resistances \( R_t(d) \) offer the possibility to determine rather than just estimate the barrier height \( \Phi \). For any given value of the barrier height the theory predicts a set of discrete coupling resistances and all \( R_t \)'s found in the experiment have to match one of the predicted values. Adjusting \( \Phi \) for this purpose yields a reliable value for the barrier height.

Figure 4.12 shows the result of this procedure with a optimized value of \( \Phi = 225 \, \text{meV} \), which is indeed in very good agreement with half the energy gap of the semiconducting tubes in between the surface and the bulk tube. First of all, a tunnel barrier of this height makes the tunnel process indeed temperature independent since \( k_B T \ll \Phi \) for all reasonable temperatures. As can be seen in the figure, all coupling resistances found in experiment belong to distances of more than 8 nm. The depth of the sputter damage sets a natural lower limit to the distance in which an undamaged tube can be found starting at a tube at the surface of the rope (cf. figure 4.2, the diameter of the rope sets a natural upper limit for the tunnel distance \( d \)). The emerging value of 8 nm compares well to the estimate of the sputter simulation of 6-7.5 nm depth of damage obtained in section 4.1. The fact that no coupling/tunneling to tubes closer than 8 nm is observed strongly supports the interpretation of the data and the value of the barrier height derived here.

But another point of the evaluation attracts the interest. The enormous span of two orders of magnitude in the coupling resistances \( R_t \) had already been reduced to a range of distances \( d = 8-16 \, \text{nm} \) by the exponential behavior of the tunnel process. This range is still unexpectedly large. The rope compose of 1/3 metallic tubes and 2/3 semiconducting tubes. In a random arrangement one would thus have to find in almost every possible distance from a given surface
4.4. HOW TO CHANGE THE LANE

Figure 4.12: Comparison between the experimental data for the coupling resistance (from table 4.1) to the theoretical predictions of formula 4.3 (solid grey line). The open circles mark the discrete values for the coupling resistance resulting from the discrete distances of the tubes in the rope. All experimental values (left hand side, horizontal displacement for clarity) coincide with theoretical predictions. The sputter depth of 6-7.5 nm sets a natural limit for the observable tunnel distances. The error bars for the experimental values lie within the symbol size (one exception). The tunnel barrier was assumed to be $\Phi = 225 \text{ meV}$.

tube a metallic tube to tunnel into. Even if tunneling inside the damaged region of the rope (i.e. to depth below 8 nm) is not observed, there should be an undamaged metallic tube immediately behind the sputter damage offering end states for the process. A tunnel process will always favor the closest tube and thus one should observe only tunnel distances $d \approx 8 \text{ nm}$ (and according coupling resistances $R_t \approx 2 \text{ M} \Omega$). The observation of far larger distances leaves only one conclusion: there are much less metallic tubes offering end states for the tunnel process than the usual fraction of 1/3.

The ropes under consideration do indeed consist of a mixture of tubes with one third of them being metallic judging from their roll-up vector [16]. But there are two reasons why most of them are not eligible for the tunnel process. Both were already presented in section 2.2. The first reason results from the Fermi mismatch between metallic tubes of different chirality, i.e. roll-up vector [26]. Since the tunnel process itself is momentum conserving (unless inelastic scattering events are taking place during the process), a mismatch in Fermi wave vector inhibits the coupling of the tubes. Thus a surface tube of some distinct chirality can only be coupled to a bulk tube with the same chirality. All other metallic tubes would pose an effective energy barrier for the
CHAPTER 4. CONNECTIONS

Figure 4.13: Detail of the band structure of two metallic tubes of different chirality. The band structures are depicted in the same graph in order to allow a direct comparison. Due to the different roll-up vectors the Fermi points (only one for each tube is shown) are separated by a momentum mismatch \( \Delta k_F \) (cf. figure 2.19). In order to change from one tube to the other an electron has to acquire either a momentum transfer \( \Delta k_F \) or an appropriate energy transfer \( \Delta E = \hbar v_F \Delta k_F \), supplied by a scattering partner. A single particle tunnel process, which is energy and momentum conserving, is thus not possible between these tubes. Thus the tubes pose effective tunnel barriers for each other of height \( \Delta E \). For the example of a (10,10) and a (14,5) (both metallic and of nearly identical diameter) this barrier is \( \Delta E \approx 380 \text{ meV} \).

The second, though not undisputed reason is that most of the metallic tubes are predicted to open a small gap of 10 meV due to the curvature of the graphene sheet [53]. These are tubes whose roll-up vector \((n,m)\) fulfill \(n - m = 3i, i \neq 0\). This would leave only the armchair tubes to be metallic at lowest temperatures. Following this argument, the fraction of ‘true’ metallic tubes in the rope would be reduced to about 1/16. Such a diluted occurrence of metallic tubes, too, would explain the scattering of distances (and resistances) found.

One point remains to be addressed, that is the validity of the above tunnel formula \( R_t = \hbar/(4e^2) e^{2\kappa d} \) for small distances. The value \( \kappa \) was associated with the gap energy of the semiconducting tubes in the rope lying inbetween the damaged and undamaged metallic tube. This connection was shown to be valid for large distances in figure 4.12. But ultimately, for neighboring metallic tubes,
there is no semiconducting tube inbetween. Thus, the barrier has to be supplied by another reference. In the above case, the neighboring tubes were as severely damaged as the surface tube. Thus the minimum tunnel distance was given by depth of sputter damage (≈ 6 nm) and the coupling strength to the neighboring tubes was not of interest. Fuhrer et al. [45] investigated the coupling of crossed metallic nanotubes and they found that coupling of neighboring tubes can be described by a tunnel process, too. The tunnel barrier in this case is given by the work function of the tubes, since no semiconducting tubes are present. The interconnect of these formulas for intermediate tunnel distances remains a task left for further investigations.

In conclusion, the coupling mechanism between the nanotubes in a rope was argued to be direct tunneling of electrons between the tubes via a distance d. The main results are:

- The coupling resistance \( R_t \) depends exponentially on the distance d between the tubes.
- The tunnel barrier is given by the semiconducting tubes inbetween the surface and the bulk tube. The height of the barrier is determined to be \( \Phi = 225 \text{ meV} \), corresponding to half the energy gap of these tubes.
- The coupling process is temperature independent.
- The variation of the observed tunnel distances points to additional selection rules for the coupling between nanotubes. Fermi mismatch between metallic tubes (and the presence of small gap semiconducting tubes) are argued to reduce the extent of inter-tube coupling in ropes of nanotubes.
Chapter 5

Moving On

The model presented in the last chapter has been able to describe the interaction of nanotubes in a rope. The coupling has been shown to be mediated by a direct tunneling process between the tubes. And the essential feature which has made the switching of the current between the tubes observable has been the blocking of transport in a damaged tube by localization. So far, section 4.3 has supplied hints on the scattering mechanisms governing the coherent (and incoherent) current transport in nanotubes. But no definite statement on the dephasing mechanisms has been possible. This chapter will present first efforts in a new direction in order to gain additional information on the coherence in nanotubes.

5.1 Beyond Temperature

The most prominent method to gain access to localization and interference effects in general in mesoscopic systems is applying a magnetic field. When a magnetic flux is enclosed in a localization path \( \Gamma \) (cf. figure 4.5) the vector potential results in a phase shift between the time reversed paths \( +\Gamma \) and \( -\Gamma \). Thus, a magnetic field breaks the constructive interference of the two paths. The magnetic field does not break the coherence of the wave function, just the constructive interference in coherent backscattering. Since different localization paths \( \Gamma \) enclose different areas and thus different magnetic fluxes, all paths acquire a different phase shift and the constructive interference in backscattering is lost when a magnetic field is applied. From the dependence of the localization on the magnetic field conclusions about the coherence length can be drawn. This method is very successful in two and quasi-one dimensional samples.

Indeed, a magnetic field dependence of the resistance compatible with weak localization was observed in large multi wall nanotubes (diameter of the outermost shell \( \approx 20 \text{ nm} \)) [32]. Transport in these tubes thus seems to be quasi-one dimensional with the coherence limited by Nyquist and Thouless scattering. While these same scattering mechanisms have been found in the last chapter to govern the dephasing in single wall tubes, too, they were not deduced from the magnetic field dependence of the resistance for the following reason. In
case of truly one dimensional samples, a backscattered electron retraces exactly its path in contrast to the loop-like path in figure 4.5. Thus, the localization paths in one dimension do not enclose any area and thus no flux. Consequently, transport in these systems is not influenced by a magnetic field. During the investigations of this work no magnetic field dependence of the resistance was found, supporting the statement that current transport in single wall nanotubes is one dimensional and that the interaction between tubes is very weak. Due to the one dimensional nature of current transport, information on the scattering mechanisms can not be inferred from a magneto resistance but has to be extracted for example from the temperature dependence as has been done in chapter 4.

Another approach to the dephasing mechanisms is given by a method which was already introduced in figure 3.6. In addition to the temperature, a dc voltage/current can be varied during the measurement. The resulting differential resistance in the latter case gives complementary information to the temperature dependence of the resistance in linear response acquired in the former case. The key point is, that the scattering rate for some of the dephasing mechanisms under consideration depends on the excess energy (the applied dc voltage) of the electrons. Thus, the way the dc voltage affects the localization and hence the resistance can help in determining the phase breaking mechanism.

Which of the mechanisms are sensitive to an excess energy? The Nyquist scattering can be expected to be. This process describes the scattering of an electron at the fluctuations of the system. Generating a dc current by applying a dc voltage creates additional fluctuations and thus additional scattering. The exact dependence of the scattering rate on the excess energy is not known, but following the usual rule of thumb $eU_{dc} \approx k_B T$ one would expect excess energy and temperature to produce fluctuations alike.

The Thouless dephasing does not depend on the excess energy, since this dephasing is due to an uncertainty of energy of the electronic ensemble due to the finite temperature. Applying a dc voltage alters the average energy of the electrons, but not the uncertainty of this energy. Thus, if the Thouless process dominates the phase-breaking in the sample, no dependence of the localization on the excess energy is expected.

There were two more players in the game, i.e. electron-phonon and electron-electron scattering. Both processes were recognized to supply scattering rates far below the Thouless limit in the undamaged tubes and thus to be unimportant in dephasing in undamaged tubes. But in the damaged tubes, the presence of the disorder (the defects) may increase the scattering rates and thus they can not be neglected altogether. The dependence on excess energy of these processes can be understood by inspection of the band structure of the tubes, shown in figure 5.1 a). Applying a dc voltage and thereby creating a dc current in the tube results in a splitting of the Fermi level into two quasi-levels, one for the right moving electrons in bands 1 and 2', another for the left moving electrons in bands 1' and 2. The energy difference between these quasi levels is given by the applied dc voltage. The splitting generates a non-equilibrium between the
5.1. BEYOND TEMPERATURE

Figure 5.1: a) Band structure of a metallic nanotube near the Fermi level. Applying a dc voltage $U_{dc}$ creates two quasi-Fermi levels $\mu_r$ and $\mu_l$ for the right and left moving electrons in the appropriate bands. b) electron-phonon scattering for electrons with different excess energy. Every electron can only scatter with one specific phonon due to the conservation laws. Thus, the space space for electron-scattering does not depend on excess energy. c) Electron-electron scattering as discussed in section 3.2. While the scattering partner is predetermined by the conservation laws, the number of possible final states and thus the phase space for electron-electron scattering increases with the excess energy.

numbers of right and left moving electrons, that is a current flowing along the tube. The differential resistance is determined by the processes affecting the electrons at the Fermi level, i.e. the electrons with energy $E_F \pm eU_{dc}/2$.

Figure 5.1 b) shows the electron-phonon scattering for electrons of different energy. Due to the severe restrictions of energy and momentum conservation, an electron at any energy finds only one phonon to scatter with (cf. the discussion in section 3.2). Consequently, the electron-phonon scattering rate does not depend on the excess energy as long as no new scattering processes become pos-
## Table 5.1: Dependence of the scattering time on temperature and excess energy for different scattering processes. \( \eta \) denotes the 'effectiveness' of the excess energy on the scattering rate.

<table>
<thead>
<tr>
<th>Process</th>
<th>Temperature Dependence</th>
<th>Excess Energy Dependence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nyquist scattering</td>
<td>( \tau_N \sim T^{-2/3} )</td>
<td>yes ((\eta \neq 0))</td>
</tr>
<tr>
<td>Thouless dephasing</td>
<td>( \tau_{Th} \sim T^{-1} )</td>
<td>no ((\eta = 0))</td>
</tr>
<tr>
<td>el-ph scattering</td>
<td>( \tau_{el-ph} \sim T^{-1} )</td>
<td>no ((\eta = 0))</td>
</tr>
<tr>
<td>el-el scattering</td>
<td>( \tau_{el-el} \sim T^{-1} )</td>
<td>yes ((\eta \neq 0))</td>
</tr>
</tbody>
</table>

The electron-electron scattering process encountered in section 3.2 is sketched in figure 5.1 c). While the scattering partner is predetermined in this process by the conservation laws, there remains a freedom in the final states. All states in the energy window \( eU_{dc} \) are possible final states. Thus the phase space for scattering and the scattering rate depend on the excess energy in the same way as on the temperature.

Indeed, the dephasing mechanisms differ in the way in which they are affected by temperature and excess energy (table 5.1). This is the starting point for the investigations on the differential resistance. The following section will present first measurements and will draw preliminary conclusions about the processes limiting the coherence.

But first one has to include the applied dc voltage \( U_{dc} \) into the model developed in section 4.3. Figure 5.2 shows the model, consisting of the two parallel tubes interconnected by the coupling resistances with a voltage \( eU_0 \) applied to the sample. Due to the contact resistances, only a voltage \( eU_{dc} \neq eU_0 \) applies to the essential part of the model. In order to grossly assess the voltage drops, one has to consider the two main current paths. In the damaged surface tube, three resistances \( R_d \) are connected in series, thus at each resistance a voltage \( eU_{dc}/3 \) drops. The total resistance in the path via the undamaged tube is \( 2 \cdot R_t + 3 \cdot R_u \approx 2 \cdot R_t \). Thus the voltage \( eU_{dc} \) will essentially drop in equal shares at the two coupling resistances along this path.

How are the single resistances affected by the applied dc voltage? The case of the coupling resistances is particularly simple. The applied voltage \( eU_{dc}/2 \) at each tunnel barrier reduces the total barrier height, that is

\[
R_t(U_{dc}) = \frac{h}{4e^2} \cdot \exp \left( \frac{\Phi - eU_{dc}/2}{\hbar v_F} d \right) = R_t(0) \cdot e^{-U_{dc}d/\hbar v_F}. \tag{5.1}
\]

The resistances \( R_u \) of the undamaged tube segments are not affected, since first only the smallest part of the dc voltage drops at them, second, the dominant scattering mechanism in the undamaged tubes, electron-phonon scattering, is expected to be independent of the applied excess energy. Moreover, the exact value of \( R_u \) does not play any role for the model as long as it is much smaller...
Figure 5.2: Model network for the sputtered nanotube samples. The applied voltage $U_0$ is reduced by the voltage drop at the contact resistances to an effective voltage $U_{dc}$. In order to grossly assess the voltage drops at the single resistances, one assumes this voltage to split into equal parts along the upper current path in the damaged tube. Along the lower path, the voltage splits equally between the coupling resistances, while almost no voltage drops at the small resistances of the undamaged tube segments.

than the coupling resistance $R_t$. The resistance of the damaged tube segments, $R_d$, depends on the coherence length $L_\Phi$ (cf. formula 4.2). The temperature dependence of the coherence length was found to follow a power law $L_\Phi = A \cdot T^{-\alpha}$. The easiest way to account for an influence of the excess energy on the coherence length, in addition to the influence of the temperature, is to write

$$L_\Phi(T, U_{dc}) = A \cdot (T + \eta(eU_{dc}/3k_B))^{-\alpha}. \quad (5.2)$$

This follows the thumb rule $eU_{dc}/3 \approx k_BT$, with $\eta$ accounting for the actual 'effectiveness' of the excess energy. $\eta = 0$ would mean the excess energy has no influence at all on the dephasing mechanism (e.g. Thouless or electron-phonon scattering), while $\eta \neq 0$ means that the scattering rate depends on the excess energy (e.g. electron-electron and Nyquist scattering). In this way, the excess energy can be incorporated into the model. The parameter $\eta$ which will be found in the next section will confirm the identification of the dominant dephasing mechanisms made in chapter 4.
CHAPTER 5. MOVING ON

5.2 What Makes The Difference

The last section has stated how an applied dc voltage (or excess energy) $eU_{dc}$ can be incorporated in the model developed for the sputtered nanotube samples. This section will now use this extension of the model in order to describe the measurements of the differential resistance at two different samples. The main question is what additional information on the dephasing mechanisms can be obtained by this type of measurement.

Figure 5.3 shows the resistance for the first example as a function of temperature and excess energy. As can be seen, the resistance shows a very similar behavior on both, applying a dc voltage and raising the temperature. Thus, one is led to the conclusion that the phase breaking mechanism in this sample is sensitive to excess energy and temperature. Figure 5.4 shows the appropriate simulations of the measurements according to the model. The value of $\eta = 1.5$ found in the simulation of the differential resistance confirms that the excess energy is even more effective than the temperature in limiting the coherence of the electrons. In section 5.1 such a behavior (temperature and energy are both effective in breaking the coherence) was expected for Nyquist and electron-electron scattering. And indeed the power law behavior of the coherence length in this sample $\alpha = 0.35$ points to Nyquist scattering ($\alpha = 1/3$) being the dominant phase breaking process.

Upon close inspection of figure 5.4 b) one notes that the absolute values of $U_0$ and $U_{dc}$ differ by about a factor of ten. This difference cannot be explained by the presence of the contact resistances $R_c$ alone. This would require that these contact resistances are ten times larger than the resistance of the rope itself (represented by the network made from $R_u$, $R_d$, and $R_t$). Such large contact resistances were never observed during this investigation.

A rough estimate that confirms the absolute value for the effectively applied
5.2. WHAT MAKES THE DIFFERENCE

Figure 5.4: Simulations of the measurements from figure 5.3 according to the extended model. The applied voltage is found to be as efficient as the temperature ($\eta = 1.5$) in breaking the coherence and the localization. This corresponds to Nyquist scattering being the dominant phase breaking process in this sample as is suggested by the temperature dependence ($\alpha = 0.35$). A large discrepancy between the external voltage $U_0$ and the effectively applying voltage $U_{dc}$ is found.

Voltage $U_{dc}$ can be given by the height of the resistance maximum. The formula linking the resistance maximum to the coupling resistance $R_{4t,max} = R_t/3.41$ found in section 4.3 holds for the differential resistance measurements, too. Comparing the measurements of the temperature dependent and differential resistance in figure 5.3 one finds that the maximum values differ only by a small amount $\delta R$. From the temperature dependence a maximum value of 22 M$\Omega$ leads to a coupling resistance $R_t(U_{dc} = 0) = 75$ M$\Omega$, while from the differential resistance maximum of 20.6 M$\Omega$ a modified coupling resistance of $R_t(U_{dc}) = 70M\Omega = R_t(0) \cdot e^{-U_{dc}d/\hbar v_F}$ follows. This predicts the maximum to occur at a voltage of 3 meV, in reasonable agreement with the simulation. Thus, while the simulation explains the measurement consistently, the difference between external $U_0$ and effectively applying voltage $U_{dc}$ remains to be investigated further.

A very different behavior is seen at the second example. Figure 5.5 shows temperature dependent measurements recorded at discrete applied dc voltages and the differential resistance of the sample. The dependence of the differential resistance is very unspectacular. But the height of the resistance maximum in the temperature dependent measurements decreases strongly upon increasing the dc voltage, while the maximum shifts only marginally to lower temperatures. Again, the height of the resistance maximum can be used to asses the applied dc voltage $U_{dc}$ as was demonstrated in the last paragraph. Again, a difference between $U_0$ and $U_{dc}$ of roughly a factor of ten is found in figure 5.6 b). Once the actual voltage $U_{dc}$ is inferred from the resistance maximum, the measurements are described well by the model. But an 'efficiency' $\eta \approx 0.1$ has to be assumed.
in order to reproduce the measurements. This explains the weak dependence of the differential resistance on the applied voltage. Dephasing in this sample is almost insensitive to excess energy. In contrast to the previous sample, where Nyquist scattering has been the dominant phase breaking mechanism, for this sample the temperature dependence of the coherence length $\alpha = 0.6$ suggests another dominant phase breaking, possibly Thouless dephasing or electron-phonon scattering (both were recognized in the last section to be independent of the excess energy). Computing the coherence time $\tau_\Phi$ at 10 K from the fit parameters yields a value of 0.66 ps, close to the Thouless dephasing time $\hbar/(k_B \cdot 10 \, K) = 0.72 \, ps$. Thus, Thouless dephasing seems to be the most probable candidate for phase breaking in this sample. The weak dependence on the excess energy then has to be caused by a secondary phase breaking mechanism.

The very different behavior of the resistance for the two cases of dephasing mechanisms is visualized in figure 5.7. The plots show the four terminal resistance simulations of the two examples from above as a function of temperature and excess energy. In case of Nyquist scattering (a), where temperature and excess energy are equally affecting the coherence, the resistance maximum can be observed well in a pure measurement of the differential resistance. But in case Thouless dephasing is dominant in phase breaking (b), the localization is to first order unaffected by the excess energy and consequently no resistance maximum can be observed in the differential resistance. Here, temperature scans at moderate excess energy show the reduction of the resistance maximum due to the decrease of the coupling resistance with increasing excess energy.

The picture which already emerged in the last chapter is supported by the measurements presented in this section. Two dephasing mechanisms seem to be important in nanotubes, these are Thouless and Nyquist scattering. Which of the two is dominant in a given sample depends on reasons which could not...
Figure 5.6: a) Simulations of the measurements of figure 5.5 a) according to the extended model. b) The effectively applied voltage $U_{dc}$ is inferred from the resistance maximum. A large discrepancy between $U_0$ and $U_{dc}$ is found. The efficiency of the excess energy on phase breaking is very small. Together with the temperature dependence of the localization ($\alpha = 0.6$), this points to Thouless dephasing limiting the coherence.

be clarified during this investigation. But the temperature dependence of the coherence length as well as its dependence (or independence) on the excess energy can identify which process is the more important one.
Figure 5.7: Simulations of the four terminal resistance as a function of temperature and voltage for the two examples discussed. The simulations were made with the parameters inferred from the experimental data. a) For Nyquist scattering being responsible for phase breaking ($\alpha = 0.35$, $\eta = 1.5$), similar behavior is observed in temperature and voltage dependent measurements. b) With Thouless scattering being dominant in dephasing ($\alpha = 0.6$, $\eta \approx 0.1$), the excess energy does have (almost) no influence on the coherence. Consequently, only the coupling resistances decrease with increasing voltage and the resistance maximum is damped out. The heavy black lines in the simulations represent the measurements taken at the samples, which are depicted below the simulation graphs.
Chapter 6

It’s Not Over

This work has been able to address several questions regarding electronic transport in carbon nanotube ropes.

Are carbon nanotubes good conductors? Yes, they really are. First of all, they are nearly perfect crystals with a very low intrinsic defect density. Attaching electric contacts for measurement creates the most prominent ’defect’ scattering, due to the intimate relation between geometry and electronic in case of the tubes. Apart from that, electron-phonon scattering was shown to be responsible for the resistance in the tubes, leading to a linear temperature dependence, even at low temperatures. This is an effect of the one dimensional character of current transport in the tubes. Summing these effects, one finds a mean free path between scattering of several micrometers at room temperature. Together with the cross section of the tubes, this yields an estimate for the resistivity of nanotubes of $1 \, \mu\Omega \, \text{cm}$, in no way inferior to classical metals.

Why is this not observed commonly? Why is this not basic knowledge about the nanotubes? Two reasons were found for this. The first has already been mentioned: the close relation of geometry and electronic, that is resistance. Most of the resistance measured in common experiments is caused by the mere presence of the contacts. The second reason is that the tubes are only weakly interacting with one another and the current injected into a tube cannot run around the areas to which the contacts have been attached since it cannot change easily to another tube which is less affected by the presence of the contacts. In this work a smart way of making a ’soft’, non-invasive contact to a tube was found by attaching the current and voltage probes to different sides of the rope, i.e. below and on top of the tube, respectively. This way, the voltage probes make use of the weak coupling by studying the intrinsic properties of the current carrying tubes without causing any disturbance. But the pragmatic use of this weak interaction alone is not satisfactory.

Why is the coupling between nanotubes that weak? The answer is, it is caused by direct tunneling between the tubes. This statement was enabled by studying the current transport between tubes. This work used a controlled sputter treatment to introduce a sufficiently high defect density into the tubes.
Cooling the sample further increased the resistance in the damaged nanotubes by localization and these effects together were eventually strong enough to deteriorate current transport inside the nanotubes to a degree that inter-tube transport became observable. While this procedure allowed to study the inter-tube coupling and to identify the interaction mechanism, it yielded at the same time further insight into the current transport inside the tubes via the observed localization behavior.

What can localization in damaged nanotubes tell about the electronic properties? It supplies valuable information on scattering in nanotubes. While in 'normal' resistance measurements only scattering mechanisms which create resistance can be observed, localization is affected by all phase breaking scattering mechanisms, allowing access to an extended field of scattering. It was found that very general (extrinsic) dephasing mechanisms, namely Nyquist and Thouless dephasing, dominate scattering in the tubes, while intrinsic effects like electron-phonon and electron-electron scattering are less important. This supports the statement that the intrinsic scattering in nanotubes is very weak.

What is the implication for the use of the electronic properties of nanotubes? Is a nanoelectronic conceivable which benefits from these promising characteristics? This will show in the future. But one thing is sure judging from the results of this investigation: only a smart design of such an electronic will be successful. The interconnection of nanotubes depends dramatically on the geometry of their arrangement and is not simply realized by putting tubes onto one another. Basic research’s supply of profound knowledge about the coupling of the tubes and the fabrication of suited contacts will be crucial for any progress in this field.

'Since their discovery in 1991 [1], carbon nanotubes have attracted a great deal of attention ...'

I’m sure, they will do so in the future, too.
Appendix A

Do It Yourself

This chapter supplies several sheets of a graphene honeycomb lattice. The lines mark the bonds between atoms. The reader is welcome (if not recommended) to remove these sheets from this work in order to build his or her own nanotube models. These models will give a better understanding of the geometry of a nanotube than any textual descriptions or pictures. The vector $C = n \cdot a_1 + m \cdot a_2$ is called the roll-up vector of the tube and supplies the label $(n,m)$ to the tube. Two sheets are prepared to yield special kinds of tubes, namely the prominent (10,10) ’armchair’ tube and a (13,6) tube, which has a similar diameter but very different chirality. The tubes are formed by rolling up the sheet to a cylinder, matching the tip of the vector $C$ to its end. The vector will thus run around the circumference of the tube. The shaded area marks the surface of the cylinder. Arbitrary tubes can be made from the remaining sheets by marking a vector in the sheet and rolling the sheet up to a cylinder in a way that tip and end of the vector meet. (The vector $C$ has to connect equivalent atomic sites, that is atomic sites from which a bond is running strictly to the right, cf. the sheets for the (10,10) and (13,6) tubes.) In nature, the interatomic distance (the length of a single bond) is 1.42 Å, that is the models have a scale 33,000,000 : 1.
Appendix B

What And Where

This appendix is a selection of literature on carbon nanotubes and does not claim to be complete or comprehensive. It is designed to facilitate the entry into the nanotube business and to serve as a quick reference when searching material on a special subject which can then serve as starting point for further investigations.

Reviews:

- mechanical and electrical transport properties: [69]
- electrical transport in SWNT and MWNT: [70]
- MWNT: [71]
- hydrogen storage and field emission: [72]
- production: [13]
- mechanical properties: [73]

Experiment:

- SWNT in general: [31, 45, 17, 74, 75, 76, 12, 6, 77, 78, 11, 55, 79, 80, 81, 82, 83, 84, 85, 86, 87, 44, 88]
- MWNT in general: [47, 89, 18, 17, 1, 90, 91, 75, 51, 32, 38, 14, 19, 92, 20, 93, 57, 94, 85, 95, 96, 87, 44, 88, 97, 98, 2]
- production: [15, 83, 105, 88]
- mechanical properties: [3, 89, 18, 17, 101, 19, 20, 108, 97, 2]
• hydrogen storage: [4]
• field emission: [107, 5, 95, 120, 87, 44, 98, 111]
• electronic transport/scattering in SWNT: [31, 81, 85]
• electronic transport/scattering in MWNT: [47, 32, 85]
• electronic transport/scattering in SWNT ropes: [46, 37, 99, 65, 53, 102, 104]
• electronic transport/scattering in nanotube mats: [99, 116, 65, 81]
• band structure: [12, 11, 84]
• temperature dependence of resistance: [43, 99, 116, 65, 53, 91, 39, 32, 38, 102, 83]
• magnetoresistance: [47, 91, 32, 38, 102, 92]
• small gap: [49, 39]
• electron-electron scattering: [117]
• phonons/electron-phonon scattering: [117, 41, 118, 53, 55]
• Luttinger liquid behavior: [37, 76, 38, 55, 79, 93, 109]
• Coulomb blockade: [31, 46, 37, 76, 6, 77, 103, 94, 104, 108, 109]
• intertube coupling: [45, 93, 108, 113]
• superconductivity: [74]
• contact phenomena: [51, 57, 96]
• doping: [75, 11, 112]
• thermal properties: [49, 118]
• optical properties: [43, 121]
• field effect transistor: [75, 78]
• Transmission Electron Microscopy (TEM): [16, 1, 90, 100, 119, 14, 15, 105]
• Scanning Tunneling Microscopy (STM): [10, 119, 12, 11, 84, 106, 86, 110]
• Photo Emission Spectroscopy (PES): [68, 117, 41]
• Raman scattering: [119, 48, 105]
• Electron Spin Resonance (ESR): [114, 115]
• Electron Energy Loss Spectroscopy: [16, 50]
• X-ray diffraction: [15, 105]
• Scanning Gate Microscopy (SGM): [80, 82, 85, 113]

**Theory:**

• nanotubes in general: [8]
• mechanical properties: [122, 123]
• electronic transport/scattering: [124, 125, 28, 126, 127, 128]
• bandstructure/tight binding: [28, 27, 129, 130, 30, 26, 29, 131, 132, 133, 34]
• bandstructure/local density approximation: [27, 134, 135, 25]
• bandstructure/molecular orbitals: [129]
• temperature dependence of resistance: [28]
• magnetoresistance: [136]
• small gap: [28, 30, 133]
• electron-electron scattering: [28]
• phonons/electron-phonon scattering: [137, 138, 40, 139, 21]
• Coulomb interaction: [28, 140, 36, 141, 34]
• Luttinger liquid behavior: [36, 142, 35, 141, 34]
• intertube coupling: [134, 135, 25, 143, 142, 26, 144]
• superconductivity: [126, 138]
• Peierls transition: [138, 139]
• contact phenomena: [145, 146, 56, 147, 148, 149, 150]
• Fermi mismatch: [26]
• optical properties: [151, 24]
• Scanning Tunneling Microscopy (STM): [152]
• Raman scattering: [21]
Bibliography


[9] Pictures were taken from the Image Gallery of the Center for Nanoscale Science and Technology at Rice University under http://cnst.rice.edu/pics.html


[58] The Monte Carlo simulations were made using the program ‘SRIM, Stopping and Range of Ions in Matter’ by J. F. Ziegler and J. P. Biersack. The program is available at www.research.ibm.com/ionbeams.


[69] B. I. Yakobson and R. E. Smalley, ‘Fullerene Nanotubes: $C_{1,000,000}$ and Beyond’, *American Scientist* **85** (1997) 324


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