Electronic structure
of carbon nanotubes
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Chapter 1

Introduction

In 1991 the Japanese scientist Sumio Iijima made a discovery that was the incentive for a new research field in both chemistry and physics [1][2]. He found a molecule that was based on carbon alone and shaped as a tiny hollow wire with a diameter of about one nm and a length in the order of several μm’s (Fig. 1.1). These carbon nanotubes as they were later called, turned out to have some extraordinary properties. To start with, they are ultrastrong, chemically inert and flexible. In addition, they can be semiconducting or truly metallic and are beautiful model systems for the study of the behavior of electrons confined within a one-dimensional structure. Naturally, a broad range of scientists became interested in these structures and numerous applications have been thought of. To mention only a few ideas, nanotubes could be used as nanoscale electronic devices, as a balance to weigh small particles or as ultrasharp and crashproof tips in a scanning probe microscope (Fig. 1.2). In bulk amounts, they can be used for example as field emitters in robust and long-living lamps, as high-strength fiber materials or as a storage medium for fuel such as H₂-gas. It is the aim of this thesis to study the basic electronic structure of these exceptional molecules.

Until the 1980s carbon science was considered to be a mature field, but the discovery of the buckyball, a molecular soccer ball consisting of 60 carbon atoms (Fig. 1.3a) brought a new range of carbon materials into view. These fullerenes are structures of closed hollow networks constructed mainly from five-, six- and seven-rings of carbon. In principle an infinite number of fullerene geometries can exist of which fig. 1.3b is an exotic example. Soon it was realized that the cylindrical variety of the buckyball, the buckytube, would be particularly interesting. This molecule, now better known as the carbon nanotube, can be defined as a hollow wire of several μm’s length (Fig. 1.3c). One way to think of a carbon nanotube is as a sheet of hexagonal carbon that is rolled up into a cylinder. Already before they were actually synthesized, it was predicted that carbon nanotubes could be truly metallic, which is an unusual property for a molecule. In general, electrons tend to distribute themselves inhomogeneously in one-dimensional systems, inducing an alternate shortening and lengthening of
Chapter 1. Introduction

Figure 1.1: Images of carbon nanotubes, taken by a transmission electron microscope (TEM) (reproduced from ref. [3]). (a) An entangled web of nanotube ropes. The scale bar is 100 nm. (b) A cross section of a rope with many parallel nanotubes, packed in an ordered lattice. Each circle within the rope, with a diameter of about 1.4 nm, is a nanotube. The scale bar is 10 nm.

Figure 1.2: Various applications of carbon nanotubes. (a) Nanotubes blocks that were grown from a patterned substrate. Such samples with well-ordered nanotubes can be used for field-emission arrays. Reproduced from ref. [4]. (b) An atomic force microscope (AFM) cantilever tip to which a nanotube bundle is attached. Such probes are extremely sharp and well defined [5]. Reproduced from ref. [6]. (c) A fg nanobalance to weigh small particles. The end of the tube is loaded with a particle and is oscillating as a response to an applied alternating electric field. The resonance frequency depends on the spring constant of the nanotube and the mass of the particle. The scale bar is 1 μm. Reproduced from ref. [7].
the bonds between the atoms. A result of this effect, the Peierls instability, is an opening of a gap in the energy spectrum and therefore non-metallic behavior. Nanotubes appear to escape this disastrous effect for the conductivity because the hexagonal network of carbon atoms is stiff enough to inhibit such a distortion. Whether nanotubes could really exist and how to make them was not immediately clear. It was therefore an exciting result when Iijima from NEC laboratories in Japan found tubular structures while working on the characterization of fullerenes [1].

Scientists had in fact been looking for many years for a suitable molecule to use as a miniscule electrical wire. In a 'bottom-up' strategy proposed to design ultrasmall electronic circuits, individual atoms and molecules could be building blocks for the construction of devices. However, the fabrication of a single molecule device proved to be experimentally challenging because of the difficulty to achieve electrical contacts to molecules. Carbon nanotubes were soon recognized as ideal candidates. They are robust, flexible and long enough to bridge the gap between two microfabricated electrodes. Above all, they can be well-conducting. It took a few years however, until 1995, before it became possible to produce clean carbon nanotubes consisting of only one shell in large, practical quantities [3]. In the be-
Beginning, nanotubes were mainly of the multi-walled type and consisted of several concentric shells. For the physicists hunting for a perfect well-defined molecular wire the multi-walled nanotubes were less ideal. The first electronic conductance measurements on an individual single-walled nanotube were done in 1996 and presented a breakthrough in the field of molecular electronics [8]. Figure 1.4 shows the sample layout used in these experiments: a nanotube lying as an electronic wire across two electrodes. By applying a bias voltage over the electrodes a small current could be measured through the molecular wire at millikelvin temperatures. The current was found to increase in discrete steps as a function of the voltage. A third electrode near the nanotube was used as a gate electrode. By applying an electric field to the nanotube with the gate, the positions of the current steps were shifted. The measurements indicated that electronic transport in the nanotube occurs through well-separated discrete electronic states that extend undisturbed over the full length of the tube. A welcome conclusion from these measurements was that metallic single-walled nanotubes behave surprisingly well as molecular quantum wires. Since 1997, various groups have been studying the fundamental electronic properties through similar transport measurements. An interesting subject which currently attracts a lot of interest is the interaction between electrons in nanotubes. Electron-electron interactions are usually neglected. However, electrons confined in one-dimension behave fundamentally different than electrons in three-dimensions. Since the 1950s there exists extensive theory on one-dimensional electron liquids where the interactions between the electrons are taken into account. It is predicted that the electrons form a correlated liquid, called the Luttinger liquid, which exhibits various exceptional features such as the separation of spin and charge and a power-law dependence of the resistance on the bias voltage and the temperature. Recent experiments
Figure 1.5: An atomically resolved STM image of a chiral carbon nanotube (a) compared to a theoretical model of a nanotube with a similar chirality (b). The diameter of the tube is 1.2 nm.

strongly suggest that these Luttinger liquid signatures are indeed found in nanotubes [9, 10] which emphasizes the one-dimensional nature of carbon nanotubes.

Carbon nanotubes can be semiconducting or metallic which depends on two parameters, the diameter and the chiral winding of the carbon network along the tube shell. Although this prediction was already made in 1992, it was confirmed experimentally only six years later by scanning tunneling microscopy (STM) measurements ([11] and chapters 3-5). STM proved to be a useful technique to study nanotubes since it has the power to reveal both the atomic and electronic structure. It is possible to obtain beautiful images of atomically resolved nanotubes from which their chiralities can be obtained. An example is shown for example in Fig. 1.5 together with a theoretical model of a nanotube with a comparable chirality. The tip of an STM can also be used as a spectroscopic probe by keeping the tip fixed above the sample and measure the tunnel current as a function of the bias voltage. By taking current-voltage spectra on a large number of nanotubes with various chiralities, two classes of nanotubes could be identified (Fig. 1.6). The STM spectra for these two classes corresponded remarkably well to the predicted electronic density of states (DOS) for the metallic and the semiconducting type, respectively. Due to the quantization of available energy modes in the circumferential direction the DOS for nanotubes does not consist of one smooth band but it splits up into several subbands with sharp singularities at the onsets. These subbands represent separate one-dimensional channels for conduction along the nanotube. The subbands and their sharp onsets were indeed observed in the tunneling DOS that was obtained from the STM spectroscopy measurements.
Both the semiconducting and metallic type of nanotubes may be of use for nanoscale electronic devices. Junctions between two different nanotubes that have a different electronic character are interesting as well. Theoretical calculations have shown that two nanotubes with different chirality and similar diameter can connect to each other when defect pairs of five- and seven-rings of carbon are present in the hexagonal carbon lattice [13]. The connections appear as sharp kinks (Fig. 1.7a) which have been also observed in real nanotube material. Figure 1.7b shows for example a sharply kinked nanotube lying across electrodes. Recent electronic transport measurements on this type of sample indicate that these kinks can indeed be semiconductor-metal junctions [10]. Preliminary STM experiments on a nanotube kink are presented in chapter 5.

The mechanical properties of carbon nanotubes are also of large interest to scientists. Nanotubes may be called the ultimate fibers because of their light weight and the predicted record-high strength. According to ref. [14] they can be hundred times stronger than steel while they are one-sixth its weight. There are no experiments done yet to confirm such a high tensile strength. However, experiments have already demonstrated that nanotubes have an extremely high Young's (bending) modulus, on the order of TPa, and that they resist deformation remarkably well. When they are strongly bent, nanotubes do not break but 'buckle', which means that the cylindrical structure locally flattens, just as what happens to a drinking straw. When the bending strain is released, the nanotube resumes its original straight shape. Nanotubes therefore appear to be ideal tips for scanning probe microscopes since they are not only very small but also survive crashes with the sample surface.
Carbon nanotubes have proven to be unique materials that are interesting for applications as well as for fundamental science. This thesis aims to contribute to the understanding of the basic electronic structure of carbon nanotubes. To this end, STM has been used to probe both the atomic and electronic structure of nanotubes. Scanning probe microscopes (SPM) are in general extremely useful for studies at the nanoscale since they allow to image, measure and manipulate individual atoms and molecules. The basic idea of an SPM is to bring a sharp tip close to the surface of a sample and scan an area while measuring a specific interaction between the tip and the sample. In Atomic Force Microscopes (AFM), it is the force between the tip and the surface that is measured. AFM has for example been often used to image and characterize device structures made from nanotubes as illustrated by Fig. 1.4 and 1.7b. Nanotubes can also be moved by the AFM tip which can be a useful technique to build specific devices with nanotubes.

The STM applies a bias voltage between the tip and sample and brings the tip close enough to the surface, within a distance < 1 nm, to measure a finite tunnel current. This technique is restricted to substrates with conducting surfaces, but the advantage is that very high resolutions can be obtained. Nanotubes can indeed be imaged with atomic resolution as shown for example in Fig. 1.5. Furthermore, the STM tip can be used as a local probe to obtain current-voltage
spectra (Fig. 1.6). Such a scanning tunneling spectroscopy (STS) measurement differs fundamentally from a typical electron transport measurement where the conductance through a nanotube between two electrodes is measured. In the STS mode, the current path is perpendicular to the nanotube whereas in a transport measurement the current runs along the length of the tube. The STM setup thus does not measure the transport properties but instead the local electronic structure since the tunneling conductance is a good measure for the local electronic density of states. It is important in the STS method to consider the interaction with the underlying surface. A very useful feature of STS is that the STM tip can be moved along a nanotube, which enables to measure the electronic structure spatially resolved. In this way, the electronic properties at interesting topological sites such as kinks, bend, buckles and ends can be examined. Another application of STM is to use the tip as a tool to locally cut molecular bonds. With this method nanotubes can be shortened to any desired length and the electronic properties of nanotubes can therefore be studied at different length scales.

For the work presented in this thesis nanotube material was used that was produced by a laser evaporation technique in the group of Richard Smalley at Rice university. The synthesis consists of vaporization of graphite in an argon atmosphere at 1200°. By using Co/Ni catalysts, bundles of single-walled carbon nanotubes can be synthesized which are packed in a crystalline form. Figure 1.1 shows TEM images of this material. The nanotube material was dispersed in dichloroethane and ultrasonically agitated to unravel the bundles. The nanotubes were deposited on single-crystalline gold facets.

The outline of the thesis is as follows. Chapter 2 gives a theoretical background on carbon nanotubes and STM. The chapters 3 to 5 present the basic results of STM imaging and spectroscopy. The electronic spectra as well as the atomically resolved images are discussed in detail. Chapters 6 and 7 report on the technique of cutting nanotubes by STM nanostructuring. Chapter 8 finally describes an experiment where a metallic nanotube was cut to a short length. With spatially resolved measurements it was possible to image the electronic standing waves that corresponded to the discrete energy states in this tube.

References


[12] From work by Zhen Yao et al., (1999); see also ref. [10].
Chapter 2

Theoretical background on carbon nanotubes and STM

The first part of this chapter discusses in detail the geometric and electronic structure of carbon nanotubes. The second part gives a short overview on the theory of STM imaging and spectroscopy, which is the main technique in this thesis to study individual nanotubes.

2.1 Carbon Nanotubes

2.1.1 Carbon materials

There exists an amazing variety of materials that are all based on carbon but which exhibit very different behavior. Examples are diamond crystals, organic polymers such as polyacetylene, graphite, and the closed carbon network structures called fullerenes. This variety is a result of the several possible configurations in which carbon can bond. The four valence electrons of carbon in the 2s and 2p orbitals can easily mix with each other because of the small energy difference between these orbitals. An electron in the 2s shell can combine with either one, two or three 2p electrons, leading to different bonding configurations called sp, sp$^2$ and sp$^3$ hybridization respectively.

Carbon nanotubes are fullerenes that can be thought of as sheets of graphite rolled up into cylinders (Fig. 2.1). A graphene sheet consists of a hexagonal lattice of sp$^2$-hybridized carbon. Each carbon atom in a graphene sheet bonds strongly to its three neighbours via sp$^2$ σ-bonds which are in the same plane with angles of 120°. The fourth electron is in a π-orbital which has its lobes perpendicular to the plane of the sheet. The electronic properties of both graphene and carbon nanotubes can be well described by only taking into account the energy dispersion of the π-electrons [1-3].
Figure 2.1: A graphene sheet that can be folded into a seamless cylinder by cutting out the sheet along the dashed lines and rolling it up along vector $C$. $a_1$ and $a_2$ are the unit vectors of the hexagonal graphene sheet. The zigzag and armchair lines (dotted) are special symmetry directions. The corresponding patterns along the nanotube circumference are drawn near the dotted lines.

Figure 2.2: Models of carbon nanotubes. From top to bottom, an armchair (5,5), a zigzag (9,0) and a chiral (10,5) nanotube are shown. (From ref [4]).
2.1 Carbon Nanotubes

2.1.2 Geometric structure

Figure 2.1 shows a graphene sheet that can be cut out along the dashed lines and rolled up along vector $\mathbf{C}$ to obtain a seamless cylinder. Vector $\mathbf{C}$ is related to the unit vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ of the hexagonal lattice, $\mathbf{C} = n\mathbf{a}_1 + m\mathbf{a}_2$. The pair of indices $(n,m)$ identifies the nanotube and each $(n,m)$ pair corresponds to a specific set of chiral angle $\phi$ and diameter $d$:

$$\phi = \arccos \left[ \frac{\sqrt{3}(n + m)}{2\sqrt{n^2 + m^2 + nm}} \right]$$

$$d = \frac{a}{\pi} \sqrt{n^2 + m^2 + nm}$$

where $a = 2.46$ Å is the lattice constant. In the example of Fig. 2.1 the $(n,m)$ indices are $(12, 4)$, which corresponds to a nanotube with a diameter $d$ of 1.13 nm and a chiral angle $\phi$ of 16.1°. Vector $\mathbf{T}$ is perpendicular to $\mathbf{C}$ and it points from $(0,0)$ to the first lattice site through which the dashed line passes exactly. The area defined by $|\mathbf{T} \times \mathbf{C}|$ is the primitive unit cell from which a nanotube can be constructed.

Special symmetry directions in the graphene lattice are $(n,0)$ and $(n,n)$, called respectively the zigzag and armchair directions (dotted lines in Fig. 2.1). They differ by an angle of 30°. A sheet rolled up along one of these lines results in a nonchiral tube. Figure 2.2 shows examples of an armchair, a zigzag and a chiral nanotube. The names armchair and zigzag refer to the pattern of carbon bonds along the circumference. These patterns are also shown in Fig. 2.1. The electronic properties are found to be critically dependent on the chirality and diameter. A $(12,4)$ nanotube for example is semiconducting, but a $(12,3)$ nanotube, which has only a slightly different vector $\mathbf{C}$, is metallic.

2.1.3 Energy dispersion

Figure 2.3 shows fragments of the real and reciprocal space for a graphene sheet. There are two inequivalent sites in the hexagonal carbon lattice, points A and B. All other lattice sites can be mapped onto these two by fundamental lattice displacements, using $\mathbf{a}_1$ and $\mathbf{a}_2$. The unit cell in real space contains the two carbon atoms at A and B. In a tight binding approximation, the energy dispersion for the $\pi$-electrons forming a bonding (-) and antibonding (+) band can be found to be [5]:

$$E(k_x, k_y) = \pm \gamma_0 1 + 4 \left[ \cos \left( \frac{\sqrt{3}k_x a}{2} \right) \cos \left( \frac{k_y a}{2} \right) + 4 \cos^2 \left( \frac{k_y a}{2} \right) \right]^{1/2}$$

where $\gamma_0$ is the energy overlap integral between nearest neighbors. Figure 2.4a is a three-dimensional representation of the energy dispersion $E(k_x, k_y)$, as follows
Figure 2.3: Fragments of graphene in real space (left) and reciprocal space (right). The areas within the dashed borders are the unit cells. The unit vectors are $\mathbf{a}_1 = \left(\frac{\sqrt{3}a}{2}, \frac{a}{2}\right)$, $\mathbf{a}_2 = \left(\frac{\sqrt{3}a}{2}, -\frac{a}{2}\right)$ and $\mathbf{b}_1 = \left(\frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{a}\right)$, $\mathbf{b}_2 = \left(\frac{2\pi}{\sqrt{3}a}, -\frac{2\pi}{a}\right)$.

from Eq. (2.3). Graphene is sometimes classified as a zero-gap semiconductor, because of the vanishing energy gap at six points that coincide with the corners of the hexagonal Brillouin zone. The Fermi energy $E_F$ is thus reduced to six points. Energy contours for the bonding band are drawn in the first Brillouin zone in Fig. 2.4b. The antibonding band is similar. Also indicated are the gapless Fermi points at the corners by black dots. Two of these are inequivalent, $\mathbf{K}$ and $\mathbf{K}'$; the others can be obtained by lattice transformations along $\mathbf{b}_1$ and $\mathbf{b}_2$. The energy dispersion in the vicinity of these points is approximately radially symmetric within the $k_x, k_y$ plane. Equation 2.3 can be simplified in these regions.

Figure 2.4: Energy dispersion for graphite. (a) A three-dimensional graph of the energy dispersion as calculated with Eq. (2.3). The Fermi energy $E_F$ is reduced to six points where the bonding and antibonding bands touch. Reproduced from ref. [6] (b) The hexagonal Brillouin zone of graphene with energy contours schematically drawn for the bonding band. The Fermi level is reduced to the six corner points, indicated by black dots.
2.1 Carbon Nanotubes

Figure 2.5: Reciprocal space for an armchair (a), zigzag (b) and chiral (c and d) nanotube. The parallel lines represent the allowed values for the wavevector \( \mathbf{k} \). In all cases the tube axis direction is along the lines. For armchair nanotubes (a), the length of the first Brillouin zone for each allowed line is \( 2\pi/a \). Within the distance \( 2\pi/\sqrt{3}a \) between the center and the edge of the hexagon, a discrete number of lines fit. For zigzag nanotubes (b), the length of the first Brillouin zone for each allowed line for zigzag nanotubes is \( 2\pi/\sqrt{3}a \). The circle in (c) encloses a region of states near the Fermi level for a chiral nanotube and is shown enlarged in panel (d). The points \( K_1 \) and \( K_2 \) are points of closest approach to the Fermi level at \( K \) in the two nearest allowed \( k \)-lines.

to \( E - E_F = \sqrt{3}a \gamma_0 \mid \mathbf{k} - \mathbf{k}_F \mid \) [7, 8, 9].

In carbon nanotubes, which can be thought of as rolled up ribbons of graphene, the number of available energy modes in the circumferential direction is quantized; \( \mathbf{k} \cdot \mathbf{C} = 2\pi q \) \( (q = 0, 1, 2...) \). The electrons are therefore free to move only in the length direction. Due to this quantization a discrete number of parallel lines that represent the allowed modes of \( k \) values appear in the reciprocal space of graphene. This is shown for examples of armchair, zigzag and chiral nanotubes in Fig. 2.5.

The interline spacing \( \Delta k \) depends only on the diameter \( d \): \( \Delta k = \frac{2\pi}{(2\pi/q)} = \frac{\pi}{d} \). Each line corresponds to a one-dimensional channel for conduction along the nanotube. In the case of an armchair nanotube the quantization condition is \( n\sqrt{3}k_x a = 2\pi q \) \( (q = 0, 1, 2..., n) \) and the allowed \( k \)-lines run in the (vertical) \( k_y \) direction. For zigzag nanotubes the condition \( nk_y a = 2\pi q \) \( (q = 0, 1, 2..., n) \) applies and the allowed \( k \)-lines are in the (horizontal) \( k_x \) direction. The dispersion relations for armchair and zigzag nanotubes can be obtained by inserting these quantization conditions in Eq. (2.3), to yield:

\[
E_{\text{armchair}}(k_y) = \pm \gamma_0 \left[ 1 + 4 \cos \left( \frac{\pi q}{n} \right) \cos \left( \frac{k_y a}{2} \right) + 4 \cos^2 \left( \frac{k_y a}{2} \right) \right]^{1/2}, \quad (2.4)
\]

\[
E_{\text{zigzag}}(k_x) = \pm \gamma_0 \left[ 1 + 4 \cos \left( \frac{\sqrt{3}k_x a}{2} \right) \cos \left( \frac{\pi q}{n} \right) + 4 \cos^2 \left( \frac{\pi q}{n} \right) \right]^{1/2}. \quad (2.5)
\]
The dispersion diagrams that follow from Eqs. (2.4) and (2.5) are shown for a (5,5) and a (10,0) nanotube respectively in the left figure of Fig. 2.6 for \( k_x, k_y > 0 \). The relations are drawn for the first one-dimensional Brillouin zones, of which the boundaries are indicated in Fig. 2.5a and b by the dashed lines. In general, the length of the first Brillouin zone for each subband is \( 2\pi/|T| \), where \( |T| \) is the length of the nanotube unit cell (see also Fig. 2.1). For armchair nanotubes, \( T \) has a length \( a \), for zigzag nanotubes \( T \) has length \( a/\sqrt{3} \) and the Brillouin zones are \( 2\pi/a \) and \( 2\pi/a\sqrt{3} \) in length respectively.

As is illustrated in Fig. 2.5a, armchair nanotubes have allowed \( k \)-lines crossing the corner points of the Brillouin zone and therefore have no energy gaps. Indeed, the dispersion diagram for the (5,5) nanotube shows that there are linear bands crossing the Fermi level at \( k_F = 2\pi/3a \). The distance between the allowed \( k \)-lines for armchair nanotubes is \( \Delta k = 2\pi/n\sqrt{3}a \). Within the distance \( 2\pi/\sqrt{3}a \) between the center and the edge of the hexagon fit therefore a discrete number of \( n \) lines. For zigzag and chiral nanotubes, the allowed \( k \)-lines do not automatically cross the Fermi points. They are metallic when these lines do cross the Fermi point and semiconducting otherwise.

2.1.4 Density of States

The right figure of Fig. 2.6 schematically shows the density of states (DOS) that can be derived from the energy dispersion diagrams shown in the left figure. The linear crossing bands near the Fermi level yield a small constant DOS for the armchair nanotube. At energies away from the Fermi energy, the next subbands lead to Van Hove singularities at the onset due to the one-dimensional nature of the subbands. The energy separation between the first singularities above and below the Fermi level is here defined as \( \Delta E_{\text{sub}} \). The DOS for a semiconducting nanotube also consists of a series of sharp van Hove singularities. In this case however, there is an energy gap \( \Delta E_{\text{gap}} \).

For chiral nanotubes, the unit cell \( T \times C \) is typically an order of magnitude larger than for nonchiral nanotubes. It has been argued that a large number of subbands and therefore also many singularities in the DOS may be expected [10]. However, it has been found that near the Fermi level a universal DOS exists that scales with diameter and depends, to first order, only on the metallic or semiconducting character of a nanotube [7, 8, 9]. The DOS for a chiral nanotube with the same diameter is therefore similar to that of a zigzag or an armchair nanotube. This is illustrated in Fig. 2.5c. Near the Fermi point \( K \), the energy dispersion is approximately radially symmetric within the \( k_x, k_y \)-plane (see Fig. 2.4b). The point of closest approach from \( K \) to any allowed \( k \)-line (\( K_1 \)) yields therefore the first Van Hove singularity. The second point of closest approach (\( K_2 \)) yields the next singularity etc. A different chirality means that the allowed \( k \)-lines are rotated and oriented differently around \( K \). However, due to the discreteness of the hexagonal lattice it can be found that for semiconducting nanotubes the dis-
2.1 Carbon Nanotubes

Figure 2.6: The energy band diagram (left) and density of states (right) for a metallic (top) and a semiconducting (bottom) nanotube. The energy dispersion diagrams are calculated with Eqs. (2.4) and (2.5) for a (5,5) and (10,0) nanotube respectively. The energy is divided by the energy overlap integral $\gamma_0 = 2.9$ eV. In the density of states (DOS) diagrams a series of sharp peaks appear which are the subband onsets. The energy differences between the first two singularities near the Fermi level are indicated for the metallic and the semiconducting case by $\Delta E_{sub}$ and $\Delta E_{gap}$ respectively.

Distances from $K$ perpendicular to the nearest allowed $k$-lines, to $K_1$ and $K_2$, is always $1/3\Delta k$ and $2/3\Delta k$, irrespective of the chirality and diameter [7, 8, 9]. The next two points of closest approach in allowed $k$-lines, beyond $K_1$ and $K_2$, are at distances $4/3\Delta k$, $5/3\Delta k$ etc. The energy dispersion for a graphene sheet was found to be $E = \frac{\sqrt{3}}{2} \gamma_0 \mid k - k_F \mid$ near the Fermi points (with $E_F = 0$). For the distances $\mid k - k_F \mid$ of $1/3\Delta k$, $2/3\Delta k$ etc., and with $\Delta k = 2/d$, the singularities then appear in the valence band (-) and the conduction band (+) at $E_1 = \pm \frac{1}{3} (\frac{\sqrt{3}}{2} \gamma_0)^2 = \pm a\gamma_0/\sqrt{3}d$, $E_2 = \pm \frac{2}{3} (\frac{\sqrt{3}}{2} \gamma_0)^2 = \pm 2a\gamma_0/\sqrt{3}d$ etc. These energies only depend on the diameter $d$. For metallic nanotubes there is always
an allowed $k$-line crossing the Fermi point. The two points of closest approach in neighboring lines are therefore both exactly a distance $\Delta k$ away. The Van Hove singularities thus overlap. Other singularities appear at $2\Delta k$, $3\Delta k$, etc. This corresponds to energies $E_1 = \pm 3a\gamma_0/\sqrt{3}d$, $E_2 = \pm 6a\gamma_0/\sqrt{3}d$, $E_3 = \pm 9a\gamma_0/\sqrt{3}d$, etc and depend also only on $d$. In conclusion, nanotubes with different chiralities but similar diameter have a similar DOS near the Fermi level, either the metallic or semiconducting type. Note that the energy is radially symmetric only in the vicinity of the Fermi point. At larger energies, the scaling of Van Hove singularities positions with diameter does not apply.

In the above discussion of the energy band structure the curvature of nanotubes was neglected. However, due to the curvature, the $\pi$-lobes are not exactly parallel but have an angle to each other. It has been shown in refs. [2, 11] that this shifts the Fermi points in reciprocal space away from $\mathbf{K}$ and $\mathbf{K}'$, which induces a small energy gap for chiral metallic nanotubes. For nanotubes of about 1.4 nm in diameter, this gap is estimated to be of the order of 10 meV [11]. These curvature induced gaps have not been yet confirmed experimentally.

2.1.5 Low energy properties of finite nanotubes

Each subband corresponds to a conduction channel for electronic transport along a nanotube. At low energies, there are two open channels for metallic nanotubes. In the case of armchair nanotubes the Fermi wavevectors are $k_y = 2\pi/3a$ and $k_y = -2\pi/3a$. These wavevectors correspond to the two inequivalent Fermi points $\mathbf{K}$ and $\mathbf{K}'$. Near the Fermi level, the subbands are approximately linear with $k_y$, $E = \frac{\sqrt{3}a}{2}\gamma_0 k_y$ where $\gamma_0 = 2.9$ eV in the case of carbon nanotubes [12]. This linear dispersion can also be written as $E = h\nu_F k_y$ with the Fermi velocity $\nu_F = 9.4 \times 10^6$ m/s. In a nanotube of finite length, electrons are no longer free to move in the length direction and from the boundary condition $k_y \cdot L = \pi p$ ($p = 0, 1, 2, \ldots$) the 'particle-in-a-box' energy level splitting of a metallic nanotube with length $L$ can be found to be $\Delta E = h\nu_F/2L$. Measurements of the conductance at low voltage bias in a single-walled carbon nanotube lying across two electrodes showed that electron transport occurs through well-separated energy levels [13, 14]. The level splitting for a 3 $\mu$m nanotube was measured to be 0.4 meV which fits quite well to the theoretical level splitting of $\Delta E \sim 0.6$ meV [13]. This indicates that the discrete energy states are quantum-mechanically coherent over long distances and that the carbon nanotube thus behaves as a perfect quantum wire. Theoretical work later showed that metallic nanotubes may be expected to be coherent one-dimensional conductors [15]. In general, electrons become localized due to residual disorder, but the effective disorder in nanotubes is averaged over the whole circumference leading to long localization lengths in the order of several $\mu$m's.

It is in principle possible to observe the wavefunctions corresponding to the discrete energy levels. In chapter 8, an experiment will be described where an
Figure 2.7: Energy dispersion for an armchair nanotube zoomed in around the Fermi level $E_F$. Due to the finite length of a nanotube the one-dimensional subbands will split up into discrete energy states (the black dots). For a nanotube supported on a metallic substrate, the Fermi level shifts down by an amount $\delta E$ from the crossing point because of charge transfer.

An armchair nanotube was cut into a piece of length $30$ nm by an STM voltage pulse. The electronic wavefunctions of several energy states can indeed be imaged as oscillations in the tunneling conductance along the length direction. Figure 2.7 shows the energy dispersion for an armchair nanotube zoomed in around the Fermi energy. The two linear crossing bands are split up into discrete energy levels with level splitting $\Delta E$ for a short nanotube. The Fermi wavelength in armchair nanotubes $\lambda_F$ is in principle $2\pi/k_F = 3a = 0.74$ nm. However, the Fermi level is shifted away from the crossing point due to doping by the underlying gold substrate on which the nanotube is supported. The Fermi wavelength $k_F$ therefore shifts to $k_F \pm \delta k$ and $\lambda_F$ becomes \( \frac{2\pi}{k_F \pm \delta k} \). The experimentally obtained wavelengths of the electronic wavefunctions corresponded well to the wavelengths of 0.69 nm (+) and 0.79 nm (-) that were calculated taking into account a shift of the Fermi level of $\delta E = 0.3$ eV.

2.2 STM imaging and spectroscopy

STM has proven to be a very useful tool to study individual carbon nanotubes. The atomic structure of carbon nanotubes can be resolved by STM imaging, and the electronic features can be probed by STM spectroscopy. This section gives a short overview on STM theory and also briefly discusses STM spectroscopy on single molecules, in particular carbon nanotubes.
Figure 2.8: C$_{60}$ molecules on Si(001) at 30 K. The tunnel current is $I = 0.1$ nA and the bias voltage is $V = -2.5$ V. The bright dots are the molecules. The underlying silicon dimer rows are clearly visible. On the right, a monoatomic terrace step can be observed. (From ref. [17]).

2.2.1 STM theory

In the Tersoff-Hamann approximation the STM tip is treated as a single $s$ orbital with a constant DOS [16]. The tunnel current $I$ that flows between the tip and sample upon applying a bias voltage $V$ is to first order:

$$I(V) \propto \int_0^{eV} \rho_s(E) \rho_t(E - eV) T(E) dE,$$

(2.6)

where $\rho_s$ is the sample electronic DOS and $\rho_t$ the DOS of the tip. $T$ is the tunneling probability and is determined by the overlap of the tip and sample wavefunctions. The wavefunctions fall off exponentially in the tunnel barrier and $T$ depends on the barrier width $W$ according to $T \propto e^{-2\kappa W}$. The decay constant $\kappa = \sqrt{2m_e \phi^2}/\hbar$ in the free electron model, where $\phi$ is the effective workfunction of the tip and sample. The STM tip probes the corrugation and electronic structure by scanning over the surface while measuring changes in the tunnel current. Topographic images are usually made in the so-called constant-current mode. In this mode, a feedback loop is used to keep the tunnel current $I$ constant. Changes in the tunnel current are compensated for by adjusting the height of the tip above the surface. A two-dimensional map of the tip height then reflects the corrugation
of the sample surface. An STM image of C_{30} molecules on clean Si(100) is shown in Fig. 2.8 as an example of the high resolution offered by STM. Both the silicon dimer rows and the molecules are clearly visible. In general, care has to be taken in the interpretation of STM topographic images, since not only the corrugation but also changes in the local electronic structure are imaged.

A tunneling spectroscopy measurement can be done to determine the tunneling DOS of a sample locally. A typical spectroscopy measurement as has been used in this work consists of keeping the position of the STM tip fixed at a constant tunnel distance \( W \) above the sample surface and recording \( I \) as a function of \( V \). The tunneling conductance \( dI/dV(V) \) that is numerically calculated from this \( I(V) \) measurement can be found to scale with the sample DOS \( \rho_s(eV) \). If the tip DOS is indeed flat and the transmission coefficient \( T \) is constant, Eq. 2.6 reduces to:

\[
I(V) \propto \int_{0}^{eV} \rho_s(E)dE
\]  

(2.7)

from which it follows that \( dI/dV(V) \propto \rho_s(V) \). However, the transmission coefficient \( T \) is not constant but depends on the applied bias voltage, which leads to deviations in particular at large bias voltages. This problem can be attacked by taking the normalized differential conductance \( dI/dV/(I/V) \). The transmission probability \( T(E) \) cancels out in this expression since it appears both in the numerator and the denominator. \( dI/dV/(I/V) \) is proportional to the normalized surface DOS and was successfully used to obtain spectroscopy data on Si(111) [19] and single adatoms [20]. In chapter 5, \( dI/dV \) data on carbon nanotubes is compared to normalized \( dI/dV/(I/V) \) data.

### 2.2.2 STM spectroscopy on single molecules

A spectroscopy measurement on a molecule absorbed on a sample surface will show a local DOS that is in fact a convolution between the molecular orbitals and the electronic structure of the substrate. Commonly, the DOS for metallic substrates is assumed to be flat and any features in the tunnel spectra are ascribed to the molecule. However, the molecular orbitals may be broadened and somewhat shifted compared to a free molecule, due to interactions with the substrate. The nature and strength of this interaction depends on the binding between the molecule and the substrate [21]. Two extremes in adsorption are physisorption and chemisorption [22]. In the first case there are only Van Der Waals interactions and the chemical structure of the molecule is not much perturbed. Chemisorption is the opposite type of binding; the interaction between the molecule and the substrate resembles the formation of covalent or ionic bonds and the electronic structure of the molecule can be strongly perturbed.

The interaction between a nanotube and a gold substrate is assumed to be mainly of van der Waals type in refs. [23, 24, 25] and the binding energy is
typically about 2 meV/atom. The total binding energy for a long nanotube adds up to a large amount if the nanotube lies flat on the surface, which prevents tubes from moving during imaging. There is however also a small charge transfer between the gold substrate and the nanotube due to a difference in workfunction. The atoms closest to the gold substrate get therefore charged by \(\sim 0.1\) extra electrons. It has been shown by first principles calculations that this charging shifts the energy levels of the system slightly but does not significantly alter the STM images [24, 25].

References


Chapter 3

Electronic structure of atomically resolved carbon nanotubes


Abstract

The remarkable electronic properties that are predicted for carbon nanotubes have been a major reason for the interest in these fullerene molecules. A carbon nanotube can be considered as a single graphene sheet wrapped into a seamless cylinder. Early after their discovery in 1991 [1] it was predicted that nanotubes can be either metallic or semiconducting depending on minor differences of the wrapping angle and diameter [2-4]. In other words, similarly shaped molecules consisting of only one element (carbon) may exhibit dramatically different electronic properties. Previous experiments on multi-wall and single-wall nanotubes [5-12] did not allow to verify this prediction. Here we present combined scanning tunneling microscopy and spectroscopy results on individual single-wall nanotubes. Atomically resolved images allow to relate the electronic spectra to the wrapping angle and diameter. Carbon nanotubes of various wrapping angles indeed appear to be either metallic or semiconducting as is demonstrated from the tunneling density of states. Nanotubes are expected to be strongly one-dimensional conductors. Van Hove singularities at the onset of one-dimensional energy bands are indeed observed. Gap values are in good agreement with theoretical predictions.
Figure 3.1: Relation between the hexagonal carbon lattice and the chirality of carbon nanotubes. (a) The construction of a carbon nanotube from a single graphene sheet. By rolling up the sheet along the wrapping vector C, i.e., such that the origin (0,0) coincides with point C, a nanotube indicated by indices (11,7) is formed. Wrapping vectors along the dotted lines lead to tubes that are zigzag or armchair. All other wrapping angles lead to chiral tubes whose wrapping angle is specified relative to either the zigzag direction ($\theta$) or to the armchair direction ($\phi = 30^\circ - \theta$). Dashed lines are perpendicular to C and run in the direction of the tube axis indicated by vector T. The solid vector H is perpendicular to the armchair direction and
(continued caption of Fig. 3.1) specifies the direction of nearest-neighbor hexagon rows indicated by the black dots. The angle between T and H is the chiral angle $\phi$. (b) Atomically resolved STM images of individual single-wall carbon nanotubes. The lattice on the surface of the cylinders allows a clear identification of the tube chirality. Dashed arrows represent the tube axis T and the solid arrows indicate the direction of nearest-neighbor hexagon rows H. Tubes #10, #11, and #1 are chiral, while #7 and #8 have a zigzag and armchair structure, respectively. Tube #10 has a chiral angle $\phi = 7^\circ$ and a diameter $d = 1.3$ nm, which corresponds to the (11,7) type of figure a. A hexagonal lattice is plotted on top of image #8 to clarify the nonchiral armchair structure. Carbon nanotubes were synthesized as described in ref. 14. TEM studies [14] have shown that the material consists mainly of ~1.4 nm thick single-wall nanotubes. These were deposited from a dispersion in 1,2 dichloroethane on single-crystalline Au(111) facets. Topographic images were obtained by recording the tip height at constant tunnel current in a home-built STM [15] operated at 4 K. The Pt/Ir tips were cut in ambient by scissors. Typical bias parameters are those of image #10, viz., a tunnel current $I = 60$ pA, and a bias voltage $V_{bias} = 500$ mV.

Figure 3.1 shows the hexagonal lattice of a single sheet of graphite. A tube can be constructed by wrapping up the sheet such that the origin (0,0) coincides with one of the equivalent sites of the lattice (point C). Vector $\mathbf{C} = n\mathbf{a}_1 + m\mathbf{a}_2$ is specified by a pair of integers $(n, m)$. A tube is called ‘armchair’ if $n$ equals $m$, and ‘zigzag’ in the case $m = 0$. All other tubes are of the ‘chiral’ type and have a finite wrapping angle $\phi$ with $0^\circ < \phi < 30^\circ$ [13]. The electronic properties of nanotubes depend strongly on the values for $n$ and $m$. To be able to correlate the electronic properties of a tube with its atomic structure, atomically resolved images are required. In Fig. 3.1 we show examples of such scanning tunneling microscopy (STM) images of single-wall carbon nanotubes. The chiral angle $\phi = 7^\circ$, and diameter $d = 1.3$ nm of tube #10 correspond to vector $\mathbf{C} = (11,7)$ in the top panel of Fig. 3.1.

The critical dependence of the electronic spectra of nanotubes on the tube indices $(n, m)$ can be understood by again taking the 2D graphene sheet as a starting point. In the circumferential direction (along $\mathbf{C}$), periodic boundary conditions apply, i.e., $\mathbf{C} \cdot \mathbf{k} = 2\pi q$, where $\mathbf{k}$ is the wave vector and $q$ an integer. Substitution of the allowed values for $k$ in the energy dispersion relation for a graphene sheet yields the dispersion relations for the tube, with $q$ labelling the various one-dimensional (1D) modes. Calculations [13] predict that armchair ($n = m$) tubes have bands crossing the Fermi level and are therefore metallic. For all other tubes (chiral and zigzag) there exist two possibilities. When $n - m = 3l$ ($l$ is an integer), tubes are also expected to be metallic. In the case $n - m \neq 3l$, tubes are predicted to be semiconducting with a substantial energy gap (of order $\sim 0.5$ eV). This gap should only depend on the diameter, viz., $E_{gap} = 2\gamma_0 a_{C-C}/d$, where $\gamma_0$ is the C-C tight-binding overlap energy, $a_{C-C}$ the nearest-neighbor C-C distance (0.142 nm) and $d$ the diameter. Atomic resolution was achieved on more than 20 tubes, corresponding to $\sim 80\%$ of the tubes investigated. In most cases
Table 3.1: \( d \) is the nanotube diameter; \( \phi \) is the chiral angle; \( E_{\text{gap}} \) is the apparent band gap in the STS \( I - V \) spectra; \( \delta E \) is the shift of the Fermi energy due to doping of the tube by the substrate. Note that a chiral angle of 0° denotes an armchair nanotube, and an angle of 30° a zigzag tube. The diameter \( d \) of the nanotubes can be determined with an accuracy of 0.1 nm. A possible systematic uncertainty in determining the diameter is due to a difference in barrier heights for the gold substrate and the tubes. The wrapping angle \( \phi \) can be determined with an accuracy of about 1°. Accuracy in \( \phi \) is limited by the curvature of the tubes. A combination of high accuracy in both \( \phi \) (\( \sim 1 \)°) and \( d \) (\( \sim 0.05 \) nm) is required for an unambiguous identification of the \( n, m \) indices. Accuracy in \( E_{\text{gap}} \) and \( \delta E \) is 0.05 - 0.1 eV. * For this sample we observe a shift in the Fermi energy towards the conduction band instead of a shift towards the valence band as observed in the other samples. We speculate that the gold substrate for this sample may have an anomalously low work function.

only a few rows of atoms on top of the tube could be imaged. Very few armchair tubes were observed, which is in apparent contrast with earlier investigations on the same type of material [14, 16]. However, contrary to these experiments we have concentrated on individual tubes and have neglected the ropes of tubes.

Figure 3.1 shows atomically resolved STM images on five different tubes. The most prominent feature is the triangular lattice of dark dots with a lattice spacing of about 0.25 nm, as expected for a graphene lattice. We attribute the dark dots to the centers of the hexagons [17]. The atomic resolution images allow to unambiguously determine the chiral angle, i.e., the angle between the hexagon rows and the tube axis. This enables to distinguish chiral, zigzag, and armchair tubes. Tubes #1, #10, and #11 have a finite wrapping angle and are chiral. A wide variety of chiral angles is observed (see Table 3.1), in contrast to earlier electron diffraction studies on ropes of single-wall nanotubes[16]. The topographic images of tube #7 and #8 show a zigzag and armchair tube, respectively. Overlay of the hexagonal lattice for tube #8 clearly reveals the nonchiral armchair structure of this tube.

The vacuum barrier between STM tip and sample forms a convenient junc-
tion for tunneling spectroscopy (STS) since it allows tunnel currents at large bias voltages. In STS, scanning and feedback are switched off and current $I$ is recorded as a function of the bias voltage $V$ applied to the sample. The differential conductance $(dI/dV)$ then can be considered to be proportional to the tube density of states (DOS). Before and after taking STS curves on a tube, reference measurements were performed on the gold substrate. Only when the curves on gold were approximately linear and did not show kinks or steps, data on a tube were recorded. $I - V$ traces were only taken far from the ends of the tube and when tubes were isolated from each other. On all the tubes reported here, STS curves taken at different positions (typically over $\sim 40$ nm) showed consistent features.

Figure 3.2a shows a selection of $I - V$ curves obtained by STS on different tubes. Most curves show a low conductance at low bias, followed by several kinks at larger bias voltages. Tubes #1-6 are chiral. From all the chiral tubes that we have investigated we can clearly distinguish two categories: One with a well-defined gap value around 0.5-0.6 eV, the other with significantly larger gap values of about 1.7-2.0 eV (cf. Table 3.1 and Fig. 3.2b). The gap values of the first category coincide very well with the expected gap values for semiconducting tubes. Figure 3.2c displays the gap versus the measured tube diameter. The solid line denotes the theoretical gap value. A good fit is obtained for $\gamma_0 = 2.7 \pm 0.1$ eV, which is close to the value $\gamma_0 = 2.5$ eV suggested for a single graphene sheet [13, 18, 19]. The very large gaps that we observe for the second category of tubes, 1.7-2.0 eV, are in good agreement with the values 1.6-1.9 eV that we obtain from 1D dispersion relations [13] for a number of metallic tubes $(n - m = 3l)$ of $\sim 1.4$ nm diameter. Metallic nanotubes are expected to have a small but finite DOS near $E_F$ and the apparent ‘gap’ is associated with DOS peaks at the band edges of the next 1D modes.

The gaps observed in Fig. 3.2 are not symmetrically positioned around zero bias voltage. This demonstrates that the tubes are doped by charge transfer from the Au(111) substrate. The latter has a work function of about 5.3 eV which is much higher than that of the nanotubes (which presumably is similar to the 4.5 eV work function of graphite). This shifts the Fermi energy towards the valence band of the tube. In the semiconducting tubes, the Fermi energy appears to have shifted from the center of the gap to the valence band edge. In the metallic tubes it is shifted by $\sim 0.3$ eV which is much lower than half of the ‘gap’. This provides experimental evidence that these tubes indeed have a finite DOS within the ‘gap’, in contrast to the zero DOS for semiconducting tubes.

The chiral tubes thus appear to be either semiconducting or metallic, with gap values as predicted. The data provide a striking verification of the band-structure calculations of nanotube electronic properties. Our electronic spectra for armchair and zigzag tubes are also consistent with the calculations, but the small number of such tubes in our experiments prevent a more general statement. For chiral metallic tubes, it has been suggested [20] that a small ($\sim 0.01$ eV) gap
Figure 3.2: (a) Current-voltage curves obtained by tunneling spectroscopy on various individual nanotubes. Tubes #1-6 are chiral, #7 is zigzag, and #8 is armchair. The bias voltage is applied to the sample, which means that the sign of $V_{bias}$ corresponds to that of the energy relative to the tube Fermi level. Curves #1-7 show a low conductance at low bias, followed by several kinks at larger bias voltages. The armchair tube does not show clear kinks in the range -1V to +1V. (b) shows the derivatives $dI/dV$. For clarity, curves are offset vertically by multiples of 0.4 nA/V. Gaps are indicated by the arrows. Two categories can be distinguished: One with gap values around 0.5-0.6 eV, the other with significantly larger gap values. The first category of tubes is identified as the semiconducting type, the second as metallic tubes. About 12 out of 18 tubes were semiconducting, in accordance to the expected ratio of 2 out of 3. Note that these tubes, besides the primary gaps, also show peaks associated with secondary and higher-order gaps. For the secondary gaps we find: 1.4 eV (#1), 1.1 eV (#2), 1.2 eV (#3), 1.4 eV (#4). All gaps appear to have shifted to the right, which indicates doping of the tubes by the substrate. We refrain from concluding a zero or finite DOS from the value of $dI/dV$ in the gap. Possible mechanisms for a small finite $dI/dV$ within the semiconducting gap are, for example, tip-induced band bending or residual tunneling through the tube to the gold substrate. The doping behavior, however, indicates a finite DOS for metallic tubes, and a zero
(continued caption of Fig. 3.2) individual $I - V$ curves for improved signal-to-noise ratio. The individual curves all contain the same essential features. (c) Energy gap $E_{gap}$ vs diameter $d$ for semiconducting chiral tubes. The data points correspond quite well to the theoretical predicted values. The solid line denotes a fit of $E_{gap} = 2\gamma_0 a_{C-C}/d$, with $\gamma_0 = 2.7$ eV. Tunnel currents $I$ are recorded as a function of the bias voltage $V$ applied to the sample while scanning and feedback were switched off.

will open up due to the tube curvature. We did not observe such a small gap at the center of the large 'gap' of chiral metallic tubes. This may be attributed to hybridization between wave functions of the tube and the gold substrate [21] which causes smoothening of small-energy features.

Sharp Van Hove singularities in the DOS are predicted at the onsets of the subsequent energy bands, reflecting the 1D character of carbon nanotubes. The derivate spectra indeed show a number of peak structures, cf. Fig. 3.2b. The peaks we observe differ in height depending on the configuration of the STM tip. On semiconductors $dI/dV/(I/V)$ has been argued to give a better representation of the DOS than the direct derivative $dI/dV$, partly because the normalization accounts for the voltage dependence of the tunnel barrier at high bias [22-25]. In Fig. 3.3 we show $dI/dV/(I/V)$ on the ordinate. Sharp peaks are observed with a shape that resembles that predicted for Van Hove singularities (see right inset of Fig. 3.3): With increasing $|V|$, $dI/dV/(I/V)$ rises steeply, followed by a slow decrease. The latter should be $\propto 1/\sqrt{|V|}$ according to the theory for the DOS near a 1D band edge. The experimental peaks have a finite height and are broadened, which again can be attributed to hybridization of wave functions.

In conclusion, individual single-wall nanotubes have been investigated by scanning tunneling microscopy and spectroscopy. Atomic-resolution images allow to determine whether tubes are chiral, zigzag or armchair. Tunneling spectra are consistent with the theoretical DOS. The results verify the central theoretical prediction that chiral tubes are either semiconducting or metallic, depending on minor variations of wrapping angle or diameter. To our knowledge the presented data constitute the first experimental test for the vast amount of bandstructure calculations that have appeared in recent years.

Acknowledgements

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Figure 3.3: $dI/dV / (I/V)$ vs $V$. This is a measure for the density of states of nanotube #9. The asymmetric peaks correspond to Van Hove singularities at the onsets of one-dimensional energy bands of the carbon nanotube. The left inset displays the raw $dI/dV$ data. The right inset is the calculated density of states for a (16,0) tube, which displays a typical example of the peak-like DOS for a semiconducting tube. The experimental peaks have a finite height and are broadened, which we attribute to hybridization between the wave functions of the tube and the gold substrate. The overall shape of the experimental peaks however still resembles that predicted by theory.

References


References

Chapter 4

Atomic structure of carbon nanotubes from scanning tunneling microscopy

L. C. Venema, V. Meunier, Ph. Lambin and C. Dekker

Abstract

The atomic structure of a carbon nanotube can be described by its chiral angle and diameter and can be specified by a pair of lattice indices \((n, m)\). The electronic and mechanical properties are critically dependent on these indices. Scanning tunneling microscopy (STM) is a useful tool to investigate carbon nanotubes since the atomic structure as well as the electronic properties of individual molecules can be determined. This paper presents a discussion of the technique to obtain \((n, m)\) indices of nanotubes from STM images in combination with current-voltage tunnel spectra. Image contrast, distortion effects, and determination of chiral angle and diameter are discussed. The procedure of \((n, m)\) identification is demonstrated for a few single-walled carbon nanotubes.

4.1 Introduction

Carbon nanotubes [1] are hollow cylindrical molecules that have unique electronic [2] and mechanical [3] properties. They can be considered as graphene sheets that are rolled up into seamless cylinders (Fig. 4.1). Each nanotube can be specified by a pair of indices \((n, m)\) that corresponds to a specific chiral angle \(\phi\) and diameter \(d\). Remarkably, nanotubes can be either semiconducting or metallic, which depends critically on the \((n, m)\) numbers [2]. These indices can in principle be obtained experimentally by measuring both \(\phi\) and \(d\) from either transmission electron microscopy (TEM) and diffraction [4] or by scanning tunneling microscopy (STM) [5, 6]. STM appears to be more suitable to
Figure 4.1: A graphene sheet that can be rolled up into a single-walled nanotube by cutting out the sheet along the dashed lines and rolling the sheet up along vector C. $a_1$ and $a_2$ are the unit vectors of the graphene lattice. The dash-dotted lines denote the main symmetry directions in the graphene sheet, $(n,0)$ and $(n,n)$, or, the zigzag and armchair directions respectively. Also shown are $(n,m)$ indices around $(14,3)$. The corresponding $\phi$, $d$ and electronic behavior for the nanotubes with these $(n,m)$ indices are given in Table 4.1. The gray trapezium represents a measurement of $\phi$ and $d$ for nanotube 2 in Fig. 4.4. The half-widths of this area are the measurement errors.

<table>
<thead>
<tr>
<th>$(n,m)$</th>
<th>$d$ (nm)</th>
<th>$\phi$ (°)</th>
<th>electronic behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>(13,3)</td>
<td>1.15</td>
<td>19.8</td>
<td>semiconductor</td>
</tr>
<tr>
<td>(14,2)</td>
<td>1.18</td>
<td>23.4</td>
<td>metal</td>
</tr>
<tr>
<td>(13,4)</td>
<td>1.21</td>
<td>17.0</td>
<td>metal</td>
</tr>
<tr>
<td>(14,3)</td>
<td>1.23</td>
<td>20.5</td>
<td>semiconductor</td>
</tr>
<tr>
<td>(15,2)</td>
<td>1.26</td>
<td>23.8</td>
<td>semiconductor</td>
</tr>
<tr>
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<tr>
<td>(15,3)</td>
<td>1.31</td>
<td>21.1</td>
<td>metal</td>
</tr>
</tbody>
</table>

Table 4.1: $(n,m)$ indices with the corresponding chiral angles, diameters and electronic behavior for the seven nanotubes indicated in Fig. 4.1.
4.2 Definition of nanotube indices

probe individual molecules. Topographic imaging can be combined with tunneling spectroscopy measurements [5, 6, 7, 8]. This is a powerful technique since the predicted relation between atomic and electronic structure can be tested. STM measurements indeed confirmed that nanotubes can be either semiconducting or metallic, depending on the chirality and diameter [5, 6].

This paper presents a discussion of \((n, m)\) identification for individual nanotubes by use of STM measurements. Section 4.2 explains how the atomic structure of a nanotube can be described by a pair of \((n, m)\) lattice indices. Section 4.3 gives the experimental details of the STM measurements. Section 4.4 explains how \(\phi\) and \(d\) are determined from images and current-voltage tunnel spectra. Also, the lattice contrast is discussed together with a number of distortion effects that have to be taken into account. Section 4.5 describes the identification of two different nanotubes, a semiconducting and a metallic example. The atomically resolved STM images of these nanotubes are compared to calculated images. Section 4.6 gives a summary of the results.

4.2 Definition of nanotube indices

As shown in Fig. 4.1, a carbon nanotube can be thought of as a cylinder constructed from a graphene sheet. A vector \(\mathbf{C}\) is defined pointing from one carbon site to another equivalent site in the hexagonal lattice. By cutting out the sheet along the dashed lines perpendicular to \(\mathbf{C}\) and wrapping up the sheet in the direction of the vector, a seamless cylinder can be obtained, with diameter \(d = |\mathbf{C}| / \pi\). The vector \(\mathbf{C}\) can be related to the unit vectors \(\mathbf{a}_1\) and \(\mathbf{a}_2\) as \(\mathbf{C} = n\mathbf{a}_1 + m\mathbf{a}_2\). The pair of indices \((n, m)\) defines the nanotube. The corresponding chiral angle \(\phi\) and diameter \(d\) are:

\[
\phi = \arccos \left[ \frac{\sqrt{3}(n+m)}{2\sqrt{n^2 + m^2 + nm}} \right]
\]
\[
d = \frac{a}{\pi} \sqrt{n^2 + m^2 + nm}
\]

where \(a = 0.246\) nm is the lattice constant. \((n, 0)\) and \((n, n)\) denote special symmetry directions in the graphene lattice, named respectively zigzag and armchair (dash-dotted lines in Fig. 4.1). They differ by an angle of 30°. A sheet rolled up along one of these lines results in a non-chiral tube, with \(\phi = 0°\) for an armchair and \(\phi = 30°\) for a zigzag nanotube.

Nanotubes can be either semiconducting or metallic. The general rule is that nanotubes are metallic when \((n-m)\) is a multiple of 3 and semiconducting otherwise [2]. As an example, Table 4.1 lists a few nanotubes with indices around \((14, 3)\), which are also indicated in Fig. 4.1. This Table shows that a high accuracy is required in both the measured diameter and the chiral angle to distinguish
between two nanotubes with neighboring \((n,m)\) indices. \((14,3)\) and \((15,3)\) for example differ only 0.08 nm in diameter and 0.6° in chiral angle. A measurement of the electronic behavior can be conclusive in this case, since the first is a semiconductor while the latter is a metal.

### 4.3 Experimental details

The measurements discussed in this paper were performed on carbon nanotubes on a Au(111) surface. Nanotubes were synthesized by laser evaporation (material provided by R. E. Smalley and co-workers [9]). TEM images show that this material consists mainly of single-walled nanotubes with a diameter of about 1.4 nm. Au(111) was prepared by flash-heating a piece of about 30 mm\(^3\) from a 99.99% pure gold wire. The single-crystalline facets appearing on the surface after cooling were used as substrates. Nanotube soot was dispersed in dichloroethane and treated in an ultrasonic bath to unravel the material into nanotube bundles and single nanotubes. A droplet of the dispersion was then deposited on the Au(111) substrates in ambient conditions.

All measurements were done in an STM operated in constant-current mode at 4 K. STM tips were mechanically cut from a Pt(90%)Ir(10%) wire. Typical tunneling parameters were 60 pA and 0.1 V. Current-voltage \((I - V)\) tunnel spectra on the nanotubes were taken by switching off the feedback and recording the current \(I\) as a function of the bias voltage \(V\) applied to the sample. The differential conductance \(dI/dV\) calculated from the \(I - V\) spectra is roughly proportional to the density of states (DOS) of the sample. For large voltage ranges \((\gtrsim \pm 1 V)\) \(dI/dV\) is usually normalized by dividing by \(I/V\) to account for the voltage dependence of the tunnel barrier [10]. We used this normalization method to analyze our spectroscopy data.

### 4.4 STM data analysis

This section discusses methods to obtain the chiral angle \(\phi\) and diameter \(d\) from STM measurements of carbon nanotubes. Part 1 of this section discusses the apparent lattice contrast in the STM images of carbon nanotubes. Often a non-hexagonal lattice is observed which can be attributed to various effects. Furthermore, the apparent chiral angle is distorted due to the cylindrical shape of nanotubes. Part 2 describes a procedure to cancel out the distortion and obtain the true chiral angle \(\phi\). In part 3, methods to obtain the diameter \(d\) are discussed.

#### 4.4.1 Atomic contrast in STM imaging

Figure 4.2 shows various examples of atomically resolved STM images of chiral carbon nanotubes with apparent chiral angles \(\phi\) indicated. Typically, STM images
4.4 STM data analysis

Figure 4.2: STM images of atomically resolved carbon nanotubes. For each nanotube the apparent angle $\phi_1$ between hexagon rows and the tube axis is indicated. The 1 nm bar indicates the scale for all four images. (a)-(b) Two chiral nanotubes with small chiral angles. (c)-(d) Two chiral nanotubes with large chiral angles (near 30°).

of nanotubes do not show a hexagonal configuration of carbon atoms. Instead, a triangular lattice of dark and white dots is usually observed as seen for example in Fig. 4.2c and d. For graphite, various effects are known that can distort the expected hexagonal pattern. The ABAB stacking sequence of the three-dimensional layered structure in graphite results in two inequivalent atomic sites in each unit cell, which leads to an asymmetry in STM images [11]. Obviously, this can be ruled out for single-walled carbon nanotubes. There are however also a number of tip-related effects that can explain the distortion of the hexagonal graphene lattice [12, 13]. The geometrical shape of the tip and the type of electronic orbitals protruding from the tip apex play an important role in the apparent contrast of the lattice. Mizes et al. [12] argued that the STM image of an hexagonal lattice is built up by three independent Fourier components of equal magnitude. Imaging with a multi-atom tip leads to a superposition of several images, where the three components that make up the total image are not equal. This can explain various anomalous images that have been observed for planar graphite, such as triangular or striped patterns. The same effect may play a role in imaging the graphene lattice of carbon nanotubes.

Recently, Kane and Mele discussed a mechanism of symmetry breaking in carbon nanotubes that would even occur in an ideal tunneling experiment with a perfect single atom tip [14]. Due to scattering of electrons at defects or ends
of nanotubes, STM images may contain interference patterns. Kane and Mele showed for example that large momentum backscattering in armchair tubes leads to a modulation into a $\sqrt{3} \times \sqrt{3}$ pattern, whereas a small momentum backscattering may give striped patterns.

Another effect that distorts the hexagonal lattice in nanotubes is the curvature of the surface. The overlap between the external lobes of the $\pi$-orbitals on neighboring carbon atoms decreases due to the curvature, except for the bonds parallel to the nanotube axis (as in zigzag nanotubes). It therefore turns out that for a nanotube with a chiral angle near $\phi = 30^\circ$, the bonds parallel or almost parallel to the tube axis are imaged as protrusions, which leads to the typical triangular pattern of white dots. When $\phi \approx 0^\circ$ (close to armchair), there are no bonds parallel to the axis and the lattice should appear more hexagonal. The nanotubes in Fig. 4.2a and b are near-armchair and indeed have a more hexagonal contrast than the near-zigzag nanotubes in (c) and (d), where the white protrusions are here the most prominent features.

### 4.4.2 Chiral angle

All the mechanisms described above can have an effect on the lattice contrast but do not distort the chiral structure of a nanotube. STM images can thus be used to determine the chirality. However, the geometrical configuration of the STM tip tunneling on a cylindrical structure (Fig. 4.3c) does lead to an overestimation of the value for the chiral angle. This effect was first noted by Ge et al. [15], and discussed in detail by Meunier et al. [16]. Figure 4.3c illustrates the distortion mechanism. A nanotube with radius $r$ lies on a substrate in the $xy$-plane with its axis in the $x$-direction. The tunnel distance $h$ is kept constant while the tip scans in constant-current mode. The shortest tunnel path from the tip to the tube is perpendicular to the substrate only when the tip is exactly on top of the tube. In general, the tunnel current flows to the side of the nanotube and the atom at site $(x, y, z)$ on the nanotube surface will therefore be projected in the STM image at $(x, (1 + h/r)y, z)$. Effectively, the hexagonal lattice is stretched by a factor of $(1 + h/r)$ in the $y$-direction, transverse to the tube axis. This effect can be considerable; for a typical tunneling distance $h$ of 0.4 nm and a tube radius of 0.7 nm, the lattice is distorted by $\sim 60\%$.

This distortion is apparent from the angle between zigzag and armchair directions in the STM images. For example, Fig. 4.3a is an uncorrected image where the angle between zigzag and armchair directions is higher, $34^\circ$, than it should be ($30^\circ$). This is due to a stretching of the lattice in the direction normal to the tube axis. The angle $\phi_1 = 6^\circ$ seen in this image is therefore not equal to the true chiral angle. To determine the true chirality, the image size is reduced in the direction normal to the nanotube tube axis until the angle between the zigzag and armchair rows fits $30^\circ$, to compensate for the asymmetric inflation. Fig. 4.3b shows the STM image after such a correction, from which a chiral angle $\phi_2 = 5^\circ$
Figure 4.3: Illustration of image distortion mechanism for nanotubes and a correction method. The 1 nm bar indicates the scale for both images in (a) and (b). (a) An uncorrected image with an angle between armchair and zigzag directions of 34° instead of 30°. This is attributed to a distortion effect which stretches the atomic lattice in the direction perpendicular to the tube. The apparent angle $\phi_1 = 6°$. (b) The same image as (a), corrected for the distortion. This is done by decreasing the image in the perpendicular direction to obtain a 30° difference between the zigzag and armchair directions. A chiral angle $\phi_2 = 5°$ is determined from this corrected image. (c) A sketch illustrating the geometrical distortion mechanism. A nanotube with radius $r$ lies in the $xy$-plane with its axis in the $z$-direction. When the STM tip tunnels to the side of the nanotube, an atom at position $(x, y, z)$ is projected in the STM-image at $(x, (1 + h/r)y, z)$.

is found. By carrying out this procedure for various armchair-zigzag angles along the nanotube $\phi_1 = 6.2 \pm 0.4$ is obtained. This angle is 32% higher than the $\phi_2$ of $4.7 \pm 0.4°$ from the corrected image. The distortion found for various nanotubes
from STM images varies between 15% and 70%.

Clauss et al. [17] discussed a distortion mechanism for the chiral angle that is not related to the STM configuration but to the geometry of a nanotube within a rope. When packed within a rope, nanotubes may be twisted. Atomically resolved STM images of ropes indeed show twisted tubes [17]. The measured angle of the lattice with respect to the nanotube axis in that case is not only related to the nanotube chirality, but also to the twist angle. We do not include this effect in the analysis of our STM images. It is unlikely that individual nanotubes separated from ropes remain twisted, because large twisting angles are energetically very unfavorable for individual nanotubes [18]. Furthermore, the energy gap in the DOS predicted to be induced by the twist is not observed in our STM spectra.

4.4.3 Diameter

The diameter of a nanotube can be obtained from a line profile perpendicular across the nanotube. The major distortion that influences the apparent tube width in such a profile arises from the geometrical convolution between the nanotube and the STM tip shape [19]. The nanotube diameter can in principle be measured from the apparent width by careful deconvolution of the tip shape. This method can be used if ultrasharp tips are available. In general however, it is hard to obtain an accurate value for the diameter since the radius of curvature of an STM tip is typically ~10 nm, i.e. more than one order of magnitude larger than the tube radius.

Alternatively, the diameter can be estimated from the height of the nanotube relative to the substrate. The van der Waals distance between the substrate and the tube, about 0.25 nm [20], then has to be taken into account. Furthermore, because of differences in electronic structure, the tunnel distances are not necessarily the same on the nanotube and the gold substrate. Since the tube height is measured relative to the substrate this difference in tunnel distances may lead to an error in the diameter. Ab initio calculations by Rubio [21] show however that the error in diameter due to this effect will be less than 1%. A more substantial error in the apparent height may arise from mechanical deformation of the nanotube. A small deformation also may arise from the van der Waals forces between the substrate and the nanotube. For an armchair nanotube with a diameter of about 1.4 nm this deformation is calculated to be only 2% [22]. As is noticed below, the typical tunnel distances appear to be small which implies that the STM tip may exert significant forces on the nanotube. This may lead to compression of nanotubes during imaging and consequently to anomalous low apparent heights (see Sec. 4.5).

Yet another way to obtain the diameter is to determine the tunneling DOS for a nanotube. Both semiconducting and metallic nanotubes have a DOS consisting of a series of one-dimensional energy subbands [23, 24]. The separation between
the band edges depends on the diameter. Figure 4.4c shows examples of STM spectra obtained for a semiconducting (1) and a metallic (2) nanotube. The band edge separations are indicated in the figure by $\Delta E_{sub}$. For semiconducting tubes this separation is an energy gap of width $\Delta E_{sub} = 2d_{nn}\gamma_0/d$, where $d_{nn}$ is the nearest neighbor distance between carbon atoms, 1.42 Å, and $\gamma_0$ is the $\pi - \pi$ energy overlap between neighboring atoms. Metallic nanotubes have a plateau of constant DOS between subbands of $\Delta E_{sub} = 6d_{nn}\gamma_0/d$. A theoretical value for $\gamma_0$ of 2.5 eV has been estimated by Mintmire et al. using a first principles local density approximation (LDA) to calculate the band structure of armchair carbon nanotubes [25]. This type of calculations however typically give a 10-20% too small value. In a recent review paper a value of $2.9 \pm 0.2$ eV was concluded to be the best estimate for $\gamma_0$ from a critical evaluation of various theoretical and experimental results [26]. In this work we determined the diameter both from the apparent height and by measuring $\Delta E_{sub}$ using this value of $\gamma_0 = 2.9 \pm 0.2$ eV.

### 4.5 Discussion of the $(n, m)$ Identification

Two examples are shown of nanotubes for which the $(n, m)$ indices are identified. Figure 4.4a shows atomically resolved STM images of these two nanotubes which both are chiral. Tunneling spectra that were taken on these tubes are shown in Fig. 4.4c. From these spectra nanotube 1 can be identified as a semiconductor and nanotube 2 as a metallic tube. Table 4.2 lists the parameters obtained from the STM analysis done for these nanotubes. Diameters are obtained by two methods, described in Sec. 4.4.3, from the apparent height and from the subband

<table>
<thead>
<tr>
<th>Tube</th>
<th>$\Delta E_{sub}$ (eV)</th>
<th>$dE_{sub}$ (nm)</th>
<th>$d_n$ (nm)</th>
<th>$\phi_2$ (°)</th>
<th>$(n, m)$</th>
<th>$d_t$ (nm)</th>
<th>$\phi_t$ (°)</th>
<th>Electronic behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.80 ± 0.05</td>
<td>1.0 ± 0.1</td>
<td>0.7 ± 0.1</td>
<td>25 ± 1</td>
<td>(12, -1)</td>
<td>0.90</td>
<td>25.7</td>
<td>semiconductor</td>
</tr>
<tr>
<td></td>
<td>semiconductor</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(13, -1)</td>
<td>0.98</td>
<td>26.0</td>
<td>semiconductor</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(14, -1)</td>
<td>1.06</td>
<td>26.3</td>
<td>metal</td>
</tr>
<tr>
<td>2</td>
<td>1.95 ± 0.05</td>
<td>1.27 ± 0.09</td>
<td>0.7 ± 0.1</td>
<td>20 ± 1</td>
<td>(14, 3)</td>
<td>1.23</td>
<td>20.5</td>
<td>semiconductor</td>
</tr>
<tr>
<td></td>
<td>metal</td>
<td></td>
<td></td>
<td></td>
<td>(15, 3)</td>
<td>1.31</td>
<td>21.1</td>
<td>metal</td>
</tr>
</tbody>
</table>

Table 4.2: The results from data analysis of the STM measurements on the two nanotubes shown in Fig. 4.4a. $\Delta E_{sub}$ is the separation between subbands and $dE_{sub}$ is the diameter that is calculated from this energy difference using $\gamma_0 = 2.9 \pm 0.2$ eV. $d_n$ is the diameter estimated from the apparent height of the nanotubes. The true chiral angle $\phi_2$ is measured from corrected STM images. Also given are $(n, m)$ indices with their corresponding $\phi_t$ and $d_t$ that fit to the experimentally obtained values. The electronic behavior for the nanotubes with these $(n, m)$ numbers is indicated in the last column.
separations. The chiral angles $\phi_2$ are obtained from the corrected atomically resolved images, following the procedure described in Sec. 4.4.2. From this correction procedure we find distortions of about 15% for nanotube 1 and 60% for nanotube 2. These distortions give a tunnel distance $h$ of respectively $\sim 0.1$ and $\sim 0.4$ nm, using the formula for distortion $(1 + h/r)$ which follows from the simple picture of Fig. 4.3c. These values indicate that the STM tip is close to the nanotube and in the case of the first tube even in contact. In view of these small values it is likely that the nanotubes are compressed during imaging due to the forces exerted by the STM tip. The effective stretching of the image perpendicular to the nanotube axis probably deviates from $(1 + h/r)$ due to a tip shape that is more complicated than a single atom and possibly also because of the compression of the nanotubes by the STM tip. The procedure to obtain the correct chiral angle by decreasing the image in the y-direction is independent of the exact amount of stretching however.

The apparent height method yields anomalously small values for the diameter $d_h$ which is most likely due to the above mentioned flattening of the nanotubes by the STM tip during imaging. This method thus appears to be unreliable. We instead determine the diameters $d_{\Delta E_{\text{sub}}}$ found from the subband separations in the DOS. The experimental results for both nanotubes are compared in Table 4.2 to theoretical values of $\phi_2$ and $d_4$ calculated for nanotubes with indices $(n, m)$ yielding the best fits. The error in determining the chiral angle is typically $\sim 1^\circ$. The error in the diameter is $\sim 0.1$ nm and is mainly determined by an uncertainty in $\gamma_0$. The measurement uncertainty area is indicated for nanotube 2 as the gray area in Fig. 4.1. For nanotube 1, $(12, -1)$, $(13, -1)$ and $(14, -1)$ fit to the observed chirality and diameter. However, $(14, -1)$ can be ruled out as a possibility since nanotube 1 is semiconducting. Nanotube 2 fits to $(14, 3)$ and $(15, 3)$, as can also be seen in Fig. 4.1, but, since it is metallic, $(15, 3)$ can be singled out as the only candidate. In general, fitting the indices for metallic nanotubes is somewhat easier since only one third of all possible $(n, m)$ nanotubes is metallic.

The experimental images are compared to calculated images in Fig. 4.4b for nanotubes with indices $(13, -1)$ and $(15, 3)$. These calculations are done by using a tight-binding $\pi$-electron Hamiltonian as described by Meunier et al. [16]. The tip was taken as a single atom with an $s$ orbital, as in the Tersoff-Hamann theory [27], and the corresponding tip density of states was assumed to have a Gaussian shape. Input parameters for these calculations are the $(n, m)$ numbers and the tunnel distance $h$ between the STM tip and the nanotube. The calculated images in Fig. 4.4b show the remarkable result that the lattice contrast deviates considerably from a hexagonal lattice, even for a perfect single-atom tip. Comparing the experimental images to these calculations, good resemblances are observed. The most prominent features for the near-zigzag nanotube 1 are the white protrusions which also appear clearly in the calculated images. The rectangular shape of these protrusions does not come out very clearly in the STM
Figure 4.4: STM images and tunnel spectra for two different carbon nanotubes. The 0.5 nm bar indicates the scale for all four images in (a) and (b). (a) Atomically resolved STM images of two nanotubes 1 and 2. (b) Two calculated images based on the \((n, m)\) indices that are found for the nanotubes shown in (a). (b) Normalized \(dI/dV\) spectra for these nanotubes. Nanotube 1 appears to be semiconducting whereas nanotube 2 is metallic. Band edge separations \(\Delta E_{\text{sub}}\) are indicated for both curves.

images. It may be expected however that the detailed structure will be influenced by the STM tip shape.

### 4.6 Summary

It has been demonstrated that the \((n, m)\) indices for a specific nanotube can be identified from STM measurements by measuring both the chiral angle and the diameter. The chiral angle \(\phi\) is determined from atomically resolved images. These images have to be corrected to account for a geometric distortion that otherwise show 15-70% overestimated chiral angles. Diameters \(d\) can be obtained from the tunneling DOS, since the energy subband separations are related to the diameters. Two nanotubes, one semiconducting and one metallic, were presented.
as examples for which $\phi$ and $d$ were obtained. For both nanotubes, $(n, m)$ indices could be found that fit to the experimentally determined $\phi$ and $d$ and electronic behavior. We conclude that, within the uncertainty of the measurements which is $1^\circ$ for $\phi$ and 0.1 nm for $d$, it is indeed possible to obtain accurate fits of the $(n, m)$ indices.

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References

Chapter 4. Atomic structure of carbon nanotubes...
Chapter 5

Spatially resolved scanning tunneling spectroscopy on single-walled carbon nanotubes


Abstract

STM spectroscopy is used to study in detail the electronic bandstructure of carbon nanotubes as well as to locally investigate electronic features of interesting topological sites such as nanotube ends and bends. From a large number of measurements of the tunneling density of states (DOS) nanotubes can be classified, according to predictions, as either semiconducting (two-third of the total number of tubes) or metallic (one-third). The energy subband separations in the tunneling DOS compare reasonably well to theoretical calculations. At nanotube ends, spatially resolved spectra show additional sharp conductance peaks that shift in energy as a function of position. Spectroscopy measurements on a nanotube kink suggest that the kink is a heterojunction between a semiconducting and a metallic nanotube.

5.1 Introduction

The electronic and atomic structure of a carbon nanotube are related to each other in a remarkable way. A nanotube can be thought of as a rolled up graphene sheet where two parameters, the chirality $\phi$ of the hexagonal lattice along the nanotube shell and the diameter $d$ fully describe its atomic structure [1]. The indices $(n, m)$ of a nanotube correspond to a specific combination of chiral angle $\phi$ and diameter $d$. Depending critically on these $(n, m)$ indices, a nanotube can
be either semiconducting or metallic [2, 3, 4]. Of all possible \((n, m)\) nanotubes, roughly one third is predicted to be metallic.

Scanning tunneling microscopy (STM) has proven to be a very useful technique to investigate carbon nanotubes since both the atomic and electronic structure can be investigated for individual nanotubes [5-14]. Atomically resolved imaging enables to observe the chiral structure of a nanotube. In addition, the electronic density of states (DOS) can be measured for the same tube by scanning tunneling spectroscopy (STS). The DOS of carbon nanotubes in theory consists of a number of one-dimensional (1D) subbands due to the quantization of available energy modes in the circumferential direction [2, 3, 4]. This may be seen for example in the theoretically calculated DOS for a semiconducting and a metallic nanotube in Fig. 5.2 (curves 1 and 6 respectively). The subband onsets are sharp Van Hove singularities due to the one-dimensional nature of the subbands. The energy intervals at which the subband onsets appear depend on whether the tube is metallic or semiconducting and on the nanotube diameter [15, 16]. Recent STS measurements verified the general features predicted for the DOS. Nanotubes were found to be either semiconducting or metallic and also Van Hove singularities could be observed [10, 11, 14]. Attention is now directed towards the electronic structure of topologically interesting sites in nanotubes, such as ends, bends and kinks. These sites can be studied spatially resolved by STS. Carrol et al. [9] observed sharp STS resonances at the tip of multi-walled nanotubes that could be associated with a particular cap structure. Recently, Kim et al. [14] also observed peaks in the DOS at the end of a metallic single-walled nanotube. They attributed this result to a specific arrangement of pentagons at the cap. Another interesting topological effect is a junction between two nanotubes with different \((n, m)\) numbers, which appears as a sharp bend, or ‘kink’. Section 5.3.2 discusses a measurement on a sharply bent nanotube that appears from spectroscopy curves above and below the kink to be a molecular semiconductor-metal heterojunction.

In this paper we review results from a large number of STS measurements on individual nanotubes. The main features of the electronic DOS as well as locally resolved data on tube ends and a tube kink are discussed in section 5.3. The following section first gives details of the sample and measurement methods.

### 5.2 Experimental details

Measurements were performed on samples of Au (111) surfaces with single-walled carbon nanotubes that were synthesized by laser evaporation (by R.E. Smalley and coworkers) [17]. The Au (111) was prepared by melting pieces of about 30 mm³ from a 99.99\% pure gold wire in a gas flame. The single-crystalline (111) facets appearing on the surface during cooling were used as substrates. Pieces of nanotube soot were dispersed in dichloroethane and ultrasonically agitated to
5.2 Experimental details

Figure 5.1: STM images at room temperature (a), and at 4 K (b)-(f). The scale bar in b-e is 10 nm. (a) Large-scale image where various nanotubes and small bundles on a surface of Au(111) can be observed. (b) Crossing of two nanotubes. The curves on the right are two height profiles taken along the dashed lines indicated in the image. \( h \) is the height, \( x \) is the coordinate along the lines. (c) A sharply bent nanotube. (d) An end of a nanotube that splits off from a bundle. The dotted line illustrates how a series of STS curves can be taken to observe gradual changes in the local DOS at the end. (e) A bundle in which individual nanotubes can be discerned. (f) Atomically resolved image of a chiral nanotube. The image is corrected for the geometrical distortion that stretches the apparent nanotube lattice in the direction normal to the tube axis [21].
unravel the bundles of tubes. A droplet of the dispersion was then deposited on the substrates of Au (111) in ambient conditions. The measurements were done in a home-built 4K STM. STM tips were mechanically cut from a Pt(90%)Ir(10%) wire. Imaging was done in constant-current mode at typical parameters of 60 pA for the tunnel current I and 0.1 V for the bias voltage V.

Some examples of nanotubes imaged with STM at room temperature (a) and at 4 K (b-f) are shown in Fig. 5.1. The scale bar in Fig. 5.1b-d corresponds to 10 nm. The apparent width of the nanotubes varies between 5 and 20 nm. This scale is determined by the size of the STM tip rather than the nanotube diameter which is in the range of 1.4 nm. Various nanotubes and small bundles can be seen in the image of Fig. 5.1a. Carbon nanotubes usually lie straight on the surface but may be deformed due to irregularities in the surface such as monoatomic steps or crossings with other tubes. Hertel et al. showed that single-walled carbon nanotubes may experience substantial deformations at surface irregularities due to the large Van Der Waals binding energies between nanotubes and the substrate surface [18]. The nanotube emerging from the left bottom corner in Fig. 5.1a is indeed bent strongly at the crossings with two other nanotubes. The total lateral extent of such bends is typically about 30 nm. The STM images of Figs. 5.1b-e show details of respectively a crossing, a sharp bend, a nanotube end and a bundle in which several individual nanotubes can be resolved. The right part of Fig. 5.1b are two height profiles h(x) that are taken along the dashed lines shown in the STM image on the left. From the top profile, the individual nanotubes have an apparent height relative to the surface of 1.70 and 1.65 nm. Taking into account a Van Der Waals distance between the tubes and the surface of about 0.25 nm [19], the diameters are 1.45 and 1.40 nm. The crossing of the two tubes, shown in the bottom h(x) profile, has a total height of 3.35 nm. This corresponds to the sum of the individual tube heights and a Van Der Waals distance between the nanotubes and between the lower nanotube and the surface. Figure 5.1c is an image of a sharply bent nanotube, or possibly of a nanotube 'kink'. As mentioned in the introduction, kinks can be junctions between different nanotubes. Figure 5.1d is zoomed in on a nanotube that splits off from a small bundle. The dotted line crossing the end of the nanotube is an example of a line along which a series of spectroscopy measurements can be taken to observe the change in the local DOS at the end of the tube. Such measurements are discussed in Sec. 5.3.2. Figure 5.1e shows a bundle of nanotubes in which the individual nanotubes can be discerned. Figure 5.1f is an atomically resolved image of a chiral nanotube. The image has been corrected for the geometric distortion that stretches the apparent carbon lattice in the direction perpendicular to the tube [20, 21]. The chiral angle obtained from Fig. 5.1f is 21 ± 1°. In general, a large variety of chiral angles could be found for this nanotube material, ranging from zigzag to armchair. Diameters that are measured from apparent height measurements are in general quite small, about 0.9 nm, which is probably due to the flattening of nanotubes by tip forces during imaging [21]. More reliable values can be obtained
5.3 Experimental results

from tunneling spectroscopy measurements. As will be discussed in detail below, the energy differences between the subbands in the DOS depend strongly on the diameter. Using this to deduce the diameter, values of $\sim 1.1 - 1.5$ nm are found, which corresponds reasonably well to TEM measurements where diameters of about 1.4 nm were determined [17].

All spectroscopy measurements presented in this paper were done at 4 K and on individual nanotubes. Current-voltage ($I-V$) tunnel spectra were taken by switching off the feedback and recording the current as a function of the bias voltage while keeping the STM tip at a fixed position. $dI/dV - V$ curves (from here called $dI/dV$ curves) were numerically calculated from $I - V$ spectra. $dI/dV$ can be taken as a measure for the DOS.

5.3 Experimental results

5.3.1 Density of States

Long nanotubes

Two classes of DOS are expected for nanotubes, one for semiconducting and one for metallic nanotubes. The curves 1 and 6 in Fig. 5.2, represent the theoretical DOS for a $(11, 7)$ and a $(9, 9)$ tube, which have approximately the same diameter but are semiconducting and metallic respectively. Two types of $dI/dV$ spectra taken with STM can indeed be distinguished for various nanotubes. Several examples are shown in Fig. 5.2. The left figure shows $dI/dV$ curves (2-5) with various peaks and a small energy gap $\Delta E_{gap}$ of about 0.7 V. The right figure, curves (7-10), have only two clear peaks or onsets in the displayed voltage range and have a large plateau of constant conductance around zero bias $\Delta E_{sub}$ of about 1.9 V in width. The experimentally obtained spectra compare well to the theoretical curves. Both energy differences $\Delta E_{gap}$ and $\Delta E_{sub}$ should scale in theory inversely linear with the diameter of a nanotube. Semiconducting nanotubes with a diameter of 1.4 nm have an energy gap $\Delta E_{gap} = 2d_{nm}\gamma_0/d \approx 0.6$ eV where $d_{nm} = 1.42$ Å is the distance between nearest neighbor carbon atoms and $\gamma_0 = 2.9$ eV is the energy overlap integral between nearest neighbors [22]. For metallic nanotubes, the separation $\Delta E_{sub}$ between the onsets is $\Delta E_{sub} = 6a\gamma_0/d \approx 1.8$ eV for $d = 1.4$ nm. In this case, there is no energy gap but the DOS between the subbands is finite (albeit small) and constant. The experimentally obtained $\Delta E_{gap}$ and $\Delta E_{sub}$ correspond to these calculated values. Out of 29 nanotubes on which $dI/dV$ spectra have been obtained, 19 were semiconducting and 10 were metallic. This result confirms the prediction that about one third of the $(n, m)$ nanotubes is metallic and two third is semiconducting.

It is well known from STS literature that at large bias voltage the tunnel barrier is reduced considerably, which leads to an overestimated DOS at higher bias [23]. To account for this effect, $dI/dV$ can be normalized by $I/V$. The top
Figure 5.2: Experimental and theoretical DOS for semiconducting (left) and metallic (right) nanotubes. For clarity the curves are vertically offset by 0.1 and 0.2 nA/V respectively. The DOS consists of a number of subbands with sharp (Van Hove) singularities at the onsets. Curves 1 and 6 represent the theoretical DOS for a (11,7) and a (9,9) nanotube, which are semiconducting and metallic respectively. Curves 2-5 are $dI/dV$ spectra taken by STM on nanotubes that can be identified as semiconducting and have an energy gap $\Delta E_{\text{gap}}$ of about 0.7 V. Curves 7-10 are spectra on nanotubes that can be identified as metallic and have a large plateau of constant conductance $\Delta E_{\text{sub}}$ of about 1.9 V. The curves 5' and 10' in the top parts are normalized curves, obtained from 5 and 10.
curves 5' and 10' in Fig. 5.2 are normalized spectra, \(dI/dV/(I/V)\), calculated from curves 5 and 10. The normalization technique is especially useful for metallic spectroscopy curves since the first onsets appear at a relatively high voltage, around \(\pm 1\) V. The peak shapes of the subband onsets are enhanced by the normalization as can be observed for the metallic curve 10'. The value for \(\Delta E_{\text{sub}}\) determined from the normalized curves is slightly smaller, by about 0.03 eV, as compared to the value found from \(dI/dV\) curves, due to a small shift of the onsets. For the semiconducting curves, the normalization does not significantly affect the intervals between the subband onsets since they are smaller. The normalized curves are smoothed near zero bias because of the large divergences from the normalization procedure. Determining the peak position of the first valence subband onset for the semiconducting curves often is problematic because small noise fluctuations may lead to spurious peaks. We therefore use the normalization technique for metallic nanotubes to obtain the most reliable value for \(\Delta E_{\text{sub}}\), but determine the intervals between subband onsets for semiconducting nanotubes from \(dI/dV\) curves.

Various energy intervals \(\Delta E_{i-j}\), both above and below the Fermi energy, are indicated for the semiconducting curve in Fig. 5.3b. The differences between the subband onsets follows within a good estimate a simple rule [15, 16]. From the approximately linear energy dispersion near the Fermi level for graphene, the first four Van Hove singularities for semiconductors can be found to appear at energies \(E_1 = \pm d_{nn} \gamma_0/d\), \(E_2 = \pm 2d_{nn} \gamma_0/d\), \(E_3 = \pm 4d_{nn} \gamma_0/d\) and \(E_4 = \pm 5d_{nn} \gamma_0/d\). The separations between the singularities are then \(\Delta E_{2-1} = d_{nn} \gamma_0/d = 1/2 \Delta E_{\text{gap}}\), \(\Delta E_{3-2} = 2d_{nn} \gamma_0/d = \Delta E_{\text{gap}}\) and \(\Delta E_{4-3} = d_{nn} \gamma_0/d = 1/2 \Delta E_{\text{gap}}\). For a metal, the Van Hove singularities appear at energies \(E_1 = \pm 3d_{nn} \gamma_0/d\), \(E_2 = \pm 6d_{nn} \gamma_0/d\) and \(E_3 = \pm 9d_{nn} \gamma_0/d\). The separations \(\Delta E_{i-j}\) are therefore all of the size \(3d_{nn} \gamma_0/d = \Delta E_{\text{sub}}\). It is difficult to observe several energy intervals in the metallic case since the onsets appear at large energies (\(|V| \gtrsim 1\) V, see for example Fig. 5.3a). However, in the semiconducting spectra, three to five subband onsets are usually visible. In Fig. 5.3c energy differences that were obtained for about 20 semiconducting nanotubes are plotted against the energy gap of each tube and compared with \(\Delta E_{\text{gap}}\) (dotted line) and 1/2\(\Delta E_{\text{gap}}\) (solid line). There is much scatter in the data, but it can be observed that the first and third subband separations (closed squares, circles and triangles) are near the 1/2\(\Delta E_{\text{gap}}\) line whereas the second subband separations (open circles) are closer to the \(\Delta E_{\text{gap}}\) line. This observation is in agreement with the simple rule of alternating subband spacings. Deviations in the positions of the subband onsets may occur due to the nonlinearity of the graphene energy dispersion far away from the Fermi energy and due to hybridization with the gold substrate.

Also indicated in Fig. 5.3a and b is the shift \(\delta E\) of the spectra relative to zero bias. This shift can be attributed to the charge transfer between the gold-nanotube interface due to the difference in work function. Au has a work function of \(\sim 5.3\) eV, whereas nanotubes were found to have a work function of
Figure 5.3: Analysis of energy intervals between subbands and the shifts of the Fermi level. (a) Metallic $dI/dV/(I/V)$ spectrum in which $\Delta E_{\text{sub}}$ and Fermi level shift $\delta E$ are indicated. (b) Semiconducting $dI/dV$ spectrum with several subband onset separations indicated, $\Delta E_{i-j}^v$ for the valence band and $\Delta E_{i-j}^c$ for the conductance band. The shift of the Fermi level $\delta E$ is also shown. (c) Subband intervals $\Delta E_{i-j}^{v,c}$ in voltage differences $\Delta V$ plotted as a function of the energy gaps for about 20 semiconducting nanotubes. The solid line represents $1/2\Delta E_{\text{gap}}$ and the dotted line $\Delta E_{\text{gap}}$.

about 4.3 eV [24, 25]. The aligning of the Fermi levels by transfer of electrons from nanotube to gold leads to an asymmetric position of the nanotube band structure relative to the Fermi level. From the STS spectra we find that $\delta E$ is about 0.3 $\pm$ 0.1 eV for both metallic and semiconducting nanotubes, independent of $\Delta E_{\text{gap}}$ and $\Delta E_{\text{sub}}$. This agrees with the theoretical Fermi level shift of about 0.2 eV as a result of the charge transfer between a metallic substrate and a nanotube [26]. In the case of the semiconducting nanotubes the Fermi level is actually shifted into the valence band. For metallic tubes the Fermi level stays well within the plateau between the subband onsets $\Delta E_{\text{sub}}$.

Often, a suppression of the tunneling conductance near zero bias can be ob-
5.3 Experimental results

erved, see for example the metallic $dI/dV$ curves 7 and 10 in Fig. 5.2. This zero bias anomaly is also sometimes present in spectra taken on the bare gold substrate away from nanotubes. The suppression of the tunneling DOS at the Fermi energy for disordered conductors is a well-known problem in the literature [27, 28]. It was found that electron-electron interactions in the presence of impurities results in a negative correction to the DOS, which is singular at the Fermi energy. This theory may apply to the present case, since the STM tip is likely to be a disordered conductor as it is made from an alloy of Pt and Ir. In a more classical point of view, the system can be described by a tunnel junction between the STM tip and the sample in series with a resistance closely. The disordered tip material leads to the resistance in this case. If the resistance is large enough to inhibit fast recharging after a tunneling event, there will be a blockade of current when the external voltage is smaller than the charging energy [29]. The zero bias anomaly in the nanotubes is possibly enhanced by the Luttinger Liquid [30, 31].

Short nanotubes

In short nanotubes the DOS may show additional structure due to finite size effects. For nanotubes of finite length the available energy states in the length direction will be quantized. For finite metallic nanotubes it has been shown that the energy bands that cross at the Fermi level consist of well-separated single electron states that are coherent over a considerable length of the nanotube [32, 33, 34]. The energy level splitting $\Delta E_L$ scales inversely linear with the length $L$, as $\Delta E_L = h v_F/2L$, where $v_F = 9 \times 10^5$ m/s is the Fermi velocity. Discrete energy levels can be observed by cutting nanotubes into small pieces using voltage pulses to the STM tip [35]. The inset of Fig. 5.4 shows a nanotube that was cut into a piece of about 40 nm. Its metallic character is apparent from $dI/dV$ measurements before the cuts, that were similar to the metallic curves in the right plot of Fig. 5.2. After the nanotube was cut into a piece of 40 nm, the DOS showed oscillatory behavior near the Fermi energy, with a peak-peak separation of about 50 meV (Fig. 5.4). More pulses were applied to cut the tube to even smaller pieces. $dI/dV$ spectra on a 16 nm piece (Fig. 5.4, top curve) also showed clear oscillations, with a peak-peak separation of about 160 meV. These values correspond reasonably well with the predicted energy level separation: the theoretical $\Delta E_L$ is 50 meV for $L = 40$ nm and 120 meV for $L = 16$ nm.

5.3.2 Spatially resolved spectroscopy

Nanotube ends

By measuring $dI/dV$ as a function of position in the length direction of a nanotube, the evolution of the DOS near special sites such as nanotube ends can be observed. The straight dotted line drawn in Fig. 5.1d crossing the end of
Figure 5.4: $dI/dV$ spectra zoomed in at low energies on a metallic nanotube that has been cut into short pieces to observe energy level splitting. The inset shows a topographic image of the tube after it was cut by voltage pulses to a piece of 40 nm. The bottom spectrum was taken on the nanotube before it was cut. The tunneling conductance shows an oscillatory behavior (middle curve) with a period of about 50 mV for the 40 nm piece. After cutting the tube to 16 nm, the period is about 160 mV (top curve). The top curve is offset vertically for clarity by 0.6 nA/V. The middle curve is not offset, but was taken at a smaller tunnel distance and therefore has a higher tunneling conductance.

A nanotube is an example of such a measurement. Figure 5.5a displays a series of curves, measured on a semiconducting nanotube, each about 2 nm apart along the dashed line indicated in the topographic image of Fig. 5.5b. The curves are offset vertically to show the gradual change of the tunneling DOS along the tube near the end. Starting from the top, the band structure can be well observed and is reproducible for adjacent curves. The energy gap $\Delta E_{\text{gap}}$ and the first subband separation $\Delta E_{2-1}^T$ are indicated for the top curves. Near the tube end, the subband edges fade out and two new peaks appear within the energy gap at about 0.3 V. These peaks also fade out again in the last two curves where the STM moves off the tube end and onto the gold substrate. In the topographic image of Fig. 5.5b, which is obtained at a bias voltage of 0.4 V, the nanotube appears brighter near the end. This corresponds to the observed higher local density of
Figure 5.5: Electronic structure of the end of a semiconducting nanotube. (a) $dI/dV$ spectra measured at positions 2 nm apart along the dashed line shown in b. The energy gap $\Delta E_{gap}$ and the subband interval $\Delta E_{2-1}$ are indicated in the top curve. From top to bottom, the bandstructure gradually fades out and conductance peaks arise at the end. (b) Topographic image of the nanotube end taken at a bias voltage of 0.4 V.

states within the energy gap in the last $\sim$10 nm.

A very illustrative way of presenting the spatially resolved data is to plot $dI/dV$ in grayscale as a function of both the voltage $V$ and the position $x$ along the nanotube. Such a grayscale graph is shown in Fig. 5.6a for a spectroscopy measurement on another semiconducting nanotube. $dI/dV$ curves are obtained about 0.15 nm apart along a line of 30 nm. At the top, where $x = 0$, the STM tip is far away from the end. After about 25 nm, the tip moves off the tube and onto the gold. A dark color in this graph corresponds to a high tunneling conductance. Figure 5.6b shows a few $dI/dV$ curves taken from horizontal cross-sections in Fig. 5.6a, at the positions #1, #2 and #3 that are indicated in the grayscale graph. The $dI/dV$ spectrum measured far away from the tube end, curve #1, indicates that this nanotube is semiconducting. The energy gap is not completely visible due to the finite $\pm 0.5$ V voltage window, but the strong rise in $dI/dV$ near zero bias corresponds to the onset of the first valence subband observed for all semiconducting curves. The zero bias anomaly can be clearly observed in the grayscale graph, as the light-gray vertical stripe at 0 V for $0 < x < 8$ nm. The most striking feature is the fading out of the band structure at $x \approx 8$ nm and the appearance of three sharp peaks that show an oscillating behavior. These three $dI/dV$ peaks can for example also be seen in curve #2. In the bottom few
Figure 5.6: Tunneling conductance measured as a function of both the bias voltage and the position along ends of semiconducting nanotubes. a) $dI/dV$ in grayscale plotted against the voltage $V$ and position $x$ along a nanotube length axis. Dark colors correspond to large tunneling conductance. In the bulk of the nanotube ($x < 8$ nm), the STM tip is far away from the end and the local DOS is similar to the semiconducting bandstructure. For $x > 8$ nm sharp peaks arise in the $dI/dV$ that fluctuate in energy as a function of position. At the last few nm, ($x > 26$ nm) the STM tip is off the tube. (b) $dI/dV$ curves that are taken from horizontal cross-sections in (a) indicated with the numbers #1, #2 and #3. (c) $dI/dV$ in grayscale versus $V$ and $x$ for another semiconducting nanotube end. The tip is off the tube at the last few nm, where $x > 13$ nm.

nm, for $x > 25$ nm, the STM tip actually measures $dI/dV$ on the gold substrate. The tunneling conductance here is indeed featureless (curve #3). Measurements on the same nanotube, taken several minutes later showed that the oscillating pattern of $dI/dV$ peaks is highly reproducible. Between measurements, voltage pulses were applied to the STM tip, away from the nanotube, to change the shape of the tip apex. Since this did not change the observed behavior in the nanotube we can exclude artefacts due to the microscopic shape of the tip. The remarkable behavior of oscillating peaks has also been observed on other semiconducting nanotubes. An example is shown in Fig. 5.6c for a semiconducting nanotube. Again, sharp peaks are observed that fluctuate along the tube.

We have no good understanding of all the observed features in $dI/dV$ at the
nanotube ends. It would be useful to know the geometry of the ends, for example whether they are closed or open. The single-walled nanotubes are assumed to be closed by caps during the growth, but it is difficult to confirm this by imaging because of the bluntness of the STM tip. In fact, STM spectroscopy can in principle be used to identify the nanotube ends [9, 36] as has been done by Carrol et. al. [9] and Kim et. al. [14]. They measured sharp resonances in the tunneling conductance at the last few nm at the end of nanotubes and identified these as localize states corresponding to a specific arrangement of pentagons at the end. In our case, sharp peaks also appear but they are found to oscillate in energy position over a large distance, 10-20 nm, which can not be explained by the presence of localized defects alone. Possibly, the gradually changing capacitance between the STM tip and nanotube when the tip scans over the end has to be taken into account. Simulations [37] show that the capacitance between the tube and tip changes at the end over a length scale corresponding to the tip size. Our STM tips are typically 10-20 nm, which is also the scale over which the fluctuation patterns are observed. However, when the tip is displaced a few nm, the change in capacitance should be of the order of a few $10^{-3}$ aF, which can not explain the large energy fluctuations of about 0.1 eV within that distance.

Nanotube kink

As discussed in Sec. 5.2, nanotubes are often continuously bent due to elastic deformations. However, sharp bends or 'kinks' may also appear due to junctions between two nanotubes with different $(n, m)$ indices. Such junctions can be possible when pentagon-heptagon defect pairs are present in the hexagonal carbon network [38, 39, 40]. In principle, nanotubes with a different electronic character can be connected to each other by such kinks, which is of interest for nanoscale electronics. Nanotube kinks have indeed been observed by TEM [41, 42] and AFM [43] imaging. A recent report of the electronic conductance of nanotube kinks provided evidence for the existence of semiconductor-metal and metal-metal heterojunctions [43]. Kink-like sharp bends are occasionally observed in STM topographic images (for example Fig. 5.1c). Figure 5.6a shows a zoomed image of such a sharply bent nanotube. At various positions, indicated by the numbers 1–5, STS measurements were done. The tunnel spectra above the kink are metallic (curve 1 and 2 in Fig. 5.7b) whereas below the kink they are semiconducting (curves 3–5). This result strongly suggests that the kink is a heterojunction between a semiconducting and metallic nanotube.

5.4 Summary

In this paper we surveyed various measurements of the tunneling DOS in single-walled carbon nanotubes on Au(111). From $dI/dV$ tunnel spectra all nanotubes
that showed various chiralities could be classified as either metallic or semiconducting, with energy subband separations that compare well to the theoretical predictions. Discrete energy levels could be measured in the local DOS at low energies for a short metallic nanotube. The measured DOS curves are positioned asymmetrically around zero bias, indicating a shift of the Fermi level towards lower energies. This can be attributed to the difference in work function between the nanotubes and the gold substrate.

Spatially resolved measurements are used to observe changes in the local DOS at interesting topological sites such as nanotube ends and kinks. Measurements on semiconducting tube ends show that sharp conductance peaks appear within the energy gap which fluctuate in energy with position along the nanotube axis in a reproducible pattern. We do not yet have an explanation for all the experimental facts. We obtained also spectroscopy data on a nanotube kink that appears to be a molecular semiconducting-metal heterojunction. These measurements show that spatially resolved STM spectroscopy can be a useful technique to study the electronic structure of carbon nanotubes and may be exploited further to characterize nanotube devices such as kink heterojunctions.
Acknowledgements

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References


[34] L.C. Venema et al., Science 283, 52 (1999).


[37] The program used for the capacitance simulations is FastCap, developed by the Research Laboratory of Electronics at MIT (1992).


Chapter 6

Length control of individual carbon nanotubes by nanostructuring with a scanning tunneling microscope


Abstract

We present a technique to control the length of carbon nanotubes. Individual carbon nanotubes can be locally cut by applying a voltage pulse to the tip of a Scanning Tunneling Microscope (STM). Topographic imaging and STM spectroscopy is subsequently used to investigate the result. The electronic properties of a nanotube can be strongly changed by reducing the size. Current-voltage curves obtained by STM spectroscopy on a 30 nm short tube created from a longer nanotube show a stepwise increase of the current, which is attributed to quantum size effects.

Carbon nanotubes [1, 2] are currently being intensively investigated because of their remarkable electronic and mechanical properties. Nanotubes can be thought of as single graphite sheets wrapped into seamless cylinders. They can be either semiconducting, semi-metallic or metallic, depending on the wrapping angle and tube diameter [2, 3]. Most nanotubes consist of several concentric layers (multi-wall nanotubes), but single-wall tubes have also been found [4]. Recently a method has been developed to synthesize single-wall carbon nanotubes with high yield and structural uniformity [5]. Metallic single-wall nanotubes are predicted to be truly one-dimensional conductors [2, 3]. It is for this reason that these nanotubes are considered as ideal quantum wires. Recent experiments by Tans et al. [6] have demonstrated the possibility to measure electrical transport through individual single-wall nanotubes on nanofabricated electrodes. These measurements, performed at low temperatures, showed that the transport characteristics
can be adequately described by taking into account single-electron tunneling and quantum-size energy-level splitting [6, 7].

The quantum transport properties of nanotubes strongly depend on their size and their capacitance to the environment. Control of the size of the nanotubes would allow investigation of the quantum transport properties at different length scales. Up till now it has not been feasible to control the length or diameter of nanotubes. In this Letter, we present a technique to cut nanotubes into shorter sections by nanostructuring with a Scanning Tunneling Microscope (STM). STM also allows investigation of the nanotubes before and after the cutting by topographic imaging and STM spectroscopy (STS). We demonstrate the possibility to strongly change the electronic properties of a nanotube by reducing its length by use of STM nanostructuring.

Carbon nanotubes are deposited from a dispersion in 1,2 Dichloroethane onto single-crystal Au (111) surfaces. The samples are dried in air. The nanotubes were synthesized by a laser vaporization technique as described in Ref. [5] and consist mainly of ~1.4-nm diameter single-wall nanotubes. The nanostructuring experiments have been carried out with an ultra-high-vacuum Omicron STM at room temperature and a home-built 4K STM [8]. The latter has been used mainly in combination with STS measurements. All measurements are performed with Pt(90%)Ir(10%) tips, which are mechanically cut in ambient. Individual carbon nanotubes can easily be imaged on the atomically flat Au surface, both at room temperature and at 4 K. On a granular Pt film nanotubes appeared to be too mobile [9]. Figure 6.1 shows a large-scale image obtained on Au (111) at room temperature. Several nanotubes are visible as well as atomic steps in the gold surface. Figure 6.2a shows a room-temperature image of an individual nanotube
Figure 6.2: Room temperature STM images of a carbon nanotube before (a) and after (b) it was cut at the position on the tube marked with the arrow by applying a voltage pulse of -6.5 V. From the line profile (c), taken along the white line in (a), the diameter of the tube is found to be about 1.4 nm. The image size is 125 x 125 nm².

together with a line profile through the molecule (Fig 6.2c). The apparent full width at half maximum of the nanotube (~5 nm) is determined by the tip size. From the height the diameter of the tube is found to be ~1.4 nm, which is a typical value.

We have found that it is possible to cut nanotubes in a controlled way by STM nanostructuring. Tubes are cut by the following procedure: During imaging, scanning is interrupted and the tip moves to a selected position on the nanotube. Feedback is then switched off and a voltage pulse between tip and sample is applied for a specified period. After this voltage pulse, the feedback is again switched on and the tip is moved back to the position where the scanning was interrupted. Scanning is then resumed. A break in the nanotube on the selected position is visible if the cutting has succeeded. Figure 6.2b shows the result of a voltage pulse of -6.5 V on the position marked in Fig. 6.2a. It appears that the cutting procedure is a reproducible technique to shorten tubes. Figure 6.3 shows an example where a nanotube was cut at 4 different positions. Imaging is typically done at a bias voltage of 100 mV and tunnel current of 20 pA. For all cutting experiments we have used a pulse length of 1 ms, but different voltages of both positive and negative sign. The lower limit for the voltage necessary to cut a tube is about 4 V. Voltage pulses of 3.5 V or lower were never successful. With voltages above 5 V, tubes are always cut. The sign of the voltage appears
not to be relevant. The determining parameter in the cutting process turns out to be the voltage rather than the current. Applying a very high tunnel current up to 50 nA at low voltages does not result in any change in the nanotube. The same procedure to cut nanotubes was also successful at 4 K.

The gap in the tube which arises after a cutting event is typically in the order of 5 to 10 nm. During the voltage pulse, carbon material from the nanotube directly under the tip is removed. Occasionally it partly stays in or near the gap, as is observed from STM images. For example in the upper left corner of Fig. 6.3, two carbon particles are visible as white dots of ~5 nm in and near the gaps in the nanotube. In most cases material is picked up by the tip, which is apparent from a sudden degradation of the imaging quality after a cutting event. By applying a voltage pulse of 6 V on a bare part of the gold substrate the tip can be cleaned again, and the quality of STM imaging restored. It can be confirmed that the tip is indeed free from dirt by carrying out STS on the bare gold substrate. The resulting current-voltage (I – V) curve will be linear, as is expected for a metal substrate, only if the tip is clean.

From our observations it can be concluded that the tubes can only be cut by applying a relatively high voltage. We speculate that electrons injected into the nanotubes with a minimum energy of about 4 eV may break up the carbon-carbon (C-C) bonds in the nanotube. The bonding of the hexagonal carbon lattice on the surface of the nanotubes can be described by a sp² hybridization with a small admixture of sp³ character due to the curvature. The bond energies in this lattice will be in between the bond energy of 3.6 eV for a single C-C bond and 6.3 eV for a double C=C bond. The minimum voltage of about 4 V to break up a tube is indeed within this range [10].

The length control of nanotubes provided by the cutting technique may be
used to investigate the electrical properties of very short nanotubes. Here we report an example where the $I-V$ characteristics observed by STM spectroscopy at 4 K changed dramatically after a long tube was shortened to a 30 nm tube section (Fig. 6.4). Before the cutting event, $I-V$ curves taken at different positions on the nanotube were approximately linear. No gap was observed near zero bias, indicating that the nanotube exhibits metallic behavior. By contrast, the $I-V$ curves on the shorter section made from the same tube show a clear step-like behavior of the current. The $I-V$ curves on the bare gold near the tube were linear, indicating that the tip is clean. We attribute these current steps to discrete energy states of the tube which line up with the tip Fermi level at increasing voltage. Discrete energy states result from quantum confinement of electrons in the length direction of the tube. The separation between the energy states ($\Delta E$) scales inversely linear with the nanotube length. In transport experiments, $\Delta E$ for a 3 $\mu$m tube was found to be $\sim 0.4$ meV [6]. We thus expect $\Delta E$ to be in the order of 40 meV for a 30 nm tube. This corresponds well to the observed step widths which vary between 30 meV and 75 meV. Single-electron tunneling due to Coulomb charging has been shown to be the dominant low-bias feature in electrical transport measurements [6, 7]. In our case, Coulomb charging is expected to be less relevant since the nanotube makes contact to the metal substrate over its full length. This results in a large capacitance of the tube to the substrate and accordingly a small Coulomb charging energy. The $I-V$ curve can not be explained by a Coulomb staircase because the steps are not equidistant.
Summing up, we have presented a method to control the length and therefore the electrical properties of individual nanotubes by STM nanostructuring. The technique of cutting nanotubes into shorter sections may also be useful for the future development of nanotechnology. Construction of devices on a molecular scale can be envisioned, where structuring and manipulation of individual nanotubes by STM is used.

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References

[10] It is possible that the break-up mechanism bears a resemblance to the STM-induced dissociation of Si-H bonds as reported by T. C. Shen et al., Science 268, 1590 (1995).
Chapter 7

A mechanism for cutting carbon nanotubes with a scanning tunneling microscope

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Abstract

We discuss the local cutting of single-walled carbon nanotubes by a voltage pulse to the tip of a scanning tunneling microscope. The external tip voltage (| V | ≥ 3.8 ± 0.2 eV) is the key physical quantity in the cutting process. After reviewing several possible physical mechanisms we conclude that the cutting process relies on the weakening of the carbon-carbon bonds through a combination of localized particle-hole excitations induced by inelastically tunneling electrons and elastic deformation due to the electric field between tip and sample. The excitations occur around 3.6 eV which agrees with the experimental threshold voltage for cutting of 3.8 ± 0.2 V. The carbon network will release part of the induced mechanical stress by forming topological defects that act as nucleation centers for the formation of dislocations, leading eventually to bond-breaking.

7.1 Introduction

Since the discovery of carbon nanotubes in 1991 [1] a lot of progress has been made in the synthesis as well as in the characterization of the electronic, optical and mechanical properties of these remarkable molecules [2-5]. They are often regarded as promising structures to use as components in submicrometer-scale devices [6, 7] and as nanocomposites [8]. A carbon nanotube can be thought of as
a graphite sheet rolled up seamlessly into cylinders with diameters in the range of 0.6-30 nm and lengths of many \(\mu\)m's. Depending on the synthesis conditions they can appear in multi-walled or single-walled configurations [1, 9, 10]. They can be either metallic or semiconducting which is critically determined by the chirality and the diameter [3]. Furthermore, they are mechanically robust and flexible and have a low mass density. The special geometry and electronic properties makes carbon nanotubes excellent candidates for mesoscopic quantum wires. Low temperature electronic transport measurements on single-walled nanotubes showed that they behave as ideal quantum wires [11]. The electronic properties can be studied at small length scales by cutting nanotubes into shorter pieces with voltage pulses applied to the tip of a scanning tunneling microscope (STM) [12]. Discrete energy states could be measured with STM spectroscopy in a short tube [12, 13]. The energy level separation scales with the inverse length of the nanotube, consistent with a 1D particle-in-a-box model [13,14]. The possibility to control the length of nanotubes by the cutting technique is of interest for various applications of carbon nanotubes in nanoscale devices [5, 6].

In this paper we discuss a number of possible mechanisms that can explain the cutting of single-walled tubes by a voltage pulse to the STM tip. In the following section the experimental data is briefly described. In Sec. 7.3, we discuss various relevant physical mechanisms that can result in breaking of tubes and select the most likely scenario. We analyze the mechanisms involved in more detail in Sec. 7.4. The paper ends with a short discussion and outlook.
7.2 Experimental results

Figure 7.2: Cutting efficiency versus applied voltage \( V \). Efficiency is defined as the number of successful cuts divided by the total number of applied pulses at that specific voltage. About 150 voltage pulses were applied on various nanotubes. The feedback current was varied between 20 pA and 1 nA, the feedback voltage between 0.1 V and 3V.

7.2 Experimental results

As found earlier, individual carbon nanotubes can be locally cut by applying a voltage pulse to the tip of a scanning tunneling microscope (STM) [12]. The carbon nanotubes that were studied were single-walled, synthesized by a laser vaporization technique and consisted mainly of \( \sim 1.4 \) nm diameter nanotubes [9]. Samples were prepared by depositing a dispersion of nanotubes in 1,2-dichloroethane onto single-crystal Au(111) surfaces. The experiments were done both at room temperature and at 4 K.

Nanotubes are cut by the following procedure: During imaging of a nanotube in constant-current mode, scanning is interrupted and the STM tip moves to a selected position on the nanotube. Feedback is then switched off and a voltage pulse between tip and sample is applied for 1 ms. After this pulse, the feedback is switched on again and scanning resumes where imaging was interrupted. The distance between the STM tip and the nanotube during a pulse is determined by the settings for the feedback current and voltage. Fig. 7.1b shows an example of a nanotube that has been cut into various smaller tube pieces as a result of voltage pulses of -3.75 V applied at the positions marked in Fig. 7.1a.

The cutting efficiency as a function of the bias voltage applied during a pulse is shown in Fig. 7.2. This experimental result provides essential input for the theoretical modeling of the cutting mechanism described in the next sections. The efficiency at a specific voltage is defined as the number of successful cutting events divided by the total number of applied pulses at that voltage. A large
number (about 150) of voltage pulses were applied at room temperature in a range of 1 to 6 V, at positive and negative polarity. The pulses were applied on various nanotubes, both semiconducting and metallic. To study the dependence of cutting efficiency on the distance between the STM tip and the nanotube during a pulse, feedback currents were varied between 20 pA and 1 nA and feedback voltages between 0.1 and 3 V were used. No dependence of cutting efficiency on the tunnel distance was found. Pulses applied with various feedback currents and voltages are therefore included in the same graph of Fig. 7.2. The main experimental results are listed below:

- A threshold for the voltage during a pulse of $3.8 \pm 0.2$ V is found for cutting nanotubes, independent on polarity. Below 3.5 V, nanotubes could almost never be cut. Above 4 V, tubes were almost always cut.

- The cutting efficiency is independent of the feedback tunnel current or voltage. The tunnel resistance has been varied over three orders of magnitude, which should change the tunnel distance significantly. This suggests that the physical quantity triggering the cutting is the voltage, rather than the electric field.

- The cutting procedure appears to be reproducible for different types of nanotubes. There is no dependence on the electronic character i.e. semiconducting or metallic, of a tube.

- Nanotubes can be cut at room temperature as well as at 4 K.

- Nanotubes within bundles can be cut as efficiently as isolated single-wall tubes (see for example, Fig. 7.3).

- Decreasing the tunnel distance considerably, by increasing the tunnel current beyond 1 nA, results in moving the nanotubes away laterally by the STM tip during scanning.

Figure 7.3: Room temperature image of a bundle of nanotubes. An individual nanotube within the bundle, indicated by the arrow, could be cut by a voltage pulse.
Figure 7.4: Room temperature images of a strongly bent nanotube (a) before and (b) after it was cut near the two positions marked with crosses in (a). The three separated tube parts appear to be displaced as a result of the cutting events. Image (b) is an enlargement of the area within the square in (a).

- The separation between nanotube ends created by a cut varies significantly in size from a few nm to 20 nm.

Often, tube parts beneath the STM tip are picked up during a pulse. This usually leads to degradation of the tip quality. Cleaning of the tip can then be done by applying voltages on the gold surface, away from the nanotube. Sometimes, the tube ends are displaced after the cut. Fig. 7.4 for example shows a strongly bent nanotube on which two voltage pulses were applied near the marked positions. Fig. 7.4b shows that the three tube parts separated by the cuts were moved significantly by the cutting events. Most likely, the nanotube was fixed on the substrate under some strain that was released by the cutting.

### 7.3 Physical concepts for the cutting mechanism

In this section we survey a number of physical mechanisms that can lead to the breaking of nanotubes. These mechanisms are related to each other in various degrees. As a starting point, a strong binding between nanotubes and the substrate is necessary either chemically or through van der Waals dispersion forces.
Based on experiments [15] and first-principle calculations [14], we expect the tubes to have a good binding to the gold substrate. It is typically of the order of 2 meV/atom and adds up to a significant amount of binding energy for a long nanotube.

1. "Shear" pressure; Crashing the STM tip into a nanotube could be a possible cutting mechanism. However, experimentally we found that the tubes are moved laterally when the tip is brought close to the tube. This is related to the large reversible elastic response (flexibility) exhibited by the carbon nanotubes [16]. Simulations of C<sub>60</sub> molecules impact on carbon nanotubes has shown that even large radial forces produce reversible elastic distortions indicating that crashing the tip onto the tube is not be an efficient method to cut [17].

2. Crack propagation; This is related to the propagation of voids and cracks already present in as-grown nanotubes under low (tensile) loads. However, there is no evidence, from STM or otherwise, for the presence of local defects or cracks in the SWNT material studied here. This mechanism is hence not considered to be important.

3. Collective excitation (plasmon) mechanism; Plasmons excited by inelastic electron scattering of the tunneling current can decay into electron-hole pairs (or other excitations) that induce a polarization in the tube, eventually leading to a break through local heating and atom evaporation. In the case of carbon nanotubes due to their particular cylindrical geometry we expect to have a π-plasmon excitation at about 5 eV [18]. This is also confirmed experimentally [19] for SWNTs of ~ 1.4 nm diameter. The decay of the plasmon excitation into atom evaporation is a well-known phenomenon in metallic clusters where the surface-plasmon energy is of the order of the binding energy leading to atom-evaporation as an effective decaying mechanism of the collective excitations [20]. In the case of tubes with an internal binding energy greater than ~ 7 eV/atom (as for most carbon solids; see Table I) however, multiple-plasmon excitations or other mechanisms need to be active to induce transitions which weaken the carbon bonds. We expect therefore that this is not the main mechanism responsible for cutting nanotubes. However, it can enhance the probability of electronic excitations (see below).

4. Localized particle-hole excitations; This mechanism is concerned with the excitations of localized σ-electrons to states of π* character near the Fermi level. These electronic excitations leave localized σ-holes behind which weakens the C-C bonds. Electrons tunneling inelastically between tip and tube are the source for these excitations. The density of states (DOS) for a (10,10) nanotube, which is metallic, is shown in Fig. 7.5. Near the Fermi


<table>
<thead>
<tr>
<th>bond</th>
<th>( k \text{ (N/m)} )</th>
<th>( D_o \text{ (eV)} )</th>
<th>( R_{eq} \text{ (Å)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>460</td>
<td>4.0</td>
<td>1.11</td>
</tr>
<tr>
<td>C-C</td>
<td>440</td>
<td>3.4</td>
<td>1.52</td>
</tr>
<tr>
<td>C=C</td>
<td>960</td>
<td>7.4</td>
<td>1.34</td>
</tr>
<tr>
<td>C≡C</td>
<td>1560</td>
<td>10.0</td>
<td>1.21</td>
</tr>
</tbody>
</table>

Table 7.1: Typical spring constants \( k \) [N/m], energy \( D_o \) [eV] needed to break a bond at \( T=0 \), and equilibrium distances \( R_{eq} \) (Å) for different carbon bonds. In rough terms displacing an atom by 0.1 Å corresponds to an elastic energy change of 5-10 eV. (From ref. [21]).

level, the DOS is finite and constant. At higher energies, sharp peaks can be observed which are the Van Hove singularities at the subband onsets [22]. At above/below 3.6 eV from the Fermi level the interband excitations involve states with a predominant \( \sigma^*/\sigma \)-localized character with a small curvature induced \( \sigma - \pi / \sigma^* - \pi^* \) hybridization. The excitations of the \( \sigma / \sigma^* \) states have been found in nanotubes to lead to a broad spectral feature in the experimental electron-energy loss-spectra close to the \( \pi \)-plasmon excitation [19], similar to the case of \( \sigma - \pi^* \) interband transitions in graphite [3]. The interband excitations involving localized \( \sigma \)-states introduces a natural energy threshold for the cutting process to take place around 3.6 eV. This agrees quite well with the experimental observation of a sharp threshold voltage for cutting of 3.8 eV that is independent of polarity.

5. **Field-induced elastic deformation**: The large electric field from the tip apex causes significant changes (a few %) in the C-C bond lengths. This introduces a mechanical instability in the tube that triggers the formation of topological defects [23] that dynamically evolve towards breaking of the tube. This effect is enhanced by the mechanical stress introduced in the nanotube by the electronic excitation of localized \( \sigma \)-states (as discussed in the previous mechanism).

The combination of the last two processes is likely to constitute the basic mechanism for the cutting of nanotubes. The cutting process is probably triggered by the inelastic electron excitations of about 3.6 eV which accounts for the sharp voltage threshold observed in the experiments. The C-C bonds are further weakened by the mechanical stress induced by the large electric-field between tip and sample. The induced stress acts on the tube for the whole 1 ms during the applied voltage pulse which is long enough for the formation and propagation of defects. In the next section some more details on the processes involved are discussed.
Figure 7.5: Density of states (DOS) of an armchair (10,10) single-wall nanotube for various applied electric fields perpendicular to the tube axis. The electric field increases the DOS at the Fermi level. For comparison, the DOS for a single graphene layer is also shown in the top panel (dashed line).

7.4 The cutting mechanism

7.4.1 Localized electronic excitation

In order to understand better the role of electronic excitations in the bond-weakening and cutting process we show in Fig. 7.5 how the density of states of a (10,10) SWNT is modified by an external applied electric field in the direction perpendicular to the tube axis. Here the structural relaxation and electronic calculations were done in the framework of the ab-initio total-energy density-functional pseudopotential theory [24]. In the calculations shown in Fig. 7.5 the field acts on the whole tube for fixed atomic coordinates. Results are shown for typical electric fields in the experimental setup (up to 1 eV/Å). A detailed calculation should take into account the spatial variation of the applied field related to the tip-size. In that case there are distinct regions: one far from the tip where the electronic properties of the tube are dictated by the isolated tube and the other just beneath the tip where the electronic properties are modified by the applied field. From Fig. 7.5 we see that the applied field results in the appearance of
localized levels in an energy region close to the Fermi level which increases the DOS. This effect is related to the bond-weakening and bond-length increase in carbon nanotubes under an applied external voltage. The increase of the DOS near the Fermi level enhances the number of possible transitions that can take place. Semiconducting nanotubes have a DOS comparable to that of metallic nanotubes, but have an energy gap with zero DOS near the Fermi energy. However, the electric field will induce states within the gap, similar to the increase of DOS near the Fermi level for metallic nanotubes. The localized particle-hole excitations will therefore also take place in semiconducting nanotubes. This corresponds to the experimental observation that semiconducting nanotubes are as efficiently cut as metallic tubes.

It may appear that any electronic mechanism should be current dependent. However, the number of broken bonds is far less than the number of available electrons in the cutting process. A large current flows during a voltage pulse (more than 50 nA) which means that we are in a saturated regime where cutting can in principle be achieved independent of the current. This situation can be compared to the situation of cutting Si:H bonds with an STM, where the desorption yield was found to be independent of bias or current once the bias is large enough [25]. The formation of topological defects is a natural way of releasing the excitation energy and triggers the breaking process.

7.4.2 Field-induced elastic deformation and breakdown

We can study the tip-field induced mechanical stress in the nanotube within a macroscopical approach. Our argument for using a macroscopic model is that the specific elastic constants of single-walled nanotubes determined from experiments follow quite well the predictions for the macroscopic elasticity theory (in terms of the Young’s modulus, Poisson ratio and torsion and bending elastic constants [26]). Although a proper description of the fracture mechanics is a complex phenomenon that requires both macroscopic and microscopic descriptions, we rely on a continuous model to get a first estimate of the parameters involved in the process. The typical energy of the distortion process is thus such that it corresponds to bond-breaking energies for carbon compounds (see Table 1) or to displacements which fulfill a Lindeman melting criterion [27] of a 10% change in bond distance.

We consider the tube as a thin hollow rod which is clamped to the surface by van der Waals forces. In the cutting process, the tube is distorted by the tip in a region the size of the tip (length-scale L). For a hollow tube (inner radius a and outer radius b) of bending inertia I=π(b^4 - a^4)/4 and Young’s modulus Y, we expect a relative deformation δ for an applied force F of [28]
Table 7.2: Typical elasticity parameters $Y$ (Young's modulus) and $\sigma_Y$ (yield stress) for different carbon materials compared to steel. Due to the large anisotropy in the elastic constants of graphite we add those in parenthesis. They are relevant for the elastic strength and flexibility of the single wall nanotubes (SWNT).

$$\delta \approx \frac{FL^2}{NY}\frac{1}{T}$$  \hspace{1cm} (7.1)

where $N$ is a number of order 10-100 depending on details of the modeling such as force distribution and boundary conditions. We estimate the force $F$ from the interaction between a sphere of radius $R$ (representing the tip curvature) and a tube of outer radius $b$ (7.5 Å in our situation) to be [31]:

$$F = \frac{e_0}{d} \sqrt{Rb(2\pi V)^2}.$$  \hspace{1cm} (7.2)

where $V$ is the applied bias voltage. We see that the force depends inversely linear with the separation. In this equation we have neglected the hollow inner part of the tube that would reduce the force by approximately 20%. With $V=4$ Volts, a distance of $d=10$ Å and $R=100$ Å (a reasonable value in STM when simulating a tip with a sphere [32]) we find a force of 15 nN. This is independent of the polarity of the bias, thus the situation is symmetric as is also found experimentally. Soler et al. [33] found that a graphite surface would experience a 1 Å deformation in an STM configuration for a force of the order of 1 nN. Notice however that the relevant elastic constants in their case are related to the weak interlayer bonding in graphite as reflected in the corresponding $c_{33}$ and $c_{44}$ elastic constants. These are much smaller than the $c_{11}$ constant (reflecting the strong intralayer $sp^2$-like bond) which is relevant in our case (see Table II) [34].

Using now Eq. 7.1 and inserting $Y \sim 1$ TPa, we find that for a distortion $\delta/L$ higher than 10% Lindeman criterion, the cutting length $L$ has to be at least about 5-6 nm (of course strongly depending on $N$ above).
It has been shown that beyond a critical value of tension (about 5% for a (10,10) armchair nanotube) the nanotube releases its excess strain by the formation of topological defects [23]. A plausible mechanism for the creation of defects is bond rotation (also called Stone-Wales transformation [35]) which produces two pentagons and two heptagons (see Fig. 7.6). These defects behave as nucleation centers for the formation of dislocations under continued applied strain and eventually lead to breakdown.

### 7.5 Conclusions and Outlook

From the previous discussion we know that the applied voltage at the STM tip creates: (i) excitation of localized $\sigma$-bonding states and a change in the density of states around the Fermi level making the tubes more metallic-like, ii) an overall distortion of the region beneath the tip, leading to the formation and evolution of strain-induced topological defect. The field induced bond breaking through localized excitations and the overall distortion of the region beneath the tip are responsible for the cutting mechanism with the threshold voltage of $\sim 4$ volts. The proposed mechanisms rely only on the applied voltage which is responsible for the stress and change of DOS in nanotubes. It appears that within the experimental values, the tip-tube distance does not change the results. The lateral distance is as important to consider as the perpendicular one. The tip parameters versus the lateral extent of the cut needs to be investigated more carefully.

It would be interesting to attempt the cutting in multi-walled carbon nanotubes also. The cutting will probably not work for these nanotubes since the inner layers are able to withstand the stress acting on the outer layers. Furthermore we expect the inter-tube van der Waals interaction in multi-walled nanotubes to be strong enough to partially release the concentration of elastic strain so that only atoms of the outer surface will be affected. This is different to the case...
of nanotubes in bundles, where the cutting process is as effective as for isolated nanotubes (see Fig. 3). In this case the other tubes in the bundle act as a global support similar to the gold substrate for the isolated SWNTs.

It may be interesting to see if the breaking process is accompanied by photon emission to any significant degree to gain further information about the energetic of the possible processes. Photon emission provides a signal that is dependent on the local physical environment beneath the tip with a spatial resolution determined by the size of the collective mode (plasmon) involved in the photon emission. Typical resolution can be estimated as $\sqrt{Rd} \sim 20\text{Å}$ using our length scales introduced above [32]. A related topic would be field emission from nanotubes.

To summarize, we have characterized in detail the possible mechanisms responsible for the breaking up of tubes as found experimentally. Nanotube cutting is a promising technique for the emerging field of nano-manipulation and nanodevices. More studies will have to be made to understand all the interesting physics taking place at this nanoscale level.

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References


References


[18] Note that the imaginary part of the inverse dielectric function for graphite (sheet) has a peak around 6-7 eV, related to a collective plasma excitation [3]. Geometric arguments indicate that for a cylinder this excitation should move down in energy by $\sqrt{2}$.


[22] A. Rubio, Appl. Phys. A 68 275 (1999). Although interactions with the metallic substrate or other tubes introduces some modifications in the shape of the van Hove singularities and the appearance of pseudogaps close to the Fermi level, the main electronic structure is well described by the isolated tube.


[31] B. Derjagin and Z. Kolloid 69, 155 (1934); L.R. White and J. Colloid interface Sci. 95, 286 (1983). To compute the force we use the Derjagin approximation, that was later on elaborated by White. In this approach, the force between two objects is related to the curvatures involved and the interaction energy $E(d)$ per unit area for the corresponding planar situation: $F = 2\pi R_{eff} E(d)$ where $d$ is the separation between the two solids (average distance between tip and tube in our situation) and $R_{eff}$ expresses the curvatures involved and is given by: $R_{eff} = R \sqrt{\frac{b}{R+b}} \approx \sqrt{Rb}$. The latter approximation is valid when $R \gg b$, which applies to our case. The interaction energy for two planar surfaces making up a capacitor with a bias voltage $V$ is the classical charging energy: $E(d) = \frac{1}{2}CV^2$. For $C=4\pi \epsilon_0 / d$ (per unit area) we then get the final result for the force between an STM tip and a nanotube given in Eq.(7.2).


[34] The Young's modulus, $Y=k/r_o$ where $r_o$ is an interatomic distance, will be of the order of TPa (see Table II). Since the shear stress $\mu = Y/(1+\nu)$ (where $\nu \approx 0.26$ is the Poisson [26]) is of the same order of magnitude as the Young modulus, we concentrate the discussion on the strain.

Chapter 8

Imaging electron wave functions of quantized energy levels in carbon nanotubes


Abstract

Carbon nanotubes provide a unique system to study one-dimensional quantization phenomena. Scanning tunneling microscopy is used to observe the electronic wave functions that correspond to quantized energy levels in short metallic carbon nanotubes. Discrete electron waves are apparent from periodic oscillations in the differential conductance as a function of the position along the tube axis, with a period that differs from that of the atomic lattice. Wave functions can be observed for several electron states at adjacent discrete energies. The measured wavelengths are in good agreement with the calculated Fermi wavelength for armchair nanotubes.

Carbon nanotubes are molecular wires that exhibit fascinating electronic properties [1]. Electrons in these cylindrical fullerenes are confined in the radial and circumferential directions and can only propagate in the direction of the tube axis. Nanotubes are therefore interesting systems for studying the quantum behavior of electrons in one dimension (1D). Limiting the length of a carbon nanotube leads to a 'particle-in-a-box' quantization of the energy levels. Such discrete energy levels have been observed in transport experiments on individual nanotubes and ropes [2, 3]. The electron wave functions corresponding to these discrete states can in principle be imaged by Scanning Tunneling Microscopy (STM). The well-known STM work on quantum corrals demonstrated the possibility to directly image wave patterns in the local density of states of a 2D metal
Figure 8.1: STM topographic images of individual single-wall carbon nanotubes. (a) Example of a nanotube shortened by applying a voltage pulse to the STM tip above the tube ([11]). (b) Atomically resolved image of an armchair nanotube. The arrow denotes the direction of the tube axis. This nanotube can be identified as armchair-type because the hexagon rows run parallel to the direction of the tube axis (cf. overlay of the graphene lattice). The tube diameter is 1.3 nm. This image has been taken before the tube was shortened to 30 nm. Feedback parameters are $V = 0.1$ V, $I = 20$ pA. Images were taken in constant-current mode.

...surface [4]. Here, we apply this technique to map out the wave functions of single molecular orbitals in short metallic carbon nanotubes. Electronic wave functions are apparent from periodic oscillations in the low-bias differential conductance along the tube axis. To our knowledge, this is the first time that wave functions of discrete electron states have been imaged in a molecular wire.

Previous STM spectroscopy studies were done at a large ($\sim 2$ eV) energy scale to investigate the bandstructure of nanotubes [5, 6]. These experiments confirmed the prediction [7] that carbon nanotubes can be semiconducting or metallic depending on the tube diameter and the chiral angle between the tube axis and hexagon rows in the atomic lattice. In this paper we focus on the low-energy ($\sim 0.1$ eV) features of short metallic nanotubes which exhibit quantum size effects. Single-wall nanotubes with a diameter of about 1.4 nm were deposited on Au(111) substrates [5, 8]. On most tubes we were able to obtain STM images with atomic resolution [5] which allows to determine the chiral angle and diameter of the tubes[9]. The nanotube of Fig. 8.1b is identified as an ‘armchair’ tube...
Figure 8.2: STM spectroscopy measurements on a 30 nm long armchair tube. (a) Current-voltage $I(V)$ characteristics on the tube shown in Fig. 8.1b, taken at positions about 0.18 nm apart [data points 1 to 4 in (c)] on a straight line along the tube axis. Current steps correspond to discrete energy states entering the bias window. (b) Differential conductance $dI/dV$ versus $V$, as calculated from the $I(V)$ curves. Peaks appear at the voltage positions of current steps in the $I(V)$ curves. (c) Differential conductance $dI/dV$ as a function of position along the tube. Data was taken at a bias voltage of $-0.08 \text{ V}$. Data points 1 to 4 indicate the positions at which the four $I(V)$ curves plotted in (a) and $dI/dV$ curves in (b) were obtained.

from the good fit between the observed hexagon structure and the overlay of the graphene lattice. Armchair tubes have a nonchiral structure because the hexagon rows are parallel to the tube axis. This type of tubes has metallic properties [7]. Current-voltage $I(V)$ characteristics measured up to $\pm 0.5 \text{ V}$ on the armchair tube of Fig. 8.1b indeed demonstrate the simple linear behavior expected for a metallic tube. Such $I(V)$ measurements are done by keeping the STM tip stationary above the nanotube, switching off the feedback, and recording the current as a function of the voltage applied to the sample. In all our experiments the STM is operated at $4.2 \text{ K}$ [10].

In the experiments reported here, the armchair tube of Fig. 8.1b was shortened to a length of about 30 nm. This was achieved by locally cutting the tube by applying a voltage pulse of $+5 \text{ V}$ to the STM tip at a position on the tube
located 30 nm from its end [11]. STM spectroscopy was then carried out near the middle of the short tube. \( I(V) \) curves on the shortened nanotube show a step-like behavior (Fig. 8.2a), which we ascribe to quantum size effects. Steps in \( I(V) \) correspond to quantized energy levels entering the bias window upon increasing the voltage. Current steps at a voltage \( V \) thus correspond to discrete electron states at energy \( E = E_F + \alpha eV \), with \( E_F \) the Fermi energy, \( e \) the electron charge, and \( \alpha \approx 1 \) [12]. The experimentally observed width of the current plateaus between the steps ranges from 0.05 V to 0.09 V. The plateau width is determined by the total energy to add an electron to the tube. This addition energy consists of a combination of finite-size level splitting and the Coulomb charging energy that is due to the small capacitance of the tube. A simple estimate for the energy level splitting for a tube of length \( L = 30 \) nm is given by \( \Delta E = h v_F / 2L = 0.06 \) eV, where \( v_F = 8.1 \cdot 10^5 \) m/s is the Fermi velocity and \( h \) is Planck's constant. The capacitance of a nanotube lying on a metallic substrate can be approximated by the formula for a metallic wire parallel to a conducting plane, \( C = 2 \pi \varepsilon_0 L / \ln[(d + (d^2 - R^2)^{1/2})/R] \) [13], where \( \varepsilon_0 = 8.85 \cdot 10^{-12} \) F/m, \( d \) is the distance from the wire axis to the plane and \( R = 0.65 \) nm is the wire radius. Estimating \( d \approx 0.9 \) nm gives \( C \approx 2.0 \) aF, which yields a charging energy \( E_C = e^2 / C = 0.08 \) eV. Both numbers are in the same range as the observed plateau width. Since the charging energy and level splitting are of about equal magnitude, an irregular step spacing in the \( I(V) \) curve is expected [14]. For this report, the main point is that each step corresponds to a discrete energy level entering the bias window.

The central result of our experiments is that the tunneling conductance measured for such discrete states is found to oscillate along the length direction of the nanotube with a period different from the atomic lattice constant. \( I(V) \) spectroscopy curves were obtained at different locations on top of the nanotube along a line parallel to the tube axis in constant-current mode. At every point, spaced 23 pm apart, the feedback was switched off to take an \( I(V) \) curve, starting at the bias voltage used for feedback in the constant-current mode. Figure 8.2a shows several \( I(V) \) curves obtained in this way at different positions. The current displays a clear variation between maximum (dashed curves) and minimum values (solid curves) for negative bias voltage. Peaks in the differential conductance \( dI/dV \) (Fig. 8.2b) appear at the voltage positions of current steps in the \( I(V) \) curves. The height of the \( dI/dV \) peaks varies periodically with position \( x \) along the tube axis, as shown in Fig. 8.2c. The period of these oscillations in the differential conductance is about 0.4 nm, which clearly differs from the lattice constant of 0.25 nm. The periodic variation of \( dI/dV \) versus \( x \) can be attributed to the electronic wave functions in the nanotube.

The wave functions of several adjacent energy levels can be displayed simultaneously by plotting the differential conductance \( dI/dV \) as a function of the voltage and the position \( x \) along the tube (Fig. 8.3a). Wave patterns can be observed for 4 different energy levels appearing at bias voltages 0.11 V, 0.04 V, 0.00 V
Figure 8.3: Spectroscopy and topography line scans along the nanotube which show electron wave functions of discrete electron states as well as the atomic lattice. (a) Differential conductance $dI/dV$ (in gray scale) against the bias voltage ($y$-axis) and the position on a straight line along the tube ($x$-axis). This plot results from about 100 $I(V)$ curves taken at positions about 23 pm apart along the tube axis. Electron wave functions of 4 different energy levels are observed as periodic variations in $dI/dV$ along the tube at voltages of 0.11 V, 0.04 V, 0.00 V and −0.05 V. A horizontal row of about 7 $dI/dV$ maxima is observed at each energy level. Note that the exact voltages at which the peaks in $dI/dV$ appear in Fig. 2 and Fig. 3a are different [15]. (b) $dI/dV$ profiles at the 4 resolved energy levels. Fits of the function $dI/dV = A\sin^2(2\pi x/\lambda + \phi) + B$ are plotted as dashed curves. The resulting wavelengths $\lambda$ are given above the curves on the right. Curves are vertically offset for clarity. (c) Topographic height profile $z(x)$ of the nanotube. STM topographic imaging and spectroscopy was performed simultaneously by scanning the tip along the tube and recording both the tip height (with feedback on) and $I(V)$ spectroscopy curves (feedback off). Feedback parameters are $V = 0.3$ V and $I = 100$ pA.
and $-0.05 \text{ V}$ [15]. At each level a horizontal row of about 7 maxima is resolved in $dI/dV$ as a function of position $x$ along the tube (see Fig. 8.3b for the 1D spatial profile of the wave functions belonging to these states). The experimental quantity $dI/dV$ is a measure for the squared amplitude of the quantized electron wave function $|\psi(E, x)|^2$ [16]. The curves in Fig. 8.3b are fitted with a function of the form $dI/dV = A \sin^2(2\pi x/\lambda + \phi) + B$, which represents a simple trial function for $|\psi(E, x)|^2$. The separation of about 0.4 nm between peaks in $dI/dV$ corresponds to half the wavelength $\lambda$, because $dI/dV$ measures the square of the wave function. The wavelengths obtained from the fitting procedure vary from 0.66 to 0.76 nm (Fig. 8.3b). Other measurements on the same tube reproduced values for $\lambda$ in the range of 0.65 – 0.8 nm. From repeated spectroscopy measurements such as Fig. 8.3a on the same tube, we estimate the error in the wavelength to be about 0.02 nm. Note that the $dI/dV$ maxima in Fig. 8.3a occur at different positions $x$ for the different horizontal rows. This excludes many experimental artifacts such as for example oscillations in the STM and provides compelling evidence for the interpretation in terms of standing electron waves. Typically only a small number ($\sim 4$) of discrete levels were observed around zero bias. At larger bias voltages (beyond the images shown here), peaks in $dI(V)/dV$ could no longer be discerned clearly. At these voltages the broadening of energy states apparently exceeds their separation. Similar electron waves with a wavelength of about 0.7 nm were also observed in a number of other shortened metallic nanotubes. On shortened semiconducting nanotubes the level splitting could not be resolved and attempts to measure electron waves were unsuccessful. A small energy level splitting is indeed expected for semiconducting tubes since here the Fermi energy is located at the top of a band [5].

Figure 8.3c shows the topographic height profile from the constant-current measurement at $+0.3 \text{ V}$, which clearly has a different periodicity from that observed in $dI/dV$ (Fig. 8.3b). The period of 0.25 nm is in agreement with the atomic lattice constant $a_0 = 0.246 \text{ nm}$ for an armchair nanotube. Apparently we image the atomic corrugation at high bias voltage. Simultaneously, $I(V)$ spectroscopy curves are measured at every point (Fig. 8.3b and c), starting at the set-point used for feedback (100 pA and $+0.3 \text{ V}$). As a result from maintaining feedback at this voltage, the lattice periodicity is largely compensated because the STM tip follows the atomic corrugation, which makes it possible to resolve the quantized electron waves in Fig. 8.3b and c [16].

Discrete levels are probed at energies near the Fermi energy $E_F$, and therefore the wavelength of the electron waves is close to the Fermi wavelength $\lambda_F$. Electronic bandstructure calculations [1, 7] for armchair tubes yield two bands near $E_F$ with a linear energy dispersion $E(k) = E_F \pm \hbar v_F (k - k_F)$, where $\hbar = \hbar/2\pi$, $k = 2\pi/\lambda$ is the wave vector, and $k_F = 2\pi/\lambda_F$ is the Fermi wave vector. In undoped nanotubes, the two bands cross at the Fermi energy where $k = k_F = 2\pi/3a_0$. This yields $\lambda_F = 3a_0 = 0.74 \text{ nm}$, independent of the length of the tube. For nanotubes on Au(111) however, $E_F$ is shifted away from the
Figure 8.4: Pairing of conductance peaks. (a) Spectroscopy line scan where pairing of \( dI/dV \) maxima can be observed. Neighboring peaks are nonequidistant, indicating a nonsinusoidal wave function. The distance between next-nearest-neighbor peaks is approximately 0.75 nm which agrees with the Fermi wavelength. (b) Schematic of a possible arrangement of lobes of the wave function of a single molecular orbital. In a line scan along the dashed line, peaks in \( dI/dV \) will be equidistant, whereas pairing will occur if a line scan is carried out along the solid line.

crossing point to lower energy by \( \delta E = 0.3 \) eV. This is due to charge transfer as a result of a difference in workfunction with the underlying substrate [5]. This shifts \( k_F \) to \( k_F \pm \delta k \) with \( \delta k = \delta E/\hbar v_F \), and \( \lambda_F \) thus becomes \( \frac{2\pi}{k_F \pm \delta k} \approx 0.69 \) nm (+) or 0.79 nm (−). The experimentally observed wavelengths (Fig. 8.3b) correspond well to the theoretical values, confirming the predicted band structure with two linear bands crossing near \( E_F \). This result provides quantitative evidence for our interpretation of the oscillations in \( dI/dV \) in terms of wave functions of discrete electron states.

A short metallic nanotube resembles the textbook model for a particle in a 1D box. For a discrete energy state with quantum number \( n \), the corresponding wavelength \( \lambda_n = 2L/n \). The observed wavelength is much smaller than the tube length, in accordance with the fact that the number of electrons within one nanotube band is large (\( n \approx 10^6 \)). The wavelength will therefore vary only slightly (\( \lambda_n/n \approx 0.01 \) nm) for adjacent discrete energy levels in one band.

The measurements reported here are technically challenging because they require a large series of reproducible \( I(V) \) curves. Occasionally, we were able to resolve some of the spatial structure in the wave function at a length scale smaller than the Fermi wavelength, as shown in Fig. 8.4a. In this scan the peak spacing is nonequidistant, leading to an apparent ‘pairing’ of peaks. This feature indicates that the wave function does not conform to a simple sinusoidal form. Recent calculations by Rubio et al. [17] indicate a nontrivial spatial variation of the nodes in the wave function of discrete electron states in the direction perpendicular to the tube axis (compare Fig. 8.4b). Line profiles can either show pairing or an
equidistant peak spacing depending on the exact position of the line scan. The observation of pairing confirms that the relevant period in the line scans is the distance between next-nearest-neighbor peaks.

Our experiments demonstrate that individual wave functions corresponding to the quantized energy levels in a short metallic nanotube can be resolved because of the large energy level splitting. The technique for recording the wave periodicity at different energy states provides a tool for further exploration of the dispersion relation in nanotubes. Future work will include similar experiments on nanotubes with various chiral angles. The methodology presented in this paper also opens up the possibility of obtaining full 2D spatial maps of the electron wave functions in carbon nanotubes.

Acknowledgements
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References


[9] Exact identification of the exact lattice indices \((n,m)\) (see ref.[1]) of chiral nanotubes is quite difficult since both the nanotube diameter and the chiral angle between hexagon rows and the tube axis have to be measured with
high accuracy. The \((n, m)\) indices are crucial for chiral tubes because a minor change in one of these determines whether the tube is a metal or a semiconductor. For armchair tubes, however, the situation is easier. The non-chiral structure with hexagon rows running parallel to the tube axis can be easily observed from the atomically resolved images, and a precise determination of the diameter is not essential because armchair tubes of all diameters are metallic.

[10] J.W.G. Wildöer, A.J.A. van Roij, H. van Kempen and C.J.P.M. Harmans, Rev. Sci. Instrum. 65, 2849 (1994). In our setup the lateral drift is almost negligible (typically less than 1 nm per hour) because the STM is cooled in a \(^4\)He bath cryostat. Successive STM spectroscopy line scans therefore show identical results. Over a longer period, however, the tip may change position slightly as a result of residual drift as well as minor tip changes.

[11] L.C. Venema et al., Appl. Phys. Lett. 71, 2629 (1997). After this cutting event the tip was cleaned by applying voltage pulses above the gold substrate, far away from the tube. Linear \(I(V)\) spectroscopy curves on clean areas of the gold substrate demonstrated that the tip was free from any debris.

[12] The applied voltage is in principle divided into a part that drops over the tunnel gap and a part that drops between the nanotube and the substrate. The ratio \(\alpha\) between these voltages is determined by the capacitance ratio. Because the capacitance between nanotube and substrate is much larger than that between the nanotube and the STM tip, the voltage will drop almost entirely over the tunnel gap, and accordingly \(\alpha\) has a value close to 1.


[15] Note that the exact voltages at which the peaks in \(dI/dV\) appear in Fig. 8.2 and Fig. 8.3a are different. This can be attributed to variations in the offset charge caused by trapping of charge in the environment of the tube, as is well known in Coulomb charging phenomena (see e.g. R. Wilkins and R.C. Jaclevic, Phys. Rev. Lett. 63, 801 (1989); J.G.A. Dubois, E.N.G. Verheijen, J.W. Gerritsen and H. Van Kempen, Phys. Rev. B 48, 11260 (1993)). Variation of the offset charge may change the Coulomb gap and thus shift the exact voltage at which the discrete levels of the tube appear in the \(I(V)\) measurements. In fact, switching of offset charges was observed in some of our line scans. This effect is irrelevant for the observation reported here, which are the periodic oscillations in the differential conductance of discrete energy levels.
[16] The total wavefunction is in fact defined by the atomic lattice potential modulated with a standing wave profile resulting from the confinement in the length direction. Because the STM tip follows the atomic corrugation by scanning in constant-current mode at a high bias voltage, the lattice periodicity is largely compensated so that the standing waves can be resolved in the spectroscopy measurements for several discrete states at low bias.

Summary

Carbon nanotubes are hollow molecular wires with extraordinary electronic and mechanical properties. They are strong, robust, flexible, and can be either semiconducting or metallic. A carbon nanotube can be thought of as a sheet of graphite rolled up into a cylinder. The atomic structure is exactly defined by a pair of indices \((n,m)\) which relates to a specific combination of chirality and diameter. Whether a nanotube is metallic or semiconducting depends critically on the \((n,m)\) indices. This is explained in chapter 2 which gives a theoretical background on the electronic structure of carbon nanotubes. In this thesis, scanning tunneling microscopy (STM) has been used to study both the atomic and electronic structure of individual carbon nanotubes. Nanotubes can be imaged with atomic resolution which enables to measure their chirality. An example of an atomically resolved nanotube image is shown on the front page of this thesis.

With STM spectroscopy, where the STM tip is used as a local electronic probe, the electronic bandstructure can be studied as well. In this spectroscopy mode, the tip is fixed above a nanotube at a constant position and the tunnel current \(I\) is measured as a function of the bias voltage \(V\) between tip and sample. From the \(I(V)\) curves \(dI/dV(V)\) can be derived which is roughly proportional to the electronic density of states (DOS).

The low-temperature (4K) STM measurements that are presented in chapter 3 were one of the first to confirm the prediction that nanotubes can be either semiconducting or metallic. Single-walled carbon nanotubes, with diameters of about 1.4 nm, were deposited on single crystalline gold surfaces. The main result of the measurements was that all \(dI/dV(V)\) spectra measured on nanotubes with various chiralities, could be divided into two classes. The first class of nanotubes showed \(dI/dV(V)\) curves with an energy gap of about 0.6 eV. The second type of curves showed a broad plateau of constant \(dI/dV\), with a width of about 1.8 eV. These two classes could be identified as the semiconducting and metallic nanotubes, respectively.

Chapter 4 discusses in more detail the images of nanotubes and the identification of the \((n,m)\) indices. In principle these indices can be obtained from STM images. However, the chirality and diameter have to be measured with a high accuracy, better than 1° and 0.1 nm respectively, to find one specific set of \((n,m)\). Chapter 4 demonstrates for two examples of nanotubes the identification of their \((n,m)\) numbers. The origin of the atomic contrast is also discussed as well as the geometric distortion effect that leads to an overestimation of 15-70% of the apparent chiral angle. A correction of the images has to be done to obtain the true chiral angle. Diameters can in principle be determined from the height profiles in the STM images. To do this correctly, the convolution of the nanotube with the shape of the STM tip and the difference in electronic structure between the nanotube and the gold substrate have to be taken into account. To circumvent these problems, we retrieve the diameter instead from the spectroscopy measure-
ments. The intervals between the subband onsets scale inversely linear with the diameter and can therefore be taken as a measure for the diameter.

Various details of the spectroscopy measurements are discussed in chapter 5. Of all 29 nanotubes that are measured, 19 are of the semiconducting type and 10 of the metallic type, which is in agreement with the prediction that two-third of the \((n, m)\) nanotubes is semiconducting and one-third is metallic. It is furthermore observed that the \(dI/dV(V)\) curves are asymmetrically positioned around zero bias voltage. This can be ascribed to a difference in workfunction between the gold substrate and the nanotubes. This difference leads to a charge transfer and for semiconducting nanotubes a shift of the Fermi level into the valence band. Chapter 5 also discusses some spatially resolved measurements. Measurements on a semiconducting nanotube end show sharp resonances in \(dI/dV(V)\). The resonance energies fluctuate as a function of position along the nanotube over a length scale of 10 to 20 nm. An explanation for this behavior is not yet available. Chapter 5 also describes a measurement where metallic- and semiconducting-type \(dI/dV(V)\) curves were taken respectively above and below a sharp bend in a nanotube. This sharp bend most likely is an example of a nanotube 'kink' which is a connection between two nanotubes with different chirality. Nanotube kinks can act as semiconductor-metal heterojunctions.

We have found that nanotubes can be cut into shorter pieces by applying voltage pulses to the STM tip above a tube. This length control can be used to observe the electronic structure of carbon nanotubes at various length scales. Chapter 6 is a first report on this technique. A possible theoretical model for the cutting is discussed in chapter 7. The important experimental input is the sharp threshold voltage for cutting, which is determined to be 3.8 ± 0.2 V, independent of voltage polarity. In the proposed mechanism electrons tunnel inelastically into the nanotubes and excite localized electrons from \(\sigma\)-states to \(\pi^*\)-states near the Fermi energy (or from \(\sigma^*\) to \(\pi\)-states), weakening the carbon-carbon bonds. The minimum energy difference between the \(\sigma\)- and \(\pi^*\)-states, around 3.6 eV, can explain the threshold voltage for cutting of about 3.8 V. The bonds are further weakened by the strong electric field under the STM tip.

Chapter 8 discusses an experiment where a metallic nanotube was cut to a length of about 30 nm. The \(I(V)\) curves obtained on the short piece showed a step-like behavior. The step onsets lead to peaks in the tunneling conductance \(dI/dV(V)\) and correspond to discrete energy levels of the tube. The spacing between the peaks, about 70 meV, fits with the theoretical energy level splitting for a tube of length 30 nm. By scanning the STM tip along the length of the nanotube and measuring the amplitude of the \(dI/dV(V)\) peaks as a function of position, the corresponding electronic wavefunctions can be imaged. The amplitudes of the peaks indeed oscillate along the nanotube with a period corresponding to the Fermi wavelength. This experiment demonstrates that a metallic nanotube behaves as a textbook example of a quantum well, with the wavefunctions of the electrons extending over the full width.
Samenvatting

Koolstof nanobuizen zijn holle moleculaire draadjes van koolstof met uitzonderlijke mechanische en elektronische eigenschappen. Ze zijn robuust en zeer sterk en kunnen zowel halfgeleidend als metallisch zijn. Een koolstof nanobuis kan beschouwd worden als een vel grafit dat is opgerold tot een cilinder. De exacte atomairestructuur is gedefinieerd door twee indices \((n, m)\) die gerelateerd zijn aan een specifieke combinatie van chiraliteit en diameter. Of een nanobuis halfgeleidend of metallisch is wordt kritisch bepaald door de \((n, m)\) indices. Dit wordt uitgelegd in hoofdstuk 2, dat een theoretische achtergrond geeft voor de elektronische structuur van nanobuizen. In dit proefschrift is scanning tunnelingmicroscopie (STM) gebruikt om zowel de elektronische als de atomaire structuur van individuele nanobuizen te bestuderen. De nanobuizen kunnen afgebeeld worden met atomaire resolutie, waarmee het mogelijk is om hun chiraliteit te bepalen. Een voorbeeld van een nanobuis afgebeeld met STM is te zien op de voorkant van dit proefschrift. Met STM spectroscopie metingen, waarbij de STM-tip gebruikt wordt als een lokale elektronische probe, kan vervolgens ook de elektronische bandstructuur gemeten worden. Een STM spectrum wordt opgenomen door de tip op een vaste positie boven een nanobuis te houden en de tunnelstroom \(I\) te meten als functie van de spanning \(V\) tussen tip en sample. Uit de \(I(V)\) spectra kan \(dI/dV(V)\) worden afgeleid wat bij benadering evenredig is met de elektronische toestandsdichtheid.

De STM metingen die gepresenteerd worden in hoofdstuk 3 waren één van de eerste waarmee de voorspelling gestaafd kon worden dat nanobuizen halfgeleidend en metallisch kunnen zijn. Nanobuizen met een diameter van 1.4 nm waren aangebracht op een substraat van vlak, één-kristallijn goud en de metingen werden uitgevoerd bij 4K. Het centrale resultaat van de metingen was dat de \(dI/dV(V)\) spectra die gemeten waren op nanobuizen met uiteenlopende chiraliteiten opgedeeld konden worden in twee klassen. De eerste klasse van nanobuizen vertoonde curves met energie gaps in de orde van 0.6 eV. De tweede klasse van nanobuizen liet een brede plateau van constante \(dI/dV\) zien, in de orde van 1.8 eV. Deze twee klassen konden geïdentificeerd worden als respectievelijk de halfgeleidende en metallische nanobuizen.

Hoofdstuk 4 gaat nader in op het afbeelden van nanobuizen en de identificatie van de \((n, m)\) indices. De \((n, m)\) indices kunnen in principe gevonden worden uit STM metingen door de chiraliteit en de diameter te bepalen. Deze parameters moeten echter met hoge nauwkeurigheid gemeten worden om een bepaalde set van \((n, m)\) te vinden, binnen 1° en 0.1 nm respectievelijk. Hoofdstuk 4 demonstreert voor twee voorbeelden van nanobuizen de identificatie van de bijbehorende \((n, m)\) indices. Ook wordt het atomaire contrast in de afbeeldingen besproken en een geometrisch effect dat ertoe leidt dat de chiraliteit van de nanobuizen 15 tot 70% te groot wordt afgebeeld. Een correctie van de afbeeldingen moet gedaan worden om de juiste chiraliteit te bepalen. De diameters kunnen in principe
bepaald worden uit de hoogte profielen in de STM afbeeldingen. Er moet dan wel rekening gehouden worden met de convolutie van de nanobuis met de vorm van de STM tip en het verschil in elektronische structuur tussen de nanobuizen en het substraat. Om deze problemen te voorkomen wordt in hoofdstuk 4 de diameter bepaald uit de spectroscopie metingen. De afstanden tussen de energie subbanden schalen omgekeerd evenredig met de diameter en kan daarom als maat voor de diameter gebruikt worden.

Hoofdstuk 5 bespreekt verschillende details van de spectroscopie metingen. Van alle 29 nanobuizen die bestudeerd zijn, zijn er 19 halfgeleidend en 10 metallich, hetgeen overeenkomt met de voorspelling dat ongeveer tweederde van alle mogelijke \((n,m)\) nanobuizen halfgeleidend zijn en éénderde metallich. Verder blijkt dat de \(dI/dV(V)\) curves een asymmetrische positie hebben rond 0 Volt. Dit kan worden toegeschreven aan het verschil in werkfuncties tussen het goud substraat en de nanobuizen. Dit verschil leidt tot een verschuiving van lading van de tube naar het goud en daardoor tot een verschuiving van het Fermi-niveau naar de valentieband. In hoofdstuk 5 worden ook enkele plaatselijk opgeloste spectroscopie metingen besproken. Metingen aan halfgeleidend nanobuis eindjes laten zien dat scherpe resonanties in de \(dI/dV(V)\) opkomen. De energiën van deze resonanties fluctueren als functie van positie langs de nanobuis over een lengteschaal van 10 tot 20 nm. We beschikken nog niet over een complete verklaring voor dit effect. Er is in hoofdstuk 5 verder een meting geïmplementeerd waarbij \(dI/dV(V)\) curves van het metallichse en halfgeleidende type opgenomen zijn respectievelijk boven en onder een scherpe buiging in een nanobuis. Deze scherpe buiging is mogelijk een voorbeeld van een nanobuis 'kink'. Een kink is een verbinding tussen twee nanobuizen met vergelijkbare diameter en verschillende chiraliteit. Kinks kunnen hierdoor halfgeleider-metaal heterojuncties zijn.

Het is mogelijk gebleken om nanobuizen in kortere stukken te knippen door met de STM tip boven een nanobuis een spanningspuls uit te voeren. De controle over de lengte kan gebruikt worden om de elektronische eigenschappen van koolstof nanobuizen op verschillende lengteschalen te bestuderen. hoofdstuk 6 is een eerste verslag van deze techniek. Een mogelijk theoretisch model voor het knippen wordt gegeven in hoofdstuk 7. Het belangrijkste gegeven uit de experimenten is dat de nanobuizen geknapt worden met een spanning die minstens 3.8 ± 0.2 V moet zijn, ongeacht de polariteit van de spanning. In het voorgestelde model tunnelen elektronen inelastisch naar de nanobuis waardoor geëxciteerd worden van \(\sigma\)-toestanden naar \(\pi^*\)-toestanden bij het Fermi niveau (en van \(\sigma^-\) naar \(\pi^-\)-toestanden). Het minimale energie verschil tussen de \(\sigma\)- en \(\pi^*\)-toestanden, ongeveer 3.6 eV, zou de scherpe drempelspanning rond 3.8 V voor het knippen kunnen verklaren. De bindingen tussen de koolstof atomen worden nog verder verzwakt door het sterke elektrische veld onder de STM tip.

Hoofdstuk 8 bespreekt een experiment waar een metallich nanobuis geknapt is tot een stukje van 30 nm. In de \(I(V)\) curves opgenomen op dit korte stuk tube neemt de stroom stappsgewijs toe met de spanning. Deze stappen leiden tot
pieken in de $dI/dV(V)$ en corresponderen met discrete energie niveaus van de tube. De afstand tussen de pieken, ongeveer 70 meV, is te fitten met de splitting van energie niveaus die te verwachten is voor een nanobuis van 30 nm. Door met de STM tip de amplitude van de $dI/dV(V)$ pieken als functie van positie langs de nanobuis te meten kunnen de bijbehorende elektronische golffuncties gemeten worden. De amplitude oscilleert inderdaad langs de nanobuis met een periode die ongeveer gelijk is aan de theoretische Fermi golflengte. Dit experiment laat zien dat de metallische nanobuis zich gedraagt als een tekstboekvoorbeeld van een één-dimensionale quantum put met golffuncties uitgespreid over de volle lengte.
Curriculum Vitae

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List of publications

Atomic structure of carbon nanotubes from scanning tunneling microscopy,
L.C. Venema, V. Meunier, Ph. Lambin and C. Dekker, to be published in Phys.

Imaging electron wave functions of quantized energy levels in carbon nanotubes,

Veelzijdige koolstofdraadjes,

Electronic structure of atomically resolved carbon nanotubes,

STM atomic resolution images of single-wall carbon nanotubes,

Electronic properties of individual single-wall nanotubes: Transport and STM
results,
C. Dekker, S.J. Tans, M.H. Devoret, L.J. Geerligs, R.J.A. Groenveld, L.C. Ve-
nema, J.W.G. Wildöer, A.R.M. Verschuren, A.Bezryadin, A. Thess, H. Dai and
R.A. Smalley, in Molecular Nanostructures (World Scientific, 1998), Eds. H.
Kuzmany, J. Fink, M. Mehring and S. Roth, p. 467-471.

Length control of individual carbon nanotubes by nanostructuring with the scan-
ning tunneling microscope,
L.C. Venema, J.W.G. Wildöer, H.L.J. Temminck Tuinstra, C. Dekker, A.G. Rinz-

STM imaging and spectroscopy of single copperphthalocyanine molecules,
C. Dekker, S.J. Tans, B. Oberndorff, R. Meyer and L. Venema, Synthetic Metals
84, 853 (1997).
Dankwoord

Met dit proefschrift is een einde gekomen aan vier jaar promotieonderzoek, dat is uitgevoerd in de vakgroep Quantum Transport onder leiding van Prof. J.E. Mooij aan de TU Delft. Het doel van dit onderzoek was om met een scanning tunnelling microscope (STM) de geleiding te meten aan individuele moleculen. Na het eerste jaar bleek dat met name koolstof nanobuizen erg interessante geleidings-eigenschappen vertonen en bijzonder geschikt zijn voor STM studies. Dit proefschrift is dan ook voornamelijk een verslag geworden van STM metingen aan koolstof nanobuizen.

In het begin leek het einddoel van het schrijven van een proefschrift erg ver weg en enigszins onwerkelijk. Nu begrijp ik natuurlijk wat iedere promotieondervindt zich na vier jaar realiseert, dat dit niet iets is wat je alleen kan doen. Het is een bijzondere ervaring geweest om te werken in het voortreffelijke wetenschappelijke klimaat van Quantum Transport. Ik wil dan ook mijn promotoren, Hans Mooij en Cees Dekker, en de overige wetenschappelijke stafleden Kees Harmans, Peter Hadley, Leo Kouwenhoven en Herre van der Zant bedanken voor alle begeleiding en hulp. Mijn directe begeleider Cees Dekker wil ik speciaal bedanken voor zijn grote enthousiasme, het vertrouwen in mij en het vele uitgebreide en nuttige commentaar op mijn schrijven. Ik wil ook dank uit spreken aan de ondersteunende staf die met hun assistentie en af en toe een frisse kijk op de zaak onmisbaar zijn geweest. Bedankt Ria van Heeren, Bram van der Enden, Leo Lander, Gerard van der Gaag, Willem den Braver, Wim Schot, Anneke Delsing, Mascha van Oossanen en Raymond Schouten.

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Another goal of my research has been to set up a vacuum system for the deposition and in situ STM studies of molecules, as a part of the NEXT (Nanoscale Experiments and Technology) laboratory. I have been somewhat distracted from this project by the nanotube research but thanks to the efforts of several other people this system is now (almost) ready to go. The work has been mainly done by Mascha van Oossanen, Andrew Dunn and Erik Svensson. I also want to acknowledge all other NEXT technicians and scientists for help and discussions.

Al met al is de vakgroep ‘QT’ een bijzondere en aangename omgeving geweest om in te werken. QT staat met de vele studenten, promovendi en postdocs uit alle windstreken garant voor een Engelse voertaal, wekelijks taart bij de koffie en gezellige TPKafee borrels. Kamer F027 is altijd een goede uitvalbasis geweest. Mijn kamergenoten Jorg Janssen en Wilfred van der Wiel zorgen in ieder geval met hun onnavolgbare humor voor het dagelijkse benodigde amusement. Ik wil hen bedanken voor een erg plezierige omgang evenals eigenlijk de hele vakgroep. Ik mag niet vergeten mijn vakgroeps- en tevens huisgenoot Hannes Majer speciaal te noemen, die me alles heeft geleerd over vortices, Zwitserland en jazzmuziek wat ik moest weten. Met zijn opgeruimde gezelschap en (Zwitserse) punctualiteit is het erg bijzonder wonen aan Storklaan 19.

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