Carbon Nanotubes: Their Synthesis and Integration into Nanofabricated Structures

PROEFSCHRIFT

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# TABLE OF CONTENTS

## CHAPTER 1. STRATEGIES TO SYNTHESIS, POST-SYNTHESIS ALIGNMENT AND IMMobilIZATION OF CARBON NANOTUBES .......................................................... 6

### ABSTRACT .......................................................................................................................... 6

1.1 INTRODUCTION .................................................................................................................. 7

1.2 SYNTHESIS ......................................................................................................................... 9

1.2.1 ARC DISCHARGE ............................................................................................................ 9

1.2.2 LASER ABLATION ........................................................................................................ 10

1.2.3 CATALYTIC CHEMICAL VAPOR DEPOSITION (CVD) ........................................... 11

1.2.4 SEPARATION AND CHARACTERIZATION OF CARBON NANOTUBES ................. 15

1.3 POST-SYNTHESIS ATTACHMENT AND ALIGNMENT OF CNTs ............................... 16

1.4 PHYSICAL ATTACHMENT AND ALIGNMENT OF CNTs ............................................. 16

1.4.1 MECHANICAL MANIPULATION OF CNTs ................................................................. 17

1.4.1.1 MOVING CNTs BY SCANNING FORCE MICROSCOPY ....................................... 17

1.4.1.2 CNT ARRANGEMENT BY MICRO- AND NANOMANIPULATORS .......................... 18

1.4.2 ALIGNING CNTs BY EMBEDDING TECHNIQUES ...................................................... 19

1.4.2.1 MATRIX-EMBEDDED CNT SYSTEMs .................................................................. 19

1.4.2.2 FORMATION OF ALIGNED ARRAYS OF CNTs BY SELECTIVE LASER ABLATION ..................................................................................................................... 20

1.4.3 FLUID DYNAMICS AS A TOOL FOR THE ALIGNMENT OF CNTs ............................ 20

1.4.3.1 GAS FLOW-INDUCED ALIGNMENT OF CNTs ...................................................... 20

1.4.3.2 CNT ORGANIZATION BY DRYING PHENOMENA ........................................... 22

1.4.4 GUIDED ASSEMBLY OF CNTs BY LITHOGRAPHIC TECHNIQUES ............................. 25

1.4.4.1 SURFACE PATTERN-GUIDED ASSEMBLY OF CNTs ............................................ 25

1.4.4.2 ALIGNMENT OF CNTs UTILIZING RESISTS AND FILTERs ............................ 28

1.5 USE OF EXTERNAL FIELDS IN ATTACHMENT AND ALIGNMENT OF CNTs ............. 29

1.5.1 MAGNETIC FIELDS FOR THE ALIGNMENT OF CNTs ............................................. 30

1.5.2 ELECTRIC FIELDS AND ELECTROPHORESIS FOR THE PLACEMENT AND ALIGNMENT OF CNTs ......................................................................................... 31

1.5.2.1 CONTROL OF INDIVIDUAL CNTs BY SCANNING FORCE TIPS ....................... 31

1.5.2.2 FIELD-INDUCED ALIGNMENT OF CNTs ............................................................ 33

1.5.3 ALIGNMENT OF CNTs UTILIZING LIQUID CRYSTALS ........................................... 37

1.6 CHEMICALLY-GUIDED ALIGNMENT AND IMMobilIZATION OF CARBON NANOTUBES ....................................................................................................................... 41

1.6.1 IMMobilIZATION OF CNTs UTILIZING SELF-ASSEMBLED MONOLAYERS .......... 41
1.6.2 Immobilization of Functionalized CNTs ..................................................45
1.6.3 Alignment of CNTs by Electrostatic Forces .............................................46
1.6.4 The Use of Biomolecules and DNA for the Selective Placement and Alignment of CNTs on Surfaces .................................................................48
1.7 Aim and Scope of the Thesis ........................................................................50
1.8 Reference ......................................................................................................53

CHAPTER 2. Synthesis of Carbon Nanotubes and Nanofibers by Microwave Irradiation .................................................................67

Abstract ..............................................................................................................67
2.1 Introduction to Microwave Irradiation ..........................................................68
2.2 Investigation of the Selective Heating Process ...........................................69
2.3 CNTs Synthesis by Microwave Irradiation ...................................................73
2.4 Influence of the Synthesis Conditions ..........................................................76
2.5 Influence of the Catalyst Material ...............................................................79
2.6 Influence of the Substrate ...........................................................................86
2.7 Investigation of the Formation of Iron Oxide Particles by Reduction with Hydrazine .................................................................89
2.8 Growth of Carbon Nanotubes on SPM Tips .............................................95
2.9 Patterned Growth of Carbon Nanotubes ....................................................100
2.10 Conclusions ................................................................................................103
2.11 Experimental .............................................................................................105
2.12 References ................................................................................................106

CHAPTER 3. Electro-Oxidative Lithography for Nanofabrication..............112

Abstract ..............................................................................................................112
3.1 Introduction to SPM Lithography .................................................................113
3.1.1 Electrochemical Oxidation Lithography ..................................................114
3.1.2 Monolayer Oxidation Mode .................................................................116
3.1.3 Chemically Active Surface Templates Created by Monolayer Oxidation .................................................................117
3.1.4 Silicon Oxide Growth Mode ...............................................................121
3.2 Conclusion ...................................................................................................124
3.3 References ................................................................................................125

CHAPTER 4. Controlled Hierarchical Lateral Placement of Carbon Nanotubes .................................................................128

Abstract ..............................................................................................................128
4.1 Introduction ................................................................................................129
CHAPTER 5. ELECTRO-OXIDATIVE LITHOGRAPHY FOR NANOMETER GAPS AND RING FABRICATION

ABSTRACT

5.1 INTRODUCTION

5.2 GAP FORMATION

5.2.1 INVESTIGATION OF MONO- AND BILAYER OXIDATIONS

5.2.2 FABRICATION OF WELL-DEFINED NANOMETRIC GAP STRUCTURES

5.3MESOSCOPIC RING STRUCTURES

5.3.1 FABRICATION OF RING STRUCTURES BY ELECTRO-OXIDATIVE LITHOGRAPHY

5.3.2 INVESTIGATION OF THE OXIDATION PARAMETERS

5.4SELECTIVE METALLIZATION OF THE RIM FEATURES

5.5 CONCLUSIONS

5.6 EXPERIMENTAL SECTION

5.7REFERENCES

EXECUTIVE SUMMARY

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LIST OF PUBLICATIONS

ACKNOWLEDGEMENTS
Chapter 1. Strategies to Synthesis, Post-Synthesis Alignment and Immobilization of Carbon Nanotubes

Abstract

Carbon nanotubes (CNTs) have developed into a standard material used as building blocks for nanotechnological developments. Based on the unique properties, that make CNTs useful for many different applications in nanotechnology, optics, electronics, and material science, there has been a rapid development of this research area. This includes the implementation of different synthesis methods that allow selective, aligned and bulk synthesis of single-wall and multi-wall carbon nanotubes. Frequently, the alignment and immobilization of CNTs play an important role for applications, e.g., in electronics and molecular computing, field emission, and membranes. Carbon nanotubes can be aligned either during their synthesis, or alignment of the CNTs can be achieved in a post-synthesis step. Recent developments of different techniques for the synthesis, post-synthesis immobilization, and alignment of carbon nanotubes are summarized in this chapter. Due to a very rapidly changing and expanding body of knowledge in this research area, the techniques for the post-synthesis alignment were classified into three main categories: physical and external forces driven immobilization and alignment, as well as the chemical approach. Many of the techniques discussed in this paragraph involve multiple preparation steps and may also cross these rather crude boundaries. Moreover, due to the wide diversity of approaches there is no ultimate technique available to align carbon nanotubes. The main part of this thesis is based on the different issues of microwave-assisted synthesis and sequential alignment of carbon nanotubes by the use of electro-oxidative lithography. Additionally, the electro-oxidative approach was used to design other nanometer scale materials.

Parts of this chapter have been published as:

1.1 INTRODUCTION

The field of nanotechnology has experienced a constantly increasing interest over the past decades both from industry and science. Nanotechnology deals with the development of new materials at the level of atoms and molecules, which exhibit different properties compared to bulk materials.\cite{1-3} Surfaces and interfaces are critical in explaining the nanomaterial's behavior. In bulk materials, only a relatively small percentage of atoms will be at or near a surface or interface. In nanomaterials, the small feature size ensures that many atoms will be near the interfaces. Thus their properties, such as energy levels, electronic structure, adhesion, reactivity and catalytic behavior can be very different from bulk materials. Size-dependent properties are observed, such as quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles, and superparamagnetism in magnetic materials. Commonly used nanomaterials include: nanowires,\cite{4-6} quantum dots,\cite{7-9} fullerenes,\cite{10-12} and carbon nanotubes.\cite{13-15} The latter example is of special interest as carbon is the most versatile element due to the type, strength, and number of bonds it can form with many different elements. In general, carbon can exist in different forms: amorphous carbon, graphite, graphene, diamond, buckyballs, and carbon nanotubes. Carbon nanotubes represent one of the most exciting and active research areas of modern nanotechnology. These nanoscale tubes are, e.g., the stiffest and strongest fibers known, with remarkable electronic,\cite{16-18} optical,\cite{19-23} photophysical,\cite{24-27} and catalytic properties,\cite{28-30} and potential application in medicine, sensing devices and a wide range of other fields have been proposed.

Carbon nanotubes are long, nanoscale cylinders formed by rolled up graphene sheets (single-wall carbon nanotubes, SWCNTs), or multiple sheets inserted one in other (multi-wall carbon nanotubes, MWCNTs). Their diameters can differ from a few Ångstroms up to 1 nm for SWCNTs and up to hundred nanometers for MWCNTs with lengths of up to several centimeters.\cite{31} Depending on how the graphite sheet is being rolled up, carbon nanotubes can form different chiral structures. The easiest way to classify the structure of a tube is in terms of the roll-up vector $\mathbf{C}$, joining two equivalent points on the original graphene sheet. The tube is produced by rolling up the sheet such that two end-points of the vector are superimposed. Figure 1-1 shows the part of the graphene sheet, with points on the lattice labeled according to the notation introduced by Dresselhaus et al.\cite{32}
Figure 1-1. Graphene layer with atoms labeled using \((n,m)\) notation. Unit vectors of the 2D lattice are also shown.

Each pair of integers \((n,m)\) represents a particular tube structure. Thus, the vector \(\mathbf{C}\) can be expressed as:

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

where \(\mathbf{a}_1\) and \(\mathbf{a}_2\) are the unit cell base vectors of the graphene sheet and \(n \geq m\). If \(m = 0\), the nanotubes are called zigzag. If \(n = m\), the nanotubes are called armchair. All other forms are called chiral (Figure 1-2).

Figure 1-2. Schematic representation of armchair, zigzag, and chiral structures of carbon nanotubes. Image adapted from ref. [33].
Because of the symmetry and unique electronic structure of graphene, the structure of a nanotube strongly affects its electrical properties. For example, all armchair \((n = m)\) nanotubes are metallic, and nanotubes with other indices can be either semiconducting or metallic due to curvature effects. Usually both ends of such cylinders are closed with hemispheres of fullerene-like structures. Since the discovery of carbon nanotubes,\(^{[34,35]}\) the interest towards this material has constantly grown and many studies have been conducted to understand the electronic properties of nanotubes and to construct nanotube-based devices. For example, SWCNTs were used to fabricate diodes\(^{[36,37]}\) and field effect transistors (FET).\(^{[38,39]}\) Combinations of different types of FETs were used in the construction of logic gates.\(^{[40]}\) In particular, nanotube-based field emitters are of potential interest and the work has primarily been driven by the prospect of using the arrays of field emitting nanotubes in flat screen displays, but there is also interest in field emission from individual tubes.\(^{[41,42]}\) For the successful implementation of carbon nanotubes into such electronic devices, customized synthesis methods have to be designed. Over the last years, significant progress has been made in terms of the synthesis of CNTs synthesis, which improved the availability of the materials and decreased the fabrication cost.

### 1.2 Synthesis

The growing demand for efficient synthesis strategies to obtain CNTs has triggered intensive research in this direction. The main processes that are used for the production of CNTs are arc discharge,\(^{[43-45]}\) laser ablation,\(^{[46-48]}\) high pressure carbon monoxide (HiPco), or chemical vapor deposition approaches.\(^{[32-50]}\) Each of these approaches has advantages and disadvantages, which are briefly summarized in the following paragraphs.

#### 1.2.1 Arc Discharge

Arc discharge was the first method for the production of SWCNTs and MWCNTs, and has been optimized to produce bulk amounts. In 1991, the group of Iijima observed the presence of multi-walled carbon nanotubes in the carbon soot of graphite electrodes during an arc discharge process, which was initially intended to yield fullerenes.\(^{[18]}\) It was later found that CNTs could also be produced from impure raw materials.\(^{[51,52]}\) The yield of CNTs was rather poor in the beginning. A significant advancement came years later when Ebbesen and Ajayan discovered that increasing the pressure up to 0.67 bar of He in the arc-evaporation chamber
improved the yield of CNTs to the macroscopic scale.\cite{53} Moreover, an efficient water cooling of the cathode improved the purity of the CNTs. Later, it was reported that also SWCNTs could be produced by arc discharge.\cite{54,55} It was found that SWCNTs can be only produced by adding a metal catalyst to the anode. Following these initial studies, a great deal of work has been carried out on optimizing the arc discharge production of single-walled tubes. This research resulted in a controllable process that utilizes optimization of the discharge conditions, as well as of the catalyst materials. Favorable catalysts used in the arc discharge process are Fe, Co, Ni\cite{43-57} and mixtures of e.g. Ni/Y,\cite{58} Rh, Pd, Pt\cite{59,60} and rare earth metals.\cite{61-63} When produced from rare earth metals the tubes tend to be shorter. Several gases were used as an alternative to He in the arc discharge process. These include H$_2$,\cite{64-66} N$_2$,\cite{67} CF$_4$\cite{68} and organic vapors.\cite{69} Another variant involves carrying out the arcing in liquid N$_2$\cite{70} or under water.\cite{71-73} It was found that CNTs grown under water were significantly more perfect compared to tubes grown under liquid N$_2$. Other researchers have described the development of an optoelectronically automated system for the arc discharge synthesis of MWCNTs in solution.\cite{74,75} Another modification to this method was the use of magnetic fields. Anazawa’s group showed that introduction of four cylindrical Nd-Fe-B magnets around the electrodes form a symmetric magnetic field which promotes the increase in the CNT yield (up to 97%).\cite{76} In general, the arc discharge technique has been the most widely-used method of nanotube synthesis. It can produce single- and multi-walled carbon nanotubes with length of up to 50 micrometers with only few structural defects. This method is simple and inexpensive compared to other methods that can be used for carbon nanotube production. However, CNTs produced by arc discharge need extensive purification before use, although they are produced in large amounts. Moreover, the tubes tend to be relatively short with random sizes.\cite{77}

### 1.2.2 Laser Ablation

Alternatively, CNTs can be synthesized in a laser ablation process. In this process, sheets of graphite are blasted off from a graphite target and form SWCNTs (Figure 1-3).
Figure 1-3. Scheme of the laser ablation apparatus for the synthesis of SWCNTs. Reproduced from ref. [78].

Typical operating conditions in the set-up are 1200 °C with inert gas (usually Ar) flowing through a tube at the contact pressure of 0.67 bar within the furnace. The ablation from a catalyst metal doped graphite target is initiated by a laser. Nanotubes are synthesized on the cooler surfaces of the reactor during the condensation of the vaporized carbon. Carbon nanotubes can be collected by introduction of a water-cooled surface. Tuning of the graphite metal catalysts resulted in a reliable process to fabricate also SWCNTs. Utilizing a composite of graphite and metal catalyst (Co, Ni) generated a yield of 70% by weight and produces mostly single-walled carbon nanotubes of different diameters which can be tuned by the reaction temperature.

In general, laser ablation methods produce single wall carbon nanotubes with good diameter control and high yield of up to 1 g per day of SWCNTs. The SWCNTs produced by this method have few defects and are very pure. The main disadvantage of this method is that it is significantly more expensive compared to arc discharge and chemical vapor deposition. This is due to the use of expensive lasers and other high-powered equipment. Useful reviews that discuss laser ablation synthesis of carbon nanotubes have been published.

1.2.3 Catalytic Chemical Vapor Deposition (CVD)

In the early 90s, the growing interest in the catalytic growth of carbon nanotubes was stimulated. During the chemical vapor deposition (CVD) process, a substrate is loaded with metal catalyst particles (nickel, cobalt, iron, or their combination). The substrate is
heated to a temperature in the range of 500 to 1200 °C, while two gases are introduced into
the reactor: a process gas (hydrogen, ammonia, or nitrogen) and a carbon-containing gas
(methane, ethylene, acetylene, or ethanol) (Figure 1-4).

![Furnace Diagram](image)

**Figure 1-4. Schematic of the chemical vapor deposition furnace.**

The carbon-containing gas decomposes at the surface of the metal catalyst particle and
carbon is transported to the edge of the particle where it forms the carbon nanotube. The size
of the metal particles determines the diameters of the carbon nanotubes. The exact formation
mechanism is still unknown and is being studied, although two different growth modes are
generally observed. The catalyst particles can propagate with the tips of the nanotubes during
the growth process or can remain at the nanotube base. Both modes are depicted in Figure
1-5.

![Schematic Diagram](image)

**Figure 1-5. Schematic of both tip growth and base growth of carbon nanotubes on a
substrate, a) tip growth mode, b) base growth mode.**

The tip growth mode (Figure 1-5a) involves the decomposition of the carbon-containing gas
on the “front” surface of the metal particles, producing carbon, which then dissolves in the
metal. The dissolved carbon then diffuses through the particles, to be deposited on the trailing
face, forming a filament. In the base growth mode (Figure 1-5b), the catalyst particle remains
attached to the surface and the nanotube is extruded upwards or along the surface. The
mechanism depends on how strongly nanoparticles adhere to the substrate or the support material. These two mechanisms have been proposed and were indirectly observed for the growth of carbon fibers, MWCNTs, and SWCNTs, depending on the catalyst type, hydrocarbon source, and growth temperature. Tip growth is considered to be the dominant mechanism for the growth of MWCNTs, while base growth is dominant for the growth of SWCNTs. Such growth mechanism is usually followed by a graphitization step. During this step, graphitization of carbon nanotube walls appear from the surface towards the inner region of the tube. Various levels of graphitization can be obtained depending on the treatment temperature. It has been shown that higher temperatures allow a better graphitization and, thus, a lower degree of defect formation during the CNTs synthesis can be obtained.

A detailed study of the MWCNTs growth using a wide range of transition metals catalysts was conducted.\cite{88} It was found that Fe, Co and Ni were the only active catalysts studied, whereas Cr, Mn, Zn, Cd, Ti, Zr, La, Cu, V and Cd showed no activity. It was proposed that the reason for the catalyst activity was the solubility of carbon in these metals. Active catalysts have a carbon solubility of 0.5-1.5 wt% carbon, while inactive catalysts do not show solubility or tend to form intermediate carbides, which hinder the diffusion required for the graphite precipitation.\cite{89} CVD processes are widely used for the commercial production of carbon nanotubes, where the metal nanoparticles are mixed with a catalyst support such as MgO or Al$_2$O$_3$ to increase the surface area for higher yields.

The CVD process can be also used for the synthesis of aligned nanotubes on substrates. Yun et al. developed a process to grow aligned carbon nanotubes up to 4 mm long.\cite{90} Such nanotubes can find application in field emission devices,\cite{91,92} photonics,\cite{93} spinning of nanotubes yarns\cite{94,95} and dry adhesives.\cite{96} A very widely used method for the synthesis of aligned CNTs involves the use of plasma.\cite{97} For this purpose, a plasma generates an excited/ionized gas by direct current (DC), radio frequency (RF) or microwave excitation. The alignment of the produced CNTs that occurs during plasma enhanced CVD process is believed to be caused by the presence of the electric field. This has been investigated by switching on and off the plasma source, which resulted in the formation of “curled” CNTs in the experiments without utilizing plasma.\cite{98,99} It was also demonstrated that CNTs can be grown at room temperature conditions.\cite{100} This was achieved by using plasma energy rather than thermal energy to decompose the carbon source, mainly CH$_4$. Such methods provide possibilities to use polymers and other temperature sensitive materials as substrates. It is also
possible to grow vertically aligned carbon nanotubes under certain reaction conditions even without plasma; closely spaced nanotubes will maintain a vertical growth direction resulting in a dense array of tubes resembling a “forest”.[101-103] Aligned MWCNTs can be also produced by decomposition of organometallic precursors, which are injected into the reactor together with the carbon source.[104,105] Alignment is here caused by self-assembly guided by van der Waals interactions. In this method, tubes can be grown parallel, as well as perpendicular to the substrate.

Various methods have been used to deposit suitable catalysts onto the substrates. Many groups have used solutions containing salts of metals, which are deposited on the substrates, dried and are then reduced to obtain catalyst particles on the surface. Other groups used physical techniques for the catalyst deposition, such as ion beam sputtering[99] or electron gun evaporation.[106] The advantage of these latter methods is that particles can be deposited in a patterned fashion on the substrate.[107]

Production of SWCNTs by CVD methods requires high control over temperature, feedstock and the nature of the catalyst particles. The temperature necessary for SWCNTs production is usually higher than for multi-walled nanotubes, and in the range of 900 to 1200 °C. This might be a problem for some feedstock since at temperatures above 900 °C, the rate of pyrolysis of many hydrocarbons is very high, resulting in the formation of amorphous carbon. For that reason many groups have chosen to use CO and CH\textsubscript{4} as carbon sources, due to their relatively high thermal stability. The addition of H\textsubscript{2}, benzene, hexane or ethylene to CH\textsubscript{4} resulted in the increase of the yield of SWCNTs.[108-110] The most suitable catalyst for SWCNTs growth is critically dependent on the chosen feedstock. The most commonly used catalysts are Fe, Co, Ni, Mo and their combinations, but oxides have also been utilized. Recently, unusual metals have been used for SWCNT growth, including Ag, Au and Cu.[111-113] In addition to supported catalysts, “floating” catalysts were also employed for single-walled tube synthesis. In this approach, ferrocene (Fe(C\textsubscript{5}H\textsubscript{5})\textsubscript{2}) vapor is used as the catalyst. It is introduced in the chamber together with the carbon source. Large-scale synthesis of SWCNTs is possible by the high-pressure CO disproportionation (HiPco) process.[114] This method is based on the decomposition of Fe(CO)\textsubscript{5} to form Fe clusters for the SWCNTs production from CO at temperatures of 1000 °C. The method allows high level fabrication of the CNTs; it produces SWCNTs without amorphous carbon compared to, e.g., the laser ablation method or arc discharge. The main challenge here is to maintain the correct temperature for the synthesis. Moreover, the as-grown HiPco CNTs are not straight or
aligned and contain large amount of metal impurities. The super-growth chemical vapor deposition is a water-assisted chemical vapor deposition process.\cite{115} Here, the lifetime and hence the activity of the catalyst is enhanced by the addition of water into the CVD reactor. Dense, millimeter long vertically aligned single-walled carbon nanotubes were produced. Using this method, Iijima’s group succeeded to produce between 1000 m$^2$/g to 2200 m$^2$/g carbon nanotubes\cite{116} which is significantly more than the value of 400 to 1000 m$^2$/g obtained for HiPco samples. The densely aligned SWNT forests can be easily separated from the catalyst, yielding clean SWNT material (purity >99.98%) without further purification. By tuning the growth conditions and the catalysts size it was possible to grow material containing SWNT, double-wall nanotubes (DWNTs), and MWNTs, and different ratios of them.\cite{117}

In general, CVD represents the most promising synthesis process for industrial-scale deposition because of its relative inexpensiveness. Long nanotubes have been produced with this method. Disadvantage of the process is the necessity to remove the catalyst support via an acid treatment, which could potentially destroy the original structure of the carbon nanotubes. Moreover, tubes fabricated by the chemical vapor deposition process often reveal many structural defects and differ in length. High temperatures are employed during the CNTs synthesis limiting the choice of the different utilized substrates.

1.2.4 SEPARATION AND CHARACTERIZATION OF CARBON NANOTUBES

Many synthetic approaches result in mixtures of tubes that differ in diameter and length, but more importantly, also in their electrical properties. Thus, separation and purification are highly desired, and represent an additional step in the processing of crude CNT materials. Carbon nanotubes can be divided into two main categories based on their electronic structure: metallic and semiconducting. Furthermore, semiconducting carbon nanotubes can be also classified by their tube diameters, and it is possible to separate metallic from semiconducting tubes by means of their different physical or chemical properties. The separation methods are based on electrophoresis, centrifugation, chromatography, selective solubilization, and selective reactions.\cite{118-121} Several excellent reviews has been published on separation of CNTs.\cite{122-127} Separation of carbon nanotubes by their diameter is more difficult due to the smaller differences in the physical or chemical properties.\cite{128-132}
Characterization of carbon involves microscopic as well as spectroscopic tools. The orientation of carbon nanotubes, their dimensions and morphology can be investigated with Scanning Electron Microscopy (SEM). The internal structure of carbon nanotubes, such as the number of the walls, distance between them and the overall diameter of the tube can be measured with High Resolution Transmission Electron Microscopes (HRTEM). Additional information about the tube diameter, number of walls and their purity can also be obtained by Raman spectroscopy. This technique is used for both quantitative and qualitative analysis.

1.3 **Post-synthesis Attachment and Alignment of CNTs**

The unique properties of carbon nanotubes allow them to be used in many different applications such as implementing CNTs in new reinforced materials, in electrical circuits, as composites in polymers, as scanning probe microscopy tips, in field-emitting displays, in gas storage, and for sensors. In particular, aligned nanotubes are of interest in this respect. For instance, many studies have been conducted on the alignment and selective placement or patterning of CNTs for applications in electronics and molecular computing, field emission, and membranes, amongst others. Direct synthesis of vertically organized CNTs was implemented by various techniques. Parallel and vertically aligned CNT configurations have also been addressed by established synthesis strategies to produce well-defined tubes. Most of the techniques, however, rely on the post-synthesis alignment and deposition of CNTs, either parallel or perpendicular to the substrate surface. Several steps or processes from a variety of different fields can be utilized to obtain arrays of organized tubes. In particular, post-synthesis manipulation techniques play an important role and some representative examples of techniques utilizing a diversity of different effects are summarized.

1.4 **Physical Attachment and Alignment of CNTs**

In the literature, a large variety of techniques to attach or align CNTs based on physical principles have been reported. In many cases, physical processes play a supporting role in enhancing or enabling a chemical process, e.g., printing a patterned SAM, which then forms chemical bonds with the individual CNTs. In other cases, physical methods play primary roles in attaching or aligning the CNTs. At the nanometer scale, however, there is often
overlap between physical and chemical processes. In this paragraph, focus is placed on highlighting some of the primarily physical procedures published in the literature. These examples are grouped into four main categories: physical manipulation, material removal and filtration, fluid dynamics, and printing as well as lithography.

1.4.1 MECHANICAL MANIPULATION OF CNTs

The mechanical manipulation of CNTs can be addressed by different methods. These include for instance the manipulation of CNTs by instrumental tools, such as, micromanipulators, or force microscopic techniques. Selected examples are summarized to discuss the possibilities emerging from these manipulation tools.

1.4.1.1 MOVING CNTs BY SCANNING FORCE MICROSCOPY

Several groups reported on techniques to use the tip of an atomic force microscope (AFM) to position CNTs on substrates,\textsuperscript{165-167} and even to manipulate the electrical properties of the CNTs by bending them.\textsuperscript{165,168}

The basic techniques utilized the cantilever of the AFM tip to physically move CNTs on the surface of the substrate. There are three methods reported, all based on different modes of operation of the AFM: 1) contact mode,\textsuperscript{168} 2) tapping mode with the feedback turned off,\textsuperscript{169} and 3) tapping mode with a high lateral speed that results in partial deactivation of the feedback.\textsuperscript{166}

Hertel \textit{et al.}\textsuperscript{168} described that the controlled movement of nanotubes on the substrate with the AFM is possible because of the strong interactions between a MWCNT and the substrate. These interactions can also be used to stabilize highly strained CNT configurations, such as bends and kinks, which showed, \textit{e.g.}, changes in the electronic structure and electrical transport properties. Postma \textit{et al.}\textsuperscript{169} described the use of the tapping mode without feedback control to translate and rotate SWCNTs on the surface of a substrate. By dragging the cantilever along a predefined path, the CNT (segments) could be moved across the surface and can be moved into desired locations or configurations. The authors described this method as being superior to the use of the contact mode because the contact mode is unable to manipulate the much smaller single wall CNTs, as their diameters can be significantly smaller than those of multiwall CNTs. Lefebvre \textit{et al.}\textsuperscript{166} reported the manipulation of CNTs
in the tapping mode with the feedback control still enabled to translate, rotate, cut, and place CNTs on top of each other by varying the tip-sample force and the tip speed. The technique allowed the construction of nanotube circuits, which were then contacted with electron beam lithography.

These scanning probe microscopy approaches allow the arrangement and investigation of the properties of individual tubes. However, it has to be critically mentioned that the manipulation time is rather long due to the relatively low scan speeds and the complexity of the moving action. Moreover, the durability of the tip material represents a critical issue that is difficult to control; even if feedback controlled manipulation procedures are implemented that allow a manipulation of the tubes under controlled conditions.

1.4.1.2 CNT ARRANGEMENT BY MICRO- AND NANOMANIPULATORS

Micro- or nanomanipulators can be utilized to move or reposition CNTs on the substrate. Yu et al.\cite{170} reported on a technique to manipulate CNTs in three dimensions inside a SEM. A piezoelectric vacuum nanomanipulator was constructed that achieved position resolutions similar to a SEM. The device was designed to handle nanometer-sized objects to facilitate investigations of mechanical and electrical properties. CNTs were successfully attached to AFM tips with this nanomanipulator, and electrical connections between different components of the manipulator could be used for electrical tests and monitoring of the conductivity of the sample being manipulated. The CNTs and CNT bundles were also bent, kinked, and broken, and the authors stated that nanosized materials could successfully be picked up and placed.

Rueckes et al.\cite{171} reported on the utilization of a micromanipulator combined with an optical microscope to attach 50 nm thick CNT ropes to electrodes. Akita et al.\cite{172} developed nanotube-based nanotweezers that were used to pick up and move nanomaterials in three dimensions. Two nanotubes were attached to silicon substrates that were electrically connected. By applying a voltage between the two CNTs, the ends of the tubes moved closer together. Above a critical voltage, the tube ends touched each other, creating the clamping action of tweezers. These tweezers were used to manipulate (translate, rotate) other CNTs.

As these manipulations are rather slow alternative approaches have been developed. These include, \textit{e.g.}, embedding approaches or the utilization of external driving forces.
1.4.2 ALIGNING CNTs BY EMBEDDING TECHNIQUES

Embedding techniques often use matrices or molds that provide access to individual CNTs in tube assemblies. This allows, e.g., the investigation of the electrical properties of individual tubes.

1.4.2.1 MATRIX-EMBEDDED CNT SYSTEMS

Ajayan\cite{173} reported on a technique to align CNTs within a polymer resin. CNTs were dispersed in dilute concentrations to minimize the entanglement of the CNTs and were incorporated into an epoxide resin. The resin was subsequently cured with an appropriate amount of hardening agents in such a way that the hardness of the resin and the CNTs were equal. Thin slices, less than 0.2 µm thick, were cut off the resin using a diamond knife in a microtome. The shear stresses resulting from the cutting action caused most of the CNTs to align along the cutting direction. The knife did not cut or break the CNTs as no change in their size distribution could be observed.

In order to study the electrical properties of individual CNTs, Smith et al.\cite{174} used a related method. The CNTs were dispersed within a polymer that was subsequently cured. The polymer was then broken to provide access to the nanotubes along the broken edge. Using SEM, individual CNTs were identified that protruded perpendicular from the surface of the break; these were used in the measurements and experiments to study the electrical properties.

Kasumov et al.\cite{175} also conducted electrical measurements on individual CNTs, and developed a laser technique utilizing a silicon membrane with electrodes printed on both sides of a 0.3 µm wide slit in the membrane. The nanotubes were first immobilized by embedding them in a polymer film or by dispersing them in a porous carbon film. The film was then placed across the electrode/slit and 10 µm over the electrode surface using a micromanipulator. A laser pulse was used to remove nanotubes from the film, whereby the nanotubes fell onto the silicon membrane. The silicon membrane was finally analyzed to identify nanotubes located across the gap and which connected the electrodes.
1.4.2 FORMATION OF ALIGNED ARRAYS OF CNTs BY SELECTIVE LASER ABLATION

Kocabas *et al.*\(^{176}\) reported on a laser technique to fabricate aligned arrays of CNTs. The technique took advantage of the anisotropic dimensions of the CNT (one dimension is smaller than the wavelength of incident light) and the fact that the interaction between CNTs and light strongly depended on the orientation of the CNT with respect to the incident electromagnetic waves. CNTs absorbed more light that was polarized along the tube length compared to light that was polarized across the tube width. As a result, polarized laser pulses with sufficiently high intensity and short pulse duration could ablate nanotubes that were in close alignment to the polarization direction, thus leaving misaligned tubes (with respect to the polarization direction) unaffected. The authors exploited this effect to create aligned CNTs from randomly-oriented deposits, with the orientation of the tubes being approximately perpendicular to the polarization direction of the incident light.

1.4.3 FLUID DYNAMICS AS A TOOL FOR THE ALIGNMENT OF CNTs

Another family of techniques useful to align CNTs post-synthesis is based upon fluid dynamics. These techniques induce drag on the CNTs, which cause them to rotate to minimize this force. Such methods are useful for simultaneously aligning great numbers of CNTs over relatively large areas and a range of surfaces. This section summarizes the main methods utilizing this effect.

1.4.3.1 GAS FLOW-INDUCED ALIGNMENT OF CNTs

Several researchers have used gas flows to orient CNTs on substrates. Xin and Woolley\(^{177}\) placed a droplet of a diluted SWCNT suspension onto an amine-functionalized silicon substrate, which was tilted 20° and placed into a quartz tube. Argon was flushed through the quartz tube at different velocities. After 10 min, the gas flow was stopped, and the droplet was pipetted off. The substrate was rinsed in DMF and water, and was dried. Upon imaging of the substrate, it was observed that 74% of the SWCNTs were aligned within ±5° of the argon flow direction, and 85% were within 10°. The control samples where no argon flow was applied, only showed random orientation of the CNTs. It was also possible to create orthogonal arrays of nanotubes by duplicating the procedure and rotating the sample by 90°. The gas flow velocity was identified as an important factor; velocities less than 6 cm/s did not show any effect on the orientation of the tubes. Although it was expected that the entire
droplet would move in the gas flow, it was observed that the droplet remained stationary and that circulation patterns within the droplet were created that guided the CNT alignment.

Lay et al.\cite{178} used a similar technique to Xin and Woolley. Silicon substrates were functionalized with amine groups to aid the deposition of CNTs. Suspensions of SWCNTs were fabricated using an anionic solution (surfactant sodium dodecyl sulfate, SDS) and sonication, followed by centrifugation and removal of the supernatant. The substrates were then gently brought into contact with the surface of the CNT suspension, resulting in a layer of the CNT solution adhering to the substrate. The substrate was then blown dry in nitrogen, resulting in a thin homogeneous film. Imaging revealed that the CNTs were aligned with the nitrogen gas flow direction. The authors explained the alignment of the SWCNTs by the shear flow of the solution resulting from the gas stream. The CNTs aligned themselves to streamline and reduce the resistance experienced from the flow. During the drying process of the solution, the CNTs diffused to the substrate surface and were attracted to the amine groups via van der Waals forces. More than 90% of the CNTs were found to be aligned within ±5° of the nitrogen flow direction.

Huang et al.\cite{179} reported on a technique using liquid flow to align CNTs on a substrate. Flow channels were created by pressing a PDMS mold against a silicon substrate. Liquid suspensions of nanowires were prepared and guided through the channels. It was discovered that the nanowires aligned themselves with the flow direction, with the degree of orientation controlled by the flow rate of the liquid. It was found that more than 80% of the nanowires aligned within ±5° with respect to the flow direction at high velocities (Figure 1-6).

![Figure 1-6. SEM image of nanowires aligned in the liquid flow direction in the channel. Reproduced from ref. [179].](image-url)
These observations supported the explanation of the findings by Lay et al. that the shear flow near the surface was the driving force of the alignment. The alignment of CNTs could be extended to hundreds of micrometers utilizing this technique. It was also found that the surface coverage was governed by the flow duration. Perpendicular arrays of nanotubes could be created by repeating the process in a layer-by-layer alignment approach.

1.4.3.2 CNT ORGANIZATION BY DRYING PHENOMENA

Tsukruk et al.\textsuperscript{[180]} described how hydrodynamics can affect the orientation of nanotubes. Both casting (similar to the method of Xin and Woolley\textsuperscript{[177]} without the gas flow) and dip-coating techniques were used to form nanotube arrays. The substrate surface was pre-patterned with alternating hydrophilic (amine-terminated) and hydrophobic (methyl-terminated) stripes by using a PDMS stamp inked with the desired self-assembly molecules. For the casting procedure, a drop of the nanotube suspension was deposited onto an inclined substrate, and the drop was dried in air. For the dip-coating technique, the prepared substrate was dipped vertically into a liquid suspension of CNTs, withdrawn at a constant rate, and dried in a vertical position. Variation of the withdrawing conditions and the casting conditions resulted in differently ordered arrays of CNTs anchored to the amine-terminated surface. The methyl-terminated surface did not host any CNTs. The results were described as a nematic type with a uniform local orientation, but no longitudinal order was observed. As there was no macroscopic flow in these experiments, the order was assumed to be caused by the receding liquid front as the solution dried along the contact line. The liquid drying resulted therefore into a directional flow within thick layers of the fluid. The CNTs attached themselves to the amine-terminated substrate surface and aligned themselves as the contact line receded. Within the droplets, the formation of looped or hooked CNTs was observed and could be explained by the attachment of CNTs at one end, while the receding front caused the CNTs to bend and fold back to form a loop.

Several other research groups used different variations of dip-coating methods to align CNTs on substrates. Shimoda et al.\textsuperscript{[181]} immersed a hydrophilic glass slide into an aqueous dispersion of acid-treated SWCNTs, which formed bundles. Initially, no CNTs deposited onto the substrate, but as the water gradually evaporated, the CNTs were observed to assemble only along the air/liquid/substrate triple line of the glass surface. As the water
Strategies to Synthesis, Post-Synthesis Alignment and Immobilization of Carbon Nanotubes

evaporated and the triple line descended, a continuous CNT film was formed. A schematic representation of this process is depicted in Figure 1-7a, b.

Figure 1-7. Schematic representation of the orientation and the assembly process of CNTs from the liquid phase (a). b) As the water evaporates, the CNTs align along the triple line. c) Due to the constantly receding contact line, a continuous and ordered CNT film is formed (adapted from ref. [181]). d) Representation of the contact line between SWNT solution and the substrate. e) Alternatively, patterned substrates consisting of hydrophilic and hydrophobic areas can be used to organize CNTs. Due to the differences in the wetting behavior of the substrate, wetting lines are formed. f) Due to the flow conditions CNTs align across the wetting line.

The thickness of the CNT film depended on the concentration of the nanotubes in solution. TEM analysis of the CNT films revealed that the CNT bundles were highly aligned along the direction of the triple line (Figure 1-7c). The ordering was described as being nematic in nature, with long-range ordering along the triple line direction, but no ordering in the perpendicular (translational) direction (Figure 1-7d). Shorter nanotubes revealed a higher degree of ordering than longer ones. The bundles formed by longer tubes showed a polycrystalline-type structure, where islands of bundles were highly ordered, but adjacent islands were only partially aligned. The driving force was described as being similar to the
formation of Langmuir-Blodgett films, where the system automatically maximizes the van der Waals interaction between adjacent CNTs. The authors noted that surface tension at the triple line likely played a role in the orientation of the CNTs as well.

A later article by the same group\cite{182} reported on a room temperature dip-coating technique that can be used for both SWCNTs and MWCNTs as well as for different substrate materials. The substrates were first patterned with alternating hydrophilic and hydrophobic regions using photolithography or thermal evaporation techniques to prepare monolayer patterns. Homogeneous suspensions of SWCNTs in water were prepared. The previously described procedure by Shimoda et al.\cite{181} was then followed, thus the substrates were vertically immersed into the CNT suspension and the solvent was allowed to evaporate, whereby the CNTs assembled and aligned at the air-liquid interface before depositing onto the substrate. It was found that the CNT film thickness could be adjusted by varying the CNT concentration in solution and the evaporation rate of the solvent; with thicker films being obtained at higher solution concentrations and lower evaporation rates. The films became discontinuous above 40 °C, or if very volatile solvents with fast evaporation rates were used (i.e., ethanol). In some cases, streaks formed because of instabilities at the receding fluid interface. It was also reported that the SWCNTs were highly aligned along the phase interface. However, on patterned substrates, with hydrophilic and hydrophobic stripes, the triple line is no longer straight and varies depending on the wetting properties of the substrate. This resulted in nearly parabolic patterns of the nanotube orientation (Figure 1-7e, f).

Widenkvist et al.\cite{183} compared three techniques for the deposition of functionalized MWCNTs onto silicon substrates: drop evaporation, vertical dipping, and the previously discussed dip evaporation. Dip evaporation did not result in uniform surface coverage of the MWCNTs, because rings formed due to the CNT accumulation at the liquid-air interface. It was also found that the dip evaporation method resulted in the formation of a striped distribution pattern; again due to the accumulation of the CNTs at the liquid-air interface. The vertical dipping procedure was suitable to obtain the most uniform surface coverage of CNTs on the substrate. This was also combined with surface patterning techniques in order to achieve area selectivity in the deposition approach.

Kim et al.\cite{184} reported on a Langmuir-Blodgett-based layer-by-layer deposition method of CNTs using horizontal lifting (similar to the technique described by Lay et al.\cite{178}) or vertical dipping to build homogeneous thin films of SWCNTs. The effects of the preparation
technique on the nanotube orientation were investigated. The authors found two mechanisms affecting the orientation of the SWCNTs; a) the compression of the LB film orienting the CNTs perpendicular to the applied force prior to the deposition on the substrate (this mechanism was observed both in the horizontal lifting and in the vertical dipping method), and b) the liquid flow causing alignment of the CNTs on the substrate (observed only in the vertical dipping mode). The orientation of the CNTs was observed in both cases, however the orientation caused by the flow of the solution in the vertical dipping technique was more efficient.

1.4.4 GUIDED ASSEMBLY OF CNTS BY LITHOGRAPHIC TECHNIQUES

Lithographic techniques can be used to create complex patterns on substrates, which are useful for structuring assemblies of CNTs for different applications. This section highlights the major developments in printing and lithography techniques that can be used for the deposition and patterning of CNTs onto substrates.

1.4.4.1 SURFACE PATTERN-GUIDED ASSEMBLY OF CNTS

Im et al.\cite{185} investigated the selective assembly of double wall carbon nanotubes (DWCNTs) as well as of MWCNTs on substrates with different polarity. Gold or SiO$_2$ substrates were patterned with a non-polar self-assembled monolayer (SAM) (either 1-octadecanethiol (ODT) or $n$-octadecyltrichlorosilane (OTS)) for the CNTs absorption and empty spaces were back-filled with a polar SAM (16-mercaptohexadecanoic acid (MHA)). For the initial process development, dip-pen lithography (DPN) was used as a patterning tool, and micro-contact printing ($\mu$CP) was used to fabricate large-scale ODT patterns on Au. Furthermore, photolithography was used to pattern OTS monolayers on SiO$_2$ surfaces. CNTs were attracted to polar SAM regions or bare surface regions and appeared to be aligned within the patterns even without any external forces after immersion of the substrate (Figure 1-8). CNTs were also successfully adsorbed onto the large patterned areas.
Figure 1-8. AFM images of a) DWCNT patterns on gold surfaces. ODT monolayers were assembled onto gold substrates to block the assembly of CNTs. They adsorbed on the bare surface areas. b) Patterns of MWCNTs were formed on a gold surface. ODT passivated the remaining surface. c) DWCNTs were adsorbed on the silica substrate, OTS was utilized to passivate the remaining area. d) Nanoscale lines were patterned to guide the assembly of DWCNTs onto the bare gold surface (dark areas). ODT inhibited the adsorption of tubes on the light areas. The x- and y-axis scales are identical in all images. Reproduced from ref. [185].

Zhou et al.\textsuperscript{186} applied a combination of two techniques to pattern CNTs. Firstly, purified arc discharge synthesized CNTs were dispersed in SDS. Then, the solution was percolated through a filter leaving a CNT film behind. Subsequently, the film was rinsed with deionized water to remove the surfactant. Polydimethylsiloxane (PDMS) stamps were then utilized to transfer the CNTs from the film onto different substrates. Polyethylene terephthalate (PET), glass, poly(methyl methacrylate) (PMMA) and silicon were used as substrates. The smallest patterned size reported was 20 µm, and the patterns of CNT films were homogeneous and highly conductive.

Huang et al.\textsuperscript{187} used a contact transfer technique to apply vertically-aligned CNTs produced by pyrolysis of iron(II) phthalocyanine to temperature-sensitive substrates. The resulting CNT films consisted of vertically aligned tubes, which were subsequently released from the substrate by HF/H\textsubscript{2}O. The resulting substrate-free film of CNTs was afterwards deposited on a TEM grid utilizing a floating and lifting-up technique. When the TEM grid was brought into contact with a polystyrene substrate, the CNTs were embedded into the polymer and remained in a normal alignment with respect to the surface.
Hannon et al.\cite{188} selectively placed CNTs on HfO$_2$ and Al$_2$O$_3$ substrates. Two different patterning techniques were utilized. The first method was micro-contact printing of acid functionalized hexadecylphosphonic acid (HDPA) on Al$_2$O$_3$ or HfO$_2$ substrates. The acid rendered the patterns hydrophobic, and the excess of the solvent was removed by heat treatment. Subsequently, the surface was placed into a suspension of SWCNTs dispersed into an organic solvent, such as 1,2-dichloroethane (DCE) or 1-methyl-2-pyrrolidone (NMP). SWCNTs were selectively placed on the non-functionalized areas. The second approach used electron-beam lithography to create 25 nm deep Al trenches of different width on a silicon substrate. This substrate was then immersed in the solution of HDPA in 2-propanol, resulting in the formation of HDPA groups on the Al lines. Subsequently, the substrate was placed in the SWCNT/DCE solution. The CNTs were attached to the SiO$_2$ regions and their assembly on the Al lines was efficiently suppressed. These two techniques represented a negative patterning approach, where the tubes did not bind to the patterned areas.

Meitl et al.\cite{189} used a transfer printing technique to pattern SWCNTs onto different substrates, including plastic sheets. SWCNTs were dispersed in an aqueous solution of SDS. A controlled flocculation (cF) process was used to deposit a film of SWCNTs onto a PDMS stamp. In this process, streams of SWCNTs solution and methanol were simultaneously applied in the center of a rotating substrate (the PDMS stamp). The methanol was utilized to remove the surfactant from the CNT solution and then evaporated. With this method, films with a controlled thickness of the SWCNT films were produced on the stamps. These were brought into contact with a substrate, and the CNTs were transferred in a dry process onto the substrate. The transfer was guided by differences in surface energies of the stamp and the substrate. This printing method could be performed several times on the substrate without difficulties. In order to transfer SWCNT patterns onto curved substrates, the substrates were simply rolled over the PDMS stamp covered with CNTs, also resulting in the carbon nanotube pattern transfer onto the curved substrate. The group also demonstrated the deposition of SWCNTs by the cF technique on different substrates, such as SiO$_2$ (aminopropyltriethoxysilane (APTS)-treated and untreated), ITO, polyimide, Au, mica (APTS-treated and untreated), PDMS, and PMMA.

Nan et al.\cite{190} used a surface condensation approach to pattern CNTs onto the surface. The SWCNTs were synthesized by arc discharge, shortened and functionalized by oxidation in a mixture of concentrated sulfuric and nitric acid. After oxidation, the CNTs were functionalized with carboxylic groups at their ends. These tubes were subsequently dispersed
in DMF. Patterns of SAMs of \( \text{NH}_2(\text{CH}_2)_{11}\text{SH} \) were created by a micro-contact printing approach on clean gold substrates. The substrates were placed in the CNT solution, to which dicyclohexylcarbodiimide (DCC) was added. The smallest patterns tested were circles with a diameter of 1.5 µm and the CNTs were selectively attached to the amine-terminated areas. Wang et al.\cite{191} created patterns of SWCNTs on gold substrates down to sub-micrometer-size. This method was based on the attraction of SWCNTs to hydrophilic regions. Gold substrates were patterned with a SAM of MHA by dip-pen lithography (DPN) or micro-contact printing. The exposed gold regions were subsequently passivated with 1-octadecanethiol (ODT). SWCNTs were dispersed in 1,2-dichlorobenzene and a drop of CNT solution was placed on a patterned gold substrate or was rolled over the substrate several times. The investigated gold substrates revealed that SWCNTs were attracted to the MHA features, specifically to the boundary between the hydrophilic MHA and hydrophobic ODT SAMs. It was proposed that evaporation caused the high concentration of SWCNTs in the boundary regions and van der Waals attractions guided CNTs to hydrophilic areas.

### 1.4.4.2 Alignment of CNTs Utilizing Resists and Filters

Choi et al.\cite{192} used PMMA masks to deposit SAMs of silane molecules in order to create the patterns for subsequent CNT placement. A 100 nm-thick PMMA resist layer was applied onto a cleaned SiO\(_2\) substrate. By using electron-beam lithography, the PMMA was patterned with lines of different widths ranging from 50 nm up to 200 nm. On the exposed SiO\(_2\) surface, a monolayer of a 1,2-aminopropyltriethoxysilane (APTS) was formed by vapor deposition. Then, substrates were immersed in a SWCNT solution. Finally, the PMMA layer was removed. SWCNTs were selectively attached to the silane-terminated pattern structures.

Two studies report on techniques that also result in aligned carbon nanotubes on a substrate. Firstly, Choi et al.\cite{193} created a 4.5 inch CNT-based field-emission display (FED) using purified SWCNTs, which were synthesized by arc discharge. Tubes were dispersed in isopropyl alcohol and mixed with nitrocellulose to form a paste. This paste containing the CNTs was squeezed through a mesh of a metal-patterned soda lime glass. By this method, CNT patterns of lines with a width of 300 µm were formed. The pattern was subsequently heated to remove the organic binder. SEM investigations showed that the CNTs were vertically aligned. This could be due to three different reasons: a) paste squeezing through the
metal mesh, b) surface rubbing, and/or c) conditioning by the electric field. A few years later, the same group used this technique to create an even larger 9 inch FED.\cite{194}

Secondly, De Heer et al.\cite{195,196} reported on a technique similar to Huang et al.\cite{187} to align large numbers of CNTs. Therefore, the CNTs were first dispersed in ethanol. The suspension was then passed through an alumina micropore filter. As a result, the CNTs got stuck in the pores of the filter, and were partially sticking out of the filter or were perpendicularly aligned to the surface. This filter was subsequently placed face down on a polymer sheet, such as Teflon\textsuperscript{TM}, with the free-standing ends of the nanotubes being embedded into the polymer. The polymer sheet was removed resulting in a polymer film with CNTs protruding more or less vertically aligned CNTs from the surface.

In the physical methods section, the techniques described are very diverse, ranging from individual CNT manipulation to large scale flow-induced alignment. The common element is that these methods heavily depend on physical forces to align and/or deposit the CNTs. Physical manipulation can be very precise for individual CNTs, but is sometimes slow and not suitable for large numbers of CNTs. These methods have additionally limited resolution and require fairly large amounts of material and, therefore, waste much material. Fluid dynamic techniques are effective for aligning CNTs across a broad range of scales, but can be slow (particularly the evaporation techniques). These methods may also have to be combined with a separate deposition technique to firmly attach the CNTs to the surface, and are typically limited to relatively simple geometries. Printing and lithography techniques are highly suited for patterning applications and are typically rather fast and simple techniques. However, the resolution is limited by the available masks and stamps, while the lifetime and reproducibility are unproven.

1.5 Use of External Fields in Attachment and Alignment of CNTs

The use of externally applied fields, such as electric or magnetic fields, can aid in the alignment of CNTs and can also be used for their deposition. Although CVD synthesis can be enhanced by external fields, such as electric fields in a cold-wall CVD reactor,\cite{197} radio-frequency plasma-enhanced CVD,\cite{198} and direct current-enhanced plasma CVD\cite{199} during CNT synthesis, the focus in the following section is placed on utilization of external fields to aid in the alignment of pre-existing CNTs in solution and/or on surfaces.
1.5.1 MagnetICT FIELDS FOR THE ALIGNMENT OF CNTs

Metallic SWNTs are paramagnetic along their long axis, while other types of CNTs are diamagnetic across their diameter. In both cases, this results in nanotubes (when free to move and not immobilized) aligning themselves parallel to the magnetic field lines, which represents their lowest energy orientation. Walters et al. estimated that a magnetic field strength of 10 T would be sufficient to align SWNTs in suspensions. The authors successfully created aligned films with field strengths as low as 7 T. The required alignment energy was observed to be dependent on the amount of carbon. As a consequence it was observed that the alignment of ropes consisting of carbon nanotubes reduced the required strength of the magnetic field to induce alignment as compared to individual CNTs of the same length. Suspensions of nanotubes with the addition of 0.05% Triton-X in ultra-pure water were filtered, and the surfactant and water were removed by flushing the system with isopropyl alcohol (IPA) to obtain the CNT ropes. The last step of the preparation was found to be critical for the formation of suitable filter cakes because the CNTs would not deposit on the filter in the presence of the surfactant.

Tumpane et al. reported that magnetic fields as weak as 0.1 T were suitable to align SWNTs; a value, which is well within the power of simple electromagnets. The very large aspect ratio of nanotubes was observed to be a determining factor for their tendency to orient in magnetic fields. Higher aspect ratios (length/diameter) resulted in higher magnetic susceptibilities of the tubes and, thus, lowered the required strength of the magnetic fields. Preventing the bundling of nanotubes in suspension helped to preserve the effective aspect ratio. The authors improved the solubility of the nanotubes, to prevent bundling, by introducing aryl groups on the side walls of the SWCNTs. However, there was agreement with the previously reported observations that CNT ropes aligned better due to their higher magnetic susceptibility. No information on the quality of the deposited CNT films on surfaces was provided. Thus, it remains unclear if hydrodynamic effects on the surface and/or the filtering processes used in the previously reported approaches played important roles in the alignment process of the CNTs.

Sano et al. reported on the use of magnetic fields to improve the field emission properties of CNT-containing films. It was found that the CNTs typically oriented in the plane of the film. However, when permanent magnets were used to create a magnetic field across the substrate during the film formation, iron-filled MWCNTs tended to arrange towards a
perpendicular orientation within the film. This alignment was used for instance to improved field emission properties.

Smith et al.\textsuperscript{[203]} and Hone et al.\textsuperscript{[204]} also demonstrated that CNTs tended to align with magnetic fields. Thick films (“buckypaper”) of SWNTs were produced by filtering a suspension of SWNTs through a nylon filter membrane in the presence of a magnetic field. These films were characterized with and without an additional annealing treatment. It was found that the nanotubes aligned with the magnetic field (perpendicular to the filter) in a mosaic spread of less than 35°. The films tended to tear in directions parallel to the magnetic field lines when peeled off from the filter. The density of the aligned NT films was higher compared to normal filter-deposited membranes, and much higher than the as-grown material. Additional tests showed that the electrical and thermal conductivities in the film were anisotropic, showing improved properties along the alignment direction with respect to the perpendicular axis and unaligned films. The authors indicated that this method for aligning CNTs may facilitate applications, such as continuous seeded growth, controlled porosity of energy storage media, and the study of tube interactions.\textsuperscript{[203]}

\subsection{1.5.2 Electric Fields and Electrophoresis for the Placement and Alignment of CNTs}

Electric driving forces can be used to improve the alignment of CNT suspensions. Here advantage is made of the conductive nature of certain types of CNTs. In addition to aligning large numbers of CNTs with respect to each other, electric fields can also be used to position individual CNTs.

\subsubsection{1.5.2.1 Control of Individual CNTs by Scanning Force Tips}

Stevens \textit{et al.}\textsuperscript{[205]} reported on a technique to attach a MWCNT onto an AFM tip. First, a CVD technique was used to grow ordered MWCNT films on a substrate. Utilizing micromanipulators under an optical microscope, an AFM tip was lowered onto the substrate. In close proximity, an electric field was applied, using the substrate of the MWCNT as the positive electrode and the AFM cantilever tip as the negative electrode. Low voltages of 3 to 10 V attracted the MWCNT to the cantilever tip and aligned it with the apex of the tip. The attraction resulted from an induced dipole moment in the MWCNT. The alignment is caused
Chapter 1

by the geometry of the field created by the cantilever. The voltage was subsequently increased from 10 to 40 V to finally disassociate the MWCNT from the substrate. Small defects in the MWCNT resulted in the nanotube splitting, as the resistance locally heated the nanotube, leading to the physical detachment of the MWCNT from the substrate. This process was comparable to an arc discharge method. The arc appears when the nanotube is brought in close contact to the AFM tip, promoting partial dissociation of the CNT end. Thus an amorphous carbon layer is formed on the apex of the AFM tip, which triggers the fusion of the CNT to the AFM tip. The nanotube was additionally stabilized by van der Waals forces between nanotube, metallic tip, and the amorphous carbon deposited during the heating process. The results of nanotube-tipped AFM cantilevers were very promising.[206]

In another study, Stevens et al.[205] indicated that this attachment method also utilized the induced current, supporting the alignment of the MWCNT with the AFM tip (Figure 1-9).

![Figure 1-9. Electron micrographs of an AFM cantilever tip with an attached MWCNT. Reproduced from ref. [205].](image)

The cantilever was coated with cobalt, which was assumed to play a critical role in the attachment of the nanotube to the tip. The plasma of the voltage-induced arc discharge was expected to be energetically strong enough to partially disassociate the end of the nanotube, and some of the carbon was evaporated as ions. These energetically disassociated positive carbon ions were attracted by the cobalt-coated, negatively charged tip. The authors assumed that this hot amorphous carbon build-up helped to fuse the nanotube to the tip and improved the stability of the CNT AFM tip.
Nakayama et al.\textsuperscript{[207]} used the electrostatic attraction generated from a DC electric field of tens of volts to move a CNT to a silicon tip. Several other methods were also used, including welding the nanotube to the tip by first bringing the CNT in contact with the tip, then running a milliamp current through it, welding them together. These CNT tips were found to function very well. Asaka et al.\textsuperscript{[208]} reported a similar method to attach MWCNTs to surfaces in order to study their field emission properties. Duan et al.\textsuperscript{[209]} reported on a nanowelding process to immobilize SWCNTs onto a substrate at specific points. A scanning probe microscope was used and a positive bias voltage was applied between the silicon substrate and the conductive scanning probe microscope (SPM) tip at a point along the length of a CNT on the substrate. The resulting electric field caused the silicon to oxidize. As SiO\textsubscript{x} is less dense than silicon, a volume expansion occurred and the SiO\textsubscript{x} grew around the CNT, which effectively fixed the tube to the silicon substrate. The process resulted in very little damage to the CNT, while making the immobilization controllable. This form of ‘spot-welding’ could be used to fix the CNT in different configurations, \textit{i.e.}, bends or kinks, and is useful to conduct in-depth studies, \textit{e.g.}, of the CNTs (mechanical) properties.

\subsection*{1.5.2.2 Field-Induced Alignment of CNTs}

Several groups have demonstrated that electric fields can induce alignment of CNTs in suspensions. The use of electric fields has also been proposed as a means of purifying nanotube suspensions of carbon particles and other debris.\textsuperscript{[210]} Yamamoto et al.\textsuperscript{[210]} ultrasonically dispersed CNTs and centrifuged the dispersion to remove the larger particles. Drops of the suspension were placed on a glass substrate facilitated with aluminum electrodes, and a direct current (DC) electric field was applied until the solvent evaporated. It was observed that the particles in suspension, which have a positive charge in isopropyl alcohol (IPA), moved towards the cathode with a velocity proportional to the strength of the electric field, similar to an electrophoretic process. It was also observed that the nanotubes moved faster compared to the particles, which was additionally beneficial for purification. Furthermore, the nanotubes aligned parallel to the electric field due to the difference between their axial and radial electrophoretic velocities; aligned nanotubes moved approximately twice as fast as those that are perpendicularly aligned with respect to the external electric field. Chains and tree-like structures of particles and CNTs were formed as a result of the fact that once a CNT touches the electrode the electrode potential is transferred to the end of the tube because of its conductivity. A theoretical analysis of the process also showed that
conductive or dielectric particles exhibited a dipole moment in electric fields that was heavily influenced by the anisotropy in the shape of the particles.\textsuperscript{[211]} The dipole moment was observed to be oriented axially within the nanotube; as a result, the tubes experienced a torque until the dipole moment, and, thus, the nanotubes, were aligned parallel with the electric field. Bubke \textit{et al.}\textsuperscript{[211]} suppressed the drifting of the CNTs suspended in ethanol in an electric field with the application of an alternating current (AC) field. However, it was found that the optical anisotropy of the suspension, a measure of the degree of the CNT alignment, decreased rapidly. The use of higher field strengths and highly purified materials was proposed to yield better results.

Yamamoto \textit{et al.}\textsuperscript{[212]} later succeeded in the alignment of nanotubes with AC electrophoresis. A previously described procedure was followed,\textsuperscript{[210]} but an AC field was applied in this case. The field strength was kept constant and the frequency was varied from 10 Hz to 10 MHz. It was observed that, at low frequencies, all CNTs and impurity particles moved towards the electrodes. This is shown in Figure 1-10, where all the particles have moved to the electrode (a), and very few remained between the electrodes (b). At high frequencies, however, the nanotubes preferentially moved towards the electrode (c), whereas the impurity particles remained between the electrodes (d).
Figure 1-10. SEM images of the substrate after IPA is evaporated in an electric field of $2.2 \times 10^3 \text{ V}_\text{RMS/cm}^{-1}$ of different frequencies. a) The edge of the left electrode (dotted line). The solution was moved with an AC frequency of 10 Hz. (b) Midpoint between the electrodes. (c) At higher frequencies of 10 MHz the edge of the left electrode (dotted line), and (d) the midpoint between the electrodes. Reproduced from ref. [212].

The movement of the CNTs and particles in an AC field was attributed to the ability of the negative ions surrounding the positively charged nanotubes and particles to move in conjunction with the external AC field. At frequencies below 10 kHz, the ions kept up with the polarity shifts. As a result, the CNTs and particles always moved towards the negative electrode at any given time. However, the CNTs and particles moved faster towards the closer electrode during its negative cycles. Thus, the particles performed a back-and-forth motion with a net movement towards the closest electrode. At frequencies higher than 10 kHz, the ions did not respond fast enough to the changing polarity. As a result, the particles and nanotubes showed induced dipoles, which supported the movement towards the closest electrode.

More recently, Lee et al.\textsuperscript{[213]} also utilized the AC electrophoresis approach to align SWCNTs. In this case, the purpose was to suspend a few CNTs between an electrode setup to create a bridge-like structure. PMMA was deposited between the electrodes to prevent the CNTs from
depositing onto the surface in between the electrodes. Various techniques, such as oxygen plasma ashing and electron-beam lithography were used to fabricate the desired structures. AC electrophoresis was used to align the CNTs between the electrodes. The CNTs were then pinned in place with a layer deposited on top of the electrodes before the PMMA support was removed from underneath the CNTs, resulting in a configuration where the CNT bridged the gap without having contact to the substrate. The authors claimed that the number of aligned CNTs could be controlled by optimizing the AC voltage amplitude and the time the field is applied. Their results also agreed with studies reported by Yamamoto et al.\cite{212} with respect to the observation that higher AC frequencies resulted in improved alignment of the CNTs. In addition, it was observed that the majority of the aligned CNTs was metallic.

Chen et al.\cite{214} also utilized AC electric fields for the alignment of CNTs. Their results largely agreed with the previously highlighted reports. Amplitude and frequency of the electric field had a significant effect on the alignment of CNTs, with a higher frequency resulting in improved alignment of CNTs. One result that did not agree with other reports, however, was the movement of CNTs in a DC electric field. It was reported by Yamamoto et al.\cite{210} that the CNTs had a positive charge when suspended in IPA and tended to move towards the cathode and align with the DC electric field. Chen et al. found that the CNTs carried a negative charge when suspended in ethanol and tended to move towards the anode without any alignment of the CNTs.

Electrospinning was also used as a method to align nanotubes. Gao et al.\cite{215} reported on a modified electrospinning technique that deposited the spun nanofibers in a controlled fashion, as opposed to the random fashion that standard electrospinning produces. In this process, SWCNTs were mixed with an organic polymer, \textit{i.e.}, poly(vinylpyrrolidone). This mixture was placed in a metallic container with a small hole and was suspended over a metal plate. A DC electric field was applied, utilizing the container as the positive electrode, and the bottom plate as the negative electrode. At a critical potential, the liquid containing the CNTs could be drawn through the hole in the container in a thin stream via electrostatic forces. The splitting of the negative electrode into two independent pieces modified the electrostatic forces, to improve the alignment of the nanofibers parallel to the counter-electrodes, controlling their deposition. By electrospinning, the CNTs were also aligned and dispersed as individual nanotubes within the nanofiber itself. The electrospinning process tended to exfoliate the nanotube bundles that SWNTs typically form. After deposition of the nanofibers, the authors used chemical vapor etching in ethanol to remove the polymer from the nanotubes. Thermal
Strategies to Synthesis, Post-Synthesis Alignment and Immobilization of Carbon Nanotubes

treatment could also be used as an alternative process. The resulting SWCNT films were patterned according to the shape of the deposited nanofibers.

Triboelectric charging can also be used as a method to vertically align carbon nanotubes in films, which is particularly useful for the fabrication of field emission displays. In this method, a polyethylene film is used to cover the CNT film surface and rubbed with a cotton ball to induce triboelectric charging, which weakly attracts the CNTs to the film. By removing the film, the CNTs are pulled into vertical alignment, more-or-less perpendicular to the CNT film surface. A closely related physical method is the use of adhesive tape. In place of inducing triboelectric charging, adhesive tape is applied to the CNT film. When the tape is removed, the CNTs are pulled upwards from the CNT film in a vertical orientation. This method, however, may result in the outright removal of some of the CNTs and may contaminate the surface with the adhesive.

1.5.3 ALIGNMENT OF CNTs UTILIZING LIQUID CRYSTALS

The use of liquid crystals (LC) was proposed as another approach to align CNTs. Dierking et al. described liquid crystals as anisotropic fluids that show molecular self-assembly. In this case, thermotropic rod-like molecules of the liquid crystal showed the tendency to orient along the long molecular axis in a preferred direction called the director. There are several possible phases of liquid crystals. The nematic phase exhibits a high orientational order of the molecules, while the centers of mass of the molecules are distributed isotropically. The ability of nematic liquid crystals to self-organize was used to align dispersed CNTs (Figure 1-11).
Figure 1-11. Alignment of CNTs with liquid crystal solvents. a) A droplet of the mixture of liquid crystals (ellipsoids) and suspended carbon nanotubes (rods) are placed on a porous membrane substrate. b) The bulk LC is aligned using a grooved surface or external fields, which, in turn, orders the nanotubes in solution. c) The LC is drained through the porous membrane leaving behind an ordered nanotube film.

Furthermore, the liquid crystal director can be reoriented by applying electric or magnetic fields, as well as by the use of grooved surfaces, patterned electrodes, and other geometric or hydrodynamic methods. This reorientation of the director resulted in the reorientation of the dissolved nanotubes. A possible application of this approach could be the fabrication of nanoswitches \cite{220,221} or the large-scale alignment of CNTs. \cite{219}

Lynch and Patrick \cite{222} reported that thermotropic liquid crystals could be used as solvents for CNTs and represent a simple, versatile, and reproducible way to control the order in SWCNT and MWCNT films. In addition, the authors stated that these properties enabled the preparation of monolayer and multilayer films with the orientation controlled by well-established methods of LC alignment, including grooved surfaces, magnetic fields, and patterned electrodes. The authors went on to demonstrate methods for the fabrication of connecting pairs of electrodes with CNT wires and the formation of uniaxial and biaxial SWCNT and MWCNT films over large length scales and with defined thicknesses.
The film thickness could be increased by repeating the process as most of the CNTs remained adsorbed to the surface of the membrane. The desired alignment direction was obtained by formation of shallow parallel scratches on the membrane, which resulted in the planar alignment of the LC solvent parallel to these grooves but did not interfere with the CNT adsorption. However, the alignment of the nanotubes was not dominated by flow or hydrodynamic effects. Due to the fact that LCs are poor solvents for CNTs, the suspensions had to be used directly after preparation to prevent flocculation. As there is a large variety of known thermotropic liquid crystals with a wide range of properties, it is likely that a suitable liquid crystal with appropriate solvent characteristics is available for most applications.

Lagerwall et al.\textsuperscript{[223]} demonstrated that lyotropic nematic liquid crystals, where the liquid crystal is a two component mixture of a surfactant and water, could be used in applications where the liquid crystal eventually has to be removed after the aligning process. Removal of thermotropic liquid crystals was found to be difficult. In contrast, the lyotropic liquid crystal can be easily removed either by washing or evaporating the solvent. An additional benefit of the lyotropic LC was that the surfactant component helped to stabilize the dissolved CNTs, preventing the clustering that typically characterizes suspensions of CNTs. These improved properties are combined with the possibility to manipulate the orientation of the director, thus, can be used as an alternative to the previously used thermotropic LCs.

Interestingly, liquid crystals not only facilitated the alignment of dissolved CNTs, but also benefited directly from their presence. Studies demonstrated that in a twisted nematic liquid crystal display the presence of CNTs effectively reduced the required DC driving voltage and improves the switching behavior,\textsuperscript{[224]} greatly decreased the residual DC,\textsuperscript{[225]} and lowered the undesired field screening effect.\textsuperscript{[226]} Thus, the performance of the device was significantly improved.

The presence of CNTs in nematic liquid crystals was also observed to have an influence on the phase transition temperature between the isotropic and the nematic phases.\textsuperscript{[227]} Additionally, in a reversal of roles, aligned CNTs attached to a substrate were used to align nematic liquid crystals.\textsuperscript{[228]} LC optical cells with aligned CNT layers showed switching in the presence of an electric field. These CNT films were introduced as a new alignment material that may eventually facilitate the fabrication of liquid crystal displays.
Zhang et al.\textsuperscript{[229]} reported a method of utilizing liquid crystals to separate and purify a mixture of CNTs by length, taking advantage of features in the phase diagram of lyotropic liquid crystals (e.g. the Flory chimney). Oxidized MWCNTs were observed to form their own lyotropic liquid crystal phase when they were dispersed in water or other aqueous solutions.\textsuperscript{[230]} Under certain conditions, a suspension of treated CNTs could be separated by size as the longer CNTs, with a higher mesogenicity, \textit{i.e.}, a greater tendency to form liquid crystals, entered the nematic phase, while the shorter CNTs and impurities remained in the isotropic phase. The two phases could subsequently be separated physically. Davis \textit{et al.}\textsuperscript{[231]} studied the phase behavior and rheology of SWCNTs in superacids. The protonation of the SWCNTs allowed them to remain dispersed in solution even at very high concentrations, thus significantly reducing their tendency to cluster. It was also discovered that a biphasic system could be formed, which consisted of a nematic phase with ‘spaghetti-like’ self-assembled supramolecular strands of solvated tubes and a dilute isotropic phase. At higher CNT concentrations, these strands self-assembled into a polydomain nematic liquid crystal. The authors claimed that this phase can be processed into highly aligned fibers of pure SWCNTs. Additives like surfactants or polymers to stabilize the fibers were not required. Additionally, highly-aligned, needle-shaped alewives of CNTs could be formed by the addition of a small amount of water.

Additionally, Badaire \textit{et al.}\textsuperscript{[232]} reported on another method to form a nematic liquid crystal phase from CNTs. Denatured DNA was used to adsorb onto the non-functionalized CNTs, which resulted in stabilizing them and provided their aggregation in aqueous solutions. This improved stability allowed much higher concentrations of CNTs in solution to be obtained, that, upon reaching a critical concentration of CNTs, resulted in a nematic liquid crystal phase with the CNTs oriented along the director.

The external field methods described here use indirect field forces to align CNTs. These forces are usually electric or magnetic fields, but nematic liquid crystals can also induce the alignment of CNTs. Such methods are usually applicable over fairly large scales, and are simple and fast for creating large arrays of aligned CNTs. However, also separate post-alignment deposition techniques are typically required.
1.6 Chemically-guided Alignment and Immobilization of Carbon Nanotubes

Many of the previously described physical and external forces methods involve chemical functionalization steps in the process to fix CNTs onto surfaces and to guide their assembly. These chemical steps constitute part of a large field of research. Examples of these chemical methods include the use of chemical vapor deposition (CVD)\textsuperscript{[84,233-239]} or pyrolysis\textsuperscript{[84,240-243]} techniques to synthesize CNTs on templated substrates. Template-free methods based on the pyrolysis of iron(II) phthalocyanine (FePc) or ferrocene are also possible,\textsuperscript{[84,244-247]} while different patterning techniques can be used to achieve region-selective deposition.\textsuperscript{[97,134,242,243,245,248,249]} This section focuses on the literature describing chemical methods to selectively attach (pattern) or align prefabricated CNTs to surfaces. The growing number of publications on the use of biomolecules and DNA is discussed in a sub-section.

1.6.1 Immobilization of CNTs Utilizing Self-Assembled Monolayers

The use of self-assembled monolayers (SAM) to attach CNTs to surfaces is a well-studied method in the literature pioneered by Liu et al.\textsuperscript{[250]} Many of the studies presented in this section are based on methods that share the same principles described by Liu’s study, but there are considerable differences. Both Nan et al.\textsuperscript{[251]} and Cai et al.\textsuperscript{[252]} reported on the deposition of SWCNTs onto amine-terminated SAMs on gold substrates. Both groups used chemical oxidation to first functionalize the tubes by cutting the ends of the tubes. As a result, carboxylic groups attach to the open ends of the tubes. The latter article by Cai et al. described the use of ozone to perform the oxidation, while Nan et al. used acid treatment. Subsequently, a gold surface was coated with a SAM that consists of a thiol group and an amine group, one at each end. In a next step, dicyclohexylcarbodiimide (DCC) was added to a solution of SWCNTs in dimethylformamide (DMF) under sonication. The carboxyl groups on the CNTs aided, on the one hand, the dispersion of the CNTs, and on the other, they were utilized for the attachment of the tubes when the SAM-covered gold surface was placed in the CNT solution. The DCC promoted a condensation reaction involving the carboxylic acid groups on the CNTs and the amine groups on the SAM, which resulted in a binding of the CNTs on the surface of the SAM. Interestingly, Cai et al. reported that the CNTs deposited in random orientations parallel to the surface, whereas Nan et al. stated that the CNTs deposited with a vertical orientation because of the fact that direct contact between the hydrophobic
side walls of the CNT and the hydrophilic amine-functionalized SAM is energetically unfavorable (Figure 1-12a).

The differences in the orientation of the tubes could be a result of the different chemical oxidation methods. Both articles stated, however, that the CNT deposition was highly selective for the amine-containing surface; no CNT deposition was observed on the SAM-free areas of the substrate, thus opening possibilities for the patterned deposition of CNTs. The remainder of this section will focus on different selective placement techniques. The following section will summarize the techniques that combine placement and alignment.

*Figure 1-12:* Schematic representation of different approaches to form dense, vertically aligned CNT films. *a*) Self-assembled monolayers consisting of a thiol binding side to covalently link to the gold substrate, and an amine functionality to link to the carboxyl-terminated carbon nanotubes provide a means to vertically organize them onto the substrate. *b*) Alternatively, carboxyl-functionalized tubes can be deprotonated and interact with metal surfaces, i.e., silver.

Choi *et al.*[253] were able to attach CNTs to the amine groups of a self-assembled monolayer on the substrate. A method was presented to pattern the CNTs on the surface of the substrates using polymer masks (Figure 1-13).
Figure 1-13. Schematic overview of an approach utilizing e-beam lithography. a) Silicon substrates are covered with a PMMA resist. b) Electronbeam lithography is performed to form grooved substrates. c) The bare substrate areas of the grooves are cleaned by oxygen plasma treatment, and d) APTS is self-assembled by chemical vapor deposition. e) CNTs are deposited from a solution containing SDS as surfactant. f) After lift-off of the PMMA mask, CNT patterned areas are formed just in the lithographically defined areas.

A similar approach was reported by Auvray and co-workers.\textsuperscript{[254]} This work also introduced a process to form metal contacts on top of the deposited CNTs.

Burghard\textit{ et al.}\textsuperscript{[255]} presented a similar approach utilizing an alternative binding mechanism. It involved the use of an alkanethiol monolayer adsorbed onto noble metal electrodes. The alkane chains of the monolayer were able to displace some of the surfactant molecules surrounding the CNTs, leading to the attachment of the CNTs, as suggested by the authors. The CNTs selectively adsorbed to the SAM-covered electrodes and avoided the unmodified surface of the silicon substrate. By further adapting the surface groups by either 1) placing an octadecanethiol SAM on the electrodes or 2) amino-silanization of the substrate’s surface together with the adsorption of 3-mercaptopropionic acid (3-MPA) on the electrodes, CNTs could be organized on predefined areas of the substrate.

Another technique using alkanethiol self-assembled monolayers on gold films was described by Wang \textit{et al.}\textsuperscript{[191]} Using dip-pen nanolithography and microcontact printing, the gold surface
was functionalized with 16-mercaptohexadecanoic acid (MHA) and the remaining free surface was passivated with 1-octadecanethiol (ODT). The mercapto- and thiol groups resulted in the formation of a SAM on the gold surface. The MHA provided a carboxyl group at the free end, while the OCT introduced a methyl group. SWCNTs, side-wall functionalized with dodecyl groups to improve the dispersion, were then dispersed in 1,2-dichlorobenzene. Subsequently, a drop of the CNT solution was placed on the substrate and the substrate was tilted back and forth several times to coat the pattern. The drop wetted the MHA regions but not the ODT regions. The CNTs assembled exclusively on the MHA regions because of strong van der Waals interactions between the carboxyl groups of the MHA SAM and the SWCNT. The CNTs were frequently located near the border between the two SAM regions. This was caused due to the length of the CNTs, which often exceeded the size of the patterned features, resulting in the CNTs bending along the longest perimeter of MHA available, which can even result in the formation of circular structures.

Im et al.\cite{256} carried out similar work to Burghard et al., studying the deposition of CNTs (double- and multiwall) onto gold, silica, and (polar and non-polar) SAM-covered surfaces. Various physical techniques, e.g. dip-pen nanolithography, micro-contact printing, and photolithography, were used to pattern the surfaces. The CNTs were dispersed in non-polar o-dichlorobenzene, which is supposed to minimize the surface charges on the surface and the CNTs. Similar to other studies, it was found that the CNTs were attracted to the polar surfaces as well as to the (almost) neutral gold surface and avoided the absorption onto the non-polar surface areas. It was postulated that the surface charges were not the primary driving force for the CNT adsorption process, but that van der Waals forces were responsible for the adsorption. The CNTs adsorbed selectively on the patterned regions and did not cross pattern boundaries, while shorter CNTs were more likely to adsorb than longer ones. Peng et al.\cite{257} carried out similar work, but covered the substrates with a pattern of polar and non-polar SAMs. The results were consistent with other findings, as the CNTs adsorbed onto the polar SAMs. This work also described a method to pattern the substrates using photolithography. Other methods were briefly introduced by Rao et al.\cite{258}

Also utilizing polar and non-polar SAMs, Hannon et al.\cite{259} described a method using phosphonic acids to facilitate the area-selective adsorption of CNTs on certain metal oxide substrates of interest for microelectronics (ZrO$_2$, HfO$_2$, Al$_2$O$_3$, TiO$_2$). Phosphonic acids were observed to have a strong affinity for metal oxide surfaces and formed dense monolayers. Additionally, they could be patterned on the metal oxide substrates using techniques such as
micro-contact printing or electron beam lithography of aluminum onto silica wafers in combination with a subsequent oxidation step. In this study, the authors reported on the use of amine- and methyl-terminated alkylphosphonic acids to bind CNTs onto the substrate. The characterization revealed that the CNTs avoided the non-polar methyl-terminated areas (negative tone patterning) and selectively attached to the polar surfaces, i.e., the bare metal oxide surface (positive tone patterning). Attaching CNTs to the pattern was also achieved by creating a SAM pattern of aminobutylphosphonic acid (ABPA) on the metal oxide substrate. The CNTs were dispersed in NMP, as it has been shown to prevent the adsorption of the tubes on SiO$_2$ while allowing them to attach to the amine groups. The use of NMP also improved the dispersion of the CNTs as compared to other surfactants, i.e., Triton X-100 and SDS.$^{[260]}$ The CNTs selectively deposited onto the surface treated with ABPA. The major challenge of this approach, according to Hannon et al., was to further increase the density of the deposited CNT film. Chen and Dai$^{[248]}$ have developed a plasma technique that is applicable for a broad range of substrates, including polymers. Photolithographic or soft-lithographic techniques were used to pattern a polymer film on the substrate, e.g., on mica. Amine groups were then placed on the substrate via the plasma-polymerization of heptylamine, followed by the removal of the rest of the polymer mask. The nature of the plasma-polymerized heptylamine surface was not described, however, the binding of CNTs was successfully achieved by the carboxylation of the CNTs by acid treatment, as described earlier. The CNTs selectively adsorbed onto the patterned amine species on the substrate. A bare mica substrate used as a control revealed no CNT deposition, indicating that the amine groups are required for the adsorption of CNTs on the surface of the substrate.

### 1.6.2 Immobilization of Functionalized CNTs

Widenkvist et al.$^{[261]}$ presented an approach that is practically reversed from the previously discussed techniques. As opposed to modifying the surface with SAMs, the CNTs were modified instead. The MWCNTs were acid-treated and cleaned, thus adding carboxyl groups at the ends and at defect sites along the CNTs. Additionally, these carboxyl groups were reacted with octadecylbromide, which resulted in long carbon chains being bound onto the carboxyl group via ester formation. Silicon substrates were etched with HF to remove the native oxide layer, resulting in silicon surfaces that can be passivated with hydrogen (Si-H). Several coating techniques (dip-coating, drop evaporation) were used to create chemically heterogenous surface areas. It was found that the CNTs, functionalized with the alkylester,
adsorbed preferentially onto the Si-H surface of the substrate because of the interaction of the non-polar alkyl chain with the non-polar silicon surface. Very few CNTs, in particular long CNTs, adsorbed also onto polar SiO\textsubscript{x} surface areas. The authors explained this by the higher defect density of longer CNTs and, thus, a higher degree of functionalization of these tubes.

Liu \textit{et al.}\textsuperscript{[262]} used a similar approach as Widenkvist \textit{et al.}, with the goal of attaching modified CNTs onto a gold surface. The SWCNTs were first acid-treated, resulting in shortened CNTs with carboxyl groups at the open ends. The CNTs were then thiol-derivatized by reacting them with cysteamine (NH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}SH) in an ethanol solution in the presence of DCC, which supported the condensation reaction\textsuperscript{[251]}

The use of covalent chemical interactions results in general in highly stable layers, which are linked to the surface. The SAM assisted methods to deposit CNTs have proven to be very effective, but have a significant limitation in the types of substrates that can be used; generally silicon, glass, and metal oxides for silanes (\textit{e.g.}, APTS) and gold as well as silver for thiols (\textit{e.g.}, alkanethiols) can be used.

1.6.3 \textbf{ALIGNMENT OF CNTS BY ELECTROSTATIC FORCES}

A deposition method developed by Cai \textit{et al.} resulted in vertically-aligned CNTs.\textsuperscript{252} A metal-assisted layer-by-layer deposition technique was used. In this case, the substrates with a SAM on the gold surface were immersed in a metal-containing (either Fe\textsuperscript{3+} or Cu\textsuperscript{2+}) aqueous solution, rinsed, and then placed in the CNT solution for deposition. Chelation effects and electrostatic interactions facilitated the CNT deposition, which resulted in a vertical alignment of the CNTs. However, no explanation for this alignment effect was given. In a similar process, Wu \textit{et al.}\textsuperscript{[263]} used acid treatment to cut and functionalize the SWCNTs with carboxyl groups to improve their solubility in water. A substrate covered with a silver film was then dip-coated in the CNT solution, resulting in deprotonation of the carboxyl groups and their attraction to the silver surface. Because the carboxyl groups were mainly located at the ends of the tubes, the CNTs self-assembled vertically onto the substrate, in particular the shorter CNTs, while longer tubes (>200 nm) often organized horizontally. A schematic representation of this process is displayed in Figure 1-12b.

Burghard \textit{et al.}\textsuperscript{[255]} and Muster \textit{et al.}\textsuperscript{[264]} also reported a related technique to deposit CNTs on a surface. Silicon wafers with a 1 µm-thick oxide layer were treated with 3-
aminopropyltriethoxysilane (APTS) solutions to create positively charged amine groups on the surface. The deposition technique was tested on both MWCNTs and SWCNTs separately. The purified CNTs were dispersed in an aqueous solution of sodium dodecylsulfate (SDS) and subjected to size-exclusion chromatography (SEC) to obtain a narrower size distribution of the CNT samples. The surfactant formed a shell around the CNTs that exposed negatively charged groups and promoted electrostatic interactions with the positively charged surfaces. The silicon wafers were then immersed in the CNT dispersion, where the CNTs deposited onto the surface. It was claimed that the deposition was initiated by the surfactant molecules acting as linkers between the CNTs and the positively charged amine groups of the APTS layer. Initially, the CNTs were attached quite strongly, but after sufficiently long exposure to water the surfactant was washed away and the CNTs desorbed from the surface. Pan et al.\cite{265} reported a method of self-assembling CNTs into aligned arrays using a mechanochemical functionalization technique. A dry mixture of SWCNTs and potassium hydroxide was ball-milled, dissolved in water, and then precipitated in methanol. This process was repeated until all of the remaining potassium hydroxide was removed. The solution was centrifuged to concentrate the CNTs and to remove excess liquid. FT-IR spectroscopy and XPS measurements provided strong indications that this process resulted in SWCNTs that were side-wall functionalized with multiple hydroxyl groups. These SWCNTs were no longer soluble in common non-polar solvents, such as dichlorobenzene, demonstrating their hydrophilic properties. The authors called these functionalized SWCNTs nanotubols. The hydroxyl content of the tubols resulted in strong intermolecular hydrogen-bonding, which led in tubols self-assembling into highly aligned arrays.

Kim and Sigmund\cite{266} reported on the self-assembly of vertically-aligned MWCNTs on a polyelectrolyte layer adsorbed on a silicon wafer. The MWCNTs were first shortened via chemical oxidation by acid treatment with the resulting formation of carboxyl groups at the open ends of the CNTs. In an experiment, the silicon substrate was dipped into an aqueous solution of poly(diallyldimethylammonium chloride) (PDAC) and, subsequently, into the MWCNT solution for several hours. The MWCNTs selectively adsorbed onto PDAC because of Coulomb interactions between the negatively charged carboxyl groups of the CNTs and the positively charged PDAC, which resulted in vertically-aligned MWCNTs. In another experiment, the substrate was dipped into aqueous solutions of PDAC and then in poly(sodium 4-styrenesulfonate) (PSS), followed by the MWCNT solution. The CNTs were repelled by the PSS layer. Multilayers of polyelectrolyte were also utilized via successive
dip-coating of the substrate, *e.g.*, PDAC-PSS-PDAC layers. The results of the deposition of the CNTs did not change; the CNTs always adsorbed on the PDAC if it was the top layer and were always repelled by the PSS if it was the top layer, regardless of the number of alternating layers. This multilayer process is thus suitable for forming patterns and arrays of adsorbed and vertically aligned CNTs.

Electrostatic forces are regarded as a strong binding mechanism that frequently results also in the formation of aligned tube assemblies. However, the strength of the electrostatic forces can be manipulated by different solvents and the pH value of the used solutions, thus aggregation and assembly of tubes might be reversible to some extend.

### 1.6.4 The Use of Biomolecules and DNA for the Selective Placement and Alignment of CNTs on Surfaces

There is considerable and growing interest in the literature for the use of biomolecules, DNA, and equivalents as biological templates to align and deposit CNTs for applications in both biological and chemical systems, because of their inherent self-assembly characteristics and unique recognition motifs. For example, DNA has been identified as a useful template because of its small diameter (~2 nm), the controllable length, and the ability to use molecular recognition principles by the interaction of complementary base pairs.

In this section, selected examples of such approaches will be highlighted.

Singh *et al.* used peptide nucleic acid (PNA), an artificial analogue of DNA, to link CNTs together in ropes as a precursor to form higher ordered structures. SWCNTs were first mildly oxidized in a low concentrated acid to limit the oxidation to the ends of the tubes. After micropore filtration, the CNT filter cake was suspended in an aqueous solution containing 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride and *N*-hydroxysuccinimide (NHS) to form SWCNT-bearing NHS esters. The PNA was functionalized at both ends with the amino acid residue glutamine to assist the linking process as only utilizing the amine group present in the PNA was found to be an insufficient linker. The filtered SWCNT-NHS tubes were added to a PNA solution, which led to SWCNT-PNA-SWCNT conjugates by the formation of an amide bond between the glutamate-terminated ends of the PNA and the ester-terminated ends of the SWCNTs, resulting in long ropes of aggregated CNTs. Further testing revealed that these ropes retained their electrical conductivity properties.
Hazani et al.\textsuperscript{[270]} have developed a method to immobilize and connect two gold electrodes with aligned CNTs using DNA as a linker. This method consisted of three major preparation steps. The overall procedure is schematically represented in Figure 1-14.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure114.png}
\caption{Schematic representation of the procedure to deposit SWCNTs across electrodes utilizing DNA hybridization. a) Oligonucleotides are self-assembled onto the gold electrode structures. The SWCNTs are functionalized with complementary oligonucleotides. b) After immersing the substrate into the SWCNT solution, hybridization of the complementary DNA fragments takes place, which results in SWCNTs bridging both electrodes. Reproduced from ref. [270].}
\end{figure}

Firstly, single-stranded DNA was self-assembled on gold electrodes by reacting them with thiol-terminated oligonucleotides. The thiol groups showed a strong affinity to the gold surface. Secondly, the SWCNTs were oxidized and modified with an amine-terminated complementary oligonucleotide in the presence of a carbodiimide and hydroxysuccinimide. After filtering and washing the substrate containing the electrodes and DNA, the SAM was finally immersed into an aqueous suspension of the CNTs, followed by an extensive washing process. The oligonucleotides on the CNTs hybridized with the complementary DNA located on the gold contacts. As both ends of the CNT contained the oligonucleotide groups, it effectively bridged the two electrodes by hybridization with a DNA molecule on each side of the gap. It remained unclear whether individual CNTs or CNT bundles were deposited across the gap. This technique, however, was observed to result in an up to two orders of magnitude higher charge transport of the gap structures compared to direct metal-SWCNT contacts.

Xin and Woolley\textsuperscript{[268]} presented another method for the controlled placement of CNTs using DNA templates. Double-stranded DNA was linearly aligned on a silicon substrate that had been treated with a solution of aqueous poly-L-lysine by moving droplets of the DNA
solution across the surface. The combination of fluid flow and surface tension at the air-
droplet interface was observed to be sufficient to straighten the DNA strands in a uniform
direction. The surface concentration of poly-L-lysine and the length of the DNA directly
influenced the alignment of the DNA on the surface of the substrate. The substrate was
subsequently immersed in a solution of DMF and 1-pyrenemethylamine hydrochloride
(PMA). Acid-treated, and thus oxidized, SWCNTs were dispersed in DMF. A droplet of the
CNT suspension was placed on the DNA-treated substrate. The PMA acted as a linker
between the DNA and the SWCNTs as its amine group interacted with the DNA backbone,
while the aromatic pyrenyl group interacted strongly with the surfaces of SWNTs. Thus,
more than 60% of the deposited CNTs were aligned on DNA molecules. These selected
examples summarize some of the additional possibilities that emerge from the integration of
biochemical building blocks, and progress in the design concepts is expected in the future.

In general, chemical methods have the following advantages: they are highly versatile and
tunable, and they typically have high resolution. However, these methods can be time-
consuming, expensive, complex, and reproducibility may be difficult to ensure.

1.7 **AIM AND SCOPE OF THE THESIS**

The current literature overview emphasizes that there are many possible techniques to
synthesize, align and deposit carbon nanotubes. Due to the fact that relatively harsh
conditions are typically used during the synthesis of aligned carbon nanotubes, the post-
assembly process of prefabricated tubes implies advantages to avoid such conditions. As a
result, these methods serve to expand the number of possible applications and can also be
applied on substrates that are incompatible with, e.g., high temperatures and aggressive
reduction compounds. The wide diversity of approaches and the utilization of a broad field of
physical and chemical effects suggests that there is, up to now, no ultimate technique
available to align carbon nanotubes. Particular applications can rely on approaches that serve
their individual requirements, and the combination of different alignment methods might
prove to be an efficient strategy.

Selected issues of different critical aspects are centered on the synthesis of CNTs under mild
conditions and the guided assembly of CNTs on chemically active surfaces; they form the
main part of the investigations which are summarized in this thesis. Microwave-assisted
synthesis and the utilization of electro-oxidative nanolithography to chemically guide the
self-assembly of CNTs on substrates are the core techniques utilized to conduct the research targets. Electro-oxidative nanolithography was identified as a very promising way to manipulate and organize CNTs but also additional possibilities of this process are discussed in relation to nanofabrication.

Chapter 1 provides the state-of-the-art of research activities related to the synthesis and alignment of CNTs. Critical issues, i.e., the crucial synthesis conditions, are highlighted and form the motivation for studies that are subsequently summarized in the individual chapters of this thesis.

Chapter 2 deals with the introduction of a new synthesis concept of CNTs that utilizes microwave irradiation. In this process, microwave irradiation is used as the heating source and ethanol was utilized as the carbon source. This method has advantages of being relatively safe, inexpensive, and fast compared to the conventional methods. As a central result of the investigations the selective heating mechanism of different materials by microwaves could be experimentally verified and a reliable process for the synthesis of carbon nanotubes could be developed. Different catalyst salts were investigated for successful growth of CNTs, and various substrates were investigated for the placement of catalyst particles. Moreover, the overall experimental conditions were investigated in detail. As an essential point, the role of suitable catalyst particles was further investigated. Thermal, as well as chemical (by hydrazine) reduction of the metal precursor materials was studied. The particle formation process could be investigated by analytical as well as microscopic tools. Furthermore, the microwave-assisted synthesis of CNTs was applied to fabricate ultra-sharp AFM tips, typically required for high resolution imaging. The AFM tips were loaded with catalyst particles and, by use of microwave-assisted synthesis, carbon nanotubes were grown directly on the apex of the AFM tips. The microwave synthesis has been also used to grow CNTs on micro- and nanoscale patterns, fabricated by electro-oxidative nanolithography. This approach allows the fabrication of desirable structures, which can be subsequently used for the placement of nanoparticles or nanotubes. Chapter 3 introduces electro-oxidative nanolithography and provides an overview of the state-of-the art of this structuring approach.

Chapter 4 describes the use of chemically active surface patterns for the selective placement of carbon nanotubes. Carbon nanotubes were suspended in different organic and aqueous solutions and then applied to the oxidized areas on the surface. The addition of suitable surfactants resulted in the most efficient placement of individual CNTs. Carbon nanotubes
were successfully placed on carboxylic as well as on amine-functionalized nano-sized patterns on silicon wafers. It was found that surfactant suspended carbon nanotubes promote the placement of individual tube on the structures. Successful sequential electro-chemically oxidation steps were performed in the vicinity of the attached carbon nanotube. This was followed by the second selective placement of the nanotubes across the previously placed tube. This fabrication process provides total control over the lateral arrangement of the individual building blocks.

Chapter 5 summarizes experiments where electro-oxidative nanolithography was utilized to guide the assembly of metal nanostructures. These include fully-scalable mesoscopic ring features, as well as gap structures that utilize different oxidation parameters required to chemically activate monolayer and bilayer structures. Studies which resulted in mesoscopic ring structures introduce the combination of two patterning regimes of electro-oxidative lithography to obtain chemically heterogeneous surface templates within one modification step.
1.8 Reference


Strategies to Synthesis, Post-Synthesis Alignment and Immobilization of Carbon Nanotubes


Chapter 2. SYNTHESIS OF CARBON NANOTUBES AND NANOFIBERS BY MICROWAVE IRRADIATION

ABSTRACT

The development of alternative processes to synthesize carbon nanotubes (CNT) in a cost-effective, fast, and safe fashion is an area of active research. Aside from the improvement of the obtained CNT material, processes that provide possibilities for the modification of sensitive substrate materials are in focus. This chapter introduces the use of direct microwave heating to develop an improved and controllable experimental set-up that permits the safe and fast fabrication of carbon objects. Further benefit derives from the selective heating of different materials, which can be used, e.g., to efficiently heat surface-bound iron nanoparticles. First experimental evidence for this effect is obtained by utilizing a self-assembled monolayer of n-octadecyltrichlorosilane (OTS), which acts as a sensitive indicator for locally elevated temperatures. Even though the catalyst materials are sufficiently heated to promote the growth of CNTs, the overall temperature of the substrate remains relatively low. This leads to improved reaction conditions suitable for a variety of different substrates. The resulting fibers and nanotubes are micrometers long and can be synthesized on short time scales, yielding dense films of CNTs with uniform height. The influence of the reaction conditions has been investigated and the importance of individual process parameters on the synthesis of CNTs is discussed. This process could be used as a cheaper and faster method to fabricate CNT-functionalized tips for scanning probe microscopy. The process was also combined with lithography to generate micro- and nanostructure films consisting of CNTs.

Parts of this chapter have been published:

2.1 Introduction to Microwave Irradiation

Carbon nanotubes\textsuperscript{[1]} and one dimensional carbon nanostructures\textsuperscript{[2]} attract special attention because of their unique properties; such materials are proposed to be employed in a large variety of applications, such as gas storage,\textsuperscript{[3]} absorption,\textsuperscript{[4]} catalyst support,\textsuperscript{[5-7]} and composite reinforced materials.\textsuperscript{[8-11]} Chemical vapor deposition methods\textsuperscript{[12]} compared to arc discharge\textsuperscript{[1]} and laser ablation,\textsuperscript{[13]} are favored methods for the synthesis of carbon nanotubes (CNTs)\textsuperscript{[14]} due to the low cost and high yield of the process. However, they suffer from demanding reaction conditions, in particular the required high temperatures.\textsuperscript{[15]} Typical temperatures that are necessary for the growth of carbon nanotubes on suitable metal catalyst particles are higher than 600 °C.\textsuperscript{[16]} Thus, the synthesis of CNTs on low-melting point materials, such as polymers, is severely limited. Therefore, the development of fabrication methods that allow CNT synthesis at relatively low temperatures, to which the substrates have to be exposed, are highly desired. New possibilities to synthesize carbon nanotubes and carbon nanofibers (CNFs) utilizing microwave irradiation by a safe and rapid procedure is regarded as an alternative process. The approach is based on two publications by Hong et al. who reported first on a microwave synthesis procedure introducing the selective heating mechanism on a theoretical base and who demonstrated a first feasibility study on the synthesis of carbon nanotubes.\textsuperscript{[17,18]}

Microwave irradiation is electromagnetic irradiation in the frequency range of 0.3 to 300 GHz. In general, domestic microwaves as well as the microwaves dedicated for chemical synthesis operate at a frequency of 2.45 GHz (corresponding a wavelength of 12.24 cm). Microwave irradiation has been successfully used for organic and polymer synthesis in the last decades.\textsuperscript{[19-22]} It was found that in many cases reaction times can be reduced in contrast to classical synthetic approaches, and the formation of undesired byproducts can be suppressed.\textsuperscript{[23,24]} Microwave-enhanced chemistry is profiting from the generation of advanced reaction conditions, \textit{e.g.}, the pressure mediated possibility to run reactions above the usual boiling points of solvents, and the efficient heating of materials by selective heat absorbance. The later process is based on the ability of suitable materials to absorb microwave energy and convert it into heat. Irradiation of the materials with microwaves results in the alignment of dipoles, ions and electrons in the applied electric field. When the applied field oscillates, the dipoles or ions attempt to align with the alternating electric field. During this process energy
is released in form of heat due to dielectric losses and molecular friction. The amount of heat
generated by this process is directly depended on the ability of the material to align itself with
the oscillating frequency of the field. Conductive materials experience a high absorption of
the microwave irradiation. The power absorbed in a unit volume of the material is the result
of interactions between the electromagnetic field and the material and can be expressed as,

\[
P = 2\pi \varepsilon'' E^2 = \sigma E^2
\]

where \( P \) is the absorbed power per unit volume, \( f \) is the frequency, \( \varepsilon'' \) is the complex
permittivity of the material, \( E \) is the electric field intensity, and \( \sigma \) is the conductance. This
power is related to the heat effectiveness. It decreases to \( 1/e \) of the original value at the
penetration depth,

\[
d_p = \varepsilon_0 \left( \frac{2\pi \varepsilon''}{1/(\pi f \mu \sigma)} \right)^\frac{1}{2}
\]

where \( d_p \) is the penetration depth, \( \varepsilon_0 \) is the dielectric constant of free space, and \( \mu \) is the
permeability of the material. The penetration depth is inversely proportional to the
conductivity. Thus, effective heating is assumed for materials with higher conductivity and
dimensions that are not exceeding the penetration depth.\textsuperscript{[25-27]} Conductors have a small
penetration depth and therefore reflect microwaves at their surface, whereas insulators appear
to be transparent to the microwave irradiation. However, metal nanoparticles with the size of
less or around the penetration depth can be effectively heated by microwave irradiation. Such
particles can be, e.g., the catalyst particles for the growth of carbon nanotubes. Therefore, the
selective heating process was investigated and a microwave-assisted synthesis approach was
developed which permits the synthesis of carbon nanotubes and nanofibers at low
temperatures, in short time scales and under cheap and safe reactions conditions.

\section{2.2 Investigation of the Selective Heating Process}

The first research target was to experimentally investigate the concept of the selective heating
mechanism. A major difficulty in such investigations is the temperature measurement, which
is performed in synthetic single-mode microwave systems by an infrared sensor that
measures only the average temperature of the reaction chamber or the vial.
Thus, it is impossible to measure the temperature directly at the catalyst particles. Therefore, an indirect measurement of the local temperatures is required.

For this purpose, a self-assembled monolayer of \( n \)-octadecyltrichlorosilane (OTS) was used as a sensitive, qualitative indicator for the local temperature in different regions of the substrate, as the monolayer will degrade upon exposure to high temperatures\(^{[28]}\). This allows a qualitative ‘ex-situ’ mapping of the local temperatures generated in different parts of the substrate during the microwave irradiation.

The patterning of the OTS monolayer allows the definition of the positions of individual catalyst particles, \( i.e. \) iron metal particles. The fabrication of such catalyst arrays on OTS monolayers is schematically depicted in Figure 2-1\(^{[29]}\). A more detailed introduction of the technique can be found in Chapter 3.

The local application of a suitable bias voltage on the OTS monolayer \( via \) a conductive Scanning probe microscopy (SPM) tip leads to the electro-chemical oxidation of the monolayer\(^{[30]}\) and generates acid functionalized areas, which can be used to site-selectively deposit nanomaterials\(^{[31-34]}\). These patterned areas can, \( e.g. \), be loaded with iron(II) acetate that develop into iron oxide particles upon a chemical reduction by the exposure to hydrazine vapor (Figure 2-1c) (followed by subsequent oxidation of the iron particles as they are kept under ambient condition). By this process, well-defined iron oxide nanoparticle arrays can be formed which can act as “antennas” for the absorption of microwave radiation. An irradiation experiment was performed on such a substrate that was patterned with a 7 by 7 grid of individual particles, spaced 100 nm apart from each other. This substrate was subjected to microwave irradiation. To maintain the controllability of the heating process, the reaction vial contained two milliliters of ethanol underneath the substrate, which was placed on a quartz glass support above the liquid (Figure 2-1d). The presence of the ethanol ensures the safe performance of the synthetic single-mode microwave set-up by absorbing the excess radiation and preventing damage to the equipment. It can, moreover, serve as a suitable carbon source in later experiments to grow carbon nanofibers and nanotubes\(^{[35]}\).
**Figure 2-1.** Schematic outline of the experiment. a) The electro-chemical patterning is performed on a n-octadecyltrichlorosilane monolayer. b) By the local application of bias voltage pulses, an electro-chemical oxidation takes place, converting the top methyl groups to carboxylic groups. c) The carboxylic acid groups serve as a template for the site-selective placement of iron(II)acetate, which can subsequently be reduced to yield magnetite nanoparticles. d) The substrate is placed in a capped pressure vial on a quartz support above a reservoir of liquid ethanol and irradiation takes place.

In a first experiment, the irradiation conditions were kept on a moderate level with overall temperatures not exceeding 120 °C, a microwave power of 150 W, and an overall irradiation time of 10 minutes. The reaction was stopped by flushing the reaction chamber with nitrogen until room temperature was reached. Subsequently, the nanoparticle array was investigated by tapping mode scanning probe microscopy (Figure 2-2).
Figure 2-2. Scanning probe microscopy images of the array of magnetite nanoparticles that are formed on a regular grid of individual surface spots, inscribed with voltage pulses of −10 V applied to the tip of the SPM. a) After microwave irradiation was applied to the particle array, a significant degradation of the underlying OTS monolayer is observed (height image). b) Phase image. c) Line profile of the corresponding height image, which provides evidence of a higher temperature in the nanoparticles’ positions due to the better absorption of the microwaves by the metallic particles.

Characteristic, uniform hole structures are observed around the remaining particles and in the positions where particles were located within the original 7 by 7 nanoparticle pattern, which are caused by the degradation of the OTS monolayer. While OTS monolayers are relatively stable, it is observed that exposure to high temperatures results in their degradation. The size of the holes significantly exceeds the size of the particles, indicating that also the vicinity of the particles is heated due to heat dissipation effects. The analysis of the depth of these holes shows depletions of 2.1 nm, which is slightly less than the expected depth estimated for a well ordered OTS monolayer, suggesting a minor degradation of the OTS monolayer also in regions without iron catalyst present. Nonetheless, the monolayer still exhibited hydrophobic surface properties, as indicated by a water contact angle of 90° to 100° (in contrast to 114°
for the untreated OTS monolayer). It is observed that most of the particles are detached from the grid structure, however the uniform diameter of the hole structures allows the conclusion that the particles were removed only after the heating process. It is not clear if the particles were removed during the cooling cycle of the microwave, which causes the condensation of ethanol vapor on the substrate, or are removed during the SPM investigation due to the scanning tip, or during the cleaning process (with adhesive tape) to which the surface was subjected. This experiment is regarded as the first experimental evidence for the selective heating mechanism of nanoparticles by microwave irradiation. However, no quantitative investigation of the obtained temperatures could be obtained.

### 2.3 CNTs SYNTHESIS BY MICROWAVE IRRADIATION

Based on the investigation of the selective heating process additional experiments have been performed to evaluate the possibility to use microwave irradiation for the synthesis of carbon nanofibers and carbon nanotubes. Thereby, advanced reaction conditions were tested. First experiments were performed on silicon substrates, where the catalyst was in a first step deposited by means of drop-casting.

Catalyst layers have been used for the irradiation experiments, and resulted in the formation of dark, black coatings on the catalyst layers. This black coating was investigated by optical microscopy and scanning electron microscopy, where morphology of the sample is analyzed (Figure 2-3).

![Figure 2-3. After microwave irradiation, a black coating is formed on the catalyst layers. a) Optical image of the black coating formed on a droplet of iron catalyst spotted on the surface. b) Dense film of nanofibers exhibiting uniform length of the nanofibers. b) Disordered film that clearly shows the presence of individual fibers.](image)
SEM reveals that the coating consists of a densely packed assembly of fibers and carbon nanotubes with diameters of typically from 40 to 100 nm and a length of several micrometers (Figure 2-3b). More disordered films, as shown in Figure 2-3c, however demonstrate more clearly the diameter and structure of the synthesized objects. It is seen that the tip growth mode occur in this case, while all the catalyst particles are at the end of the tubes. Further information on the nature of these carbon nanostructures is provided by Raman spectroscopy. Characteristic peaks at 1294 and 1556 cm\(^{-1}\) are observed (Figure 2-4), that are corresponding to the D and G modes of carbon, that are typically observed for multiwall carbon nanotube systems.\[^{36}\]

![Raman spectrum](image.png)

*Figure 2-4. Raman spectrum obtained from the black coating. Characteristic D and G modes, corresponding to the carbon nanotubes are observed.*

The so-called G mode is a characteristic feature of the graphitic layers and corresponds to the tangential vibration of the carbon atoms. The second characteristic mode is a typical indication for defects in graphitic structures (D mode). The comparison of the ratios of these two peak intensities provides a measure of the quality of bulk samples. In case of microwave synthesized carbon nanostructures the ratio of the D and G band indicate the presence of a high number of defects and a relatively low degree of graphitization. In addition, there is a third mode, named the radial breathing mode (RBM) which is very sensitive to the diameter of SWCNT and DWCNT. However, RBM modes were not detectable in these experiments due to limitations in the spectral range of the utilized Raman spectrometer.
The black coatings consisting of carbon nanotubes exhibit strong superhydrophobicity, as it was measured by contact angle experiments (Figure 2-5).

![Photographic image of the black coating containing CNTs. Contact angle measurement of the water droplet (1 µL) on the CNTs with a contact angle of 153±2°.]

**Figure 2-5.** Photographic image of the black coating containing CNTs. Contact angle measurement of the water droplet (1 µL) on the CNTs with a contact angle of 153±2°.

The measured contact angle is 153±2° (lotus leafs (Nelumbo nucifera) for example show a contact angle of 160°) due to the density of the high aspect ratio objects pointing perpendicular to the surface, resulting in a type of Cassie type wetting.[37,38]

Furthermore, characterization of individual tubes, rather than on the formed films, were performed by means of transmission electron microscopy (TEM) and SPM of tubes, which have been removed from the substrate and have subsequently been dispersed in dimethylformamide (DMF) or ethanol. These dispersions were only stable for a few minutes before the material started to precipitate. This precipitation is attributed to the bundling of the material in solution, an effect that is well known for CNTs. Droplets of the solutions were applied on silicon surfaces coated with aminopropyltrimethoxysilane (APTMS) or carbon-coated TEM grids by drop-casting directly after preparing the dispersions. Despite the low solubility and the tendency to form bundles in solution, individual fibers and tubes could be visualized by means of SPM (Figure 2-5a) and TEM (Figure 2-5b, c). Both methods clearly confirm the tube-like structures of the material and show the presence of catalyst particles, which appear as dark spots in the TEM micrographs. The layer structure of multi-walled carbon nanotubes could be resolved in Figure 2-5c.
Figure 2-6. a) Scanning probe microscopy images of individually dispersed nanotubes on an APTMS coated silicon wafer. b) and c) Transmission electron microscopy images of a bundle of carbon nanotubes. Clear evidence for the presence of the metallic seed particles is found.

In these first experiments, mainly carbon fibers with rather large diameters were observed. A careful analysis and investigation of the reaction parameters can improve the process and, thus, the quality of the obtained fibers. This is further discussed in the following section.

2.4 Influence of The Synthesis Conditions

The investigation of the individual process parameters includes the variation of the microwave power, the process temperature, the utilized carbon source, as well as the catalyst material. Several of the parameters can be directly addressed by the microwave settings itself, whereby one of the reaction parameters can be fixed, however, variation of the pressure
within the microwave vial can only performed indirectly, *e.g.*, by variation of the carbon source.

The utilized microwave setup allows applying reaction temperatures up to 250 °C and a maximum pressure within the reaction vials of 22 bar. A safety shut-down is performed when the reaction conditions exceed these limits. Direct observation of the conditions during the reaction can be performed by monitoring continuously the microwave power, the temperature of the reaction vial, and the pressure within the vials. The microwave vials are capped to allow the development of a feeding gas atmosphere upon heating. Iron acetate catalyst layers have been prepared by the drying drop method of different catalysts solutions onto the clean silicon substrates. Due to the restrictions with respect to the maximum temperature and pressure that can be applied to the reaction chamber, a careful choice of the carbon source was essential, whereby the capability of the carbon source to absorb microwaves plays a limiting role. Different carbon sources, *i.e.*, alcohols, were tested to create a set of different synthesis conditions due to the evaporation temperature of the carbon sources resulting in different pressure levels that are reached during the reaction process. The experiments were performed with a fixed microwave irradiation power of 200 W and a maximum reaction time of 5 minutes. To ensure a constant contribution of the silicon wafer to the microwave absorption wafers of similar size, loaded with the same amount of catalyst, were irradiated in the microwave in the presence of 0.5 mL of four different carbon sources. The temperature measurement shows the average temperature of the reaction vial, which is dominated by the absorption of the silicon wafer and the individual carbon source. Figure 2-7 depicts typical temperature (a) and pressure (b) curves as a function of the irradiation time.
Figure 2-7. Influence of the carbon source on the temperature and pressure conditions within the reaction vial. a) Temperature and b) pressure during the irradiation process. c) SEM images of the microwave irradiated substrates.

Comparable temperature values of 225 and 230 °C were measured for ethanol and 2-propanol; butanol generated average temperatures of 240 °C, whereas ethylene glycol showed a significantly higher average temperature of 260 °C, which also resulted in a safety shut-down of the microwave setup. Significantly different pressure values were measured using the different carbon sources ranging from maximum pressures of < 1 bar for ethylene glycol up to 18 bar for ethanol. The importance of the pressure during the reaction process became evident when the substrates were investigated by means of SEM. The microwave irradiated substrates utilizing ethanol and 2-propanol as carbon source showed the formation of carbon nanostructures (Figure 2-1c). The tubes grown with ethanol as carbon source were synthesized at the highest pressure and at a maximum temperature of 225 °C. As a result long carbon nanotubes and fibers with small diameters were produced. A similar temperature was reached using the 2-propanol carbon source; however, significantly lower pressure values were observed and the grown tubes were found to be rather short (Figure 2-7b). Butanol and
ethylene glycol environments did not result in the formation of carbon nanostructures, even if ethylene glycol showed the highest temperature values. In both cases the pressure in the reaction vial remained below 12 bar. These results clearly indicate the importance of the pressure rather than of the generated temperatures during the synthesis process to obtain the growth of CNTs. This influence could not be compensated even by the higher average temperatures that could be reached by other carbon sources. In comparison to the high pressure carbon monoxide (HiPco) process, utilized in carbon nanotubes synthesis (for more details see Chapter 1)\cite{39,40} significantly lower overall temperatures are observed and also the applied pressure remains lower. Moreover, in contrast to the high quality single-wall CNTs synthesized with the HiPco process, up to now only the formation of multiwall CNTs and CNFs has been observed in the microwave-assisted production process. An important role for the synthesis of carbon nanotubes is the choice of the catalyst material; this aspect is investigated in more detail in the next section.

### 2.5 Influence of the Catalyst Material

The development of catalyst materials and the optimization of the formulation of the catalysts are addressed by many research groups and represent a highly specialized field of research. Most catalyst materials are based on iron, nickel and cobalt, which provide suitable seed particles to initiate the growth of carbon nanotubes and nanofibers.\cite{41-44}

In the course of the screening experiments these three main classes of catalyst materials have been investigated. The catalyst layers were prepared from different iron, nickel and cobalt salts that were applied to silicon substrates by drop-casting of ethanolic solutions of these metal salts and subsequent evaporation of the solvent. The catalyst layers based on the different metal salts were subjected to microwave irradiation (200 W, 5 min) while temperature and pressure curves were recorded. Ethanol was used as carbon source as it was observed to create the highest pressure values (see the discussion above). The irradiated substrates were analyzed by means of SEM and TEM.

The results obtained for different iron based catalyst layers are summarized in Figure 2-8. The size of the particles can be measured from the SEM images, similarly the diameter of the carbon nanotubes could be measured. It was observed that mainly the size of the particle determines the diameter of the nanotube.
Figure 2-8. a), c), and e) SEM micrographs of the carbon nanofibers synthesized on substrates coated with Fe-based catalysts; b), d), and f) TEM images of the carbon nanofibers on these catalysts.

The carbon nanotubes synthesized with iron catalysts showed typical diameters of 90 to 120±40 nm (Table 2-1).

A comparison of the temperature and pressure curves (Figure 2-9) demonstrates that iron acetate and iron(II) chloride were irradiated at rather similar synthesis conditions and only iron(III) oxide showed a lower temperature as well as a significantly lower maximum pressure.
Table 2-1. Summary of tube diameters for different catalyst sources, measured by comparison to the scale bar.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Diameter, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeAc$_2$</td>
<td>100±30</td>
</tr>
<tr>
<td>FeCl$_2$</td>
<td>120±40</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>90±20</td>
</tr>
<tr>
<td>CoOCO$_3$</td>
<td>30±5</td>
</tr>
<tr>
<td>CoC$_2$O$_4$</td>
<td>50±10</td>
</tr>
<tr>
<td>CoAc$_2$</td>
<td>30±10</td>
</tr>
<tr>
<td>Ni(NO$_3$)$_2$</td>
<td>15±5</td>
</tr>
<tr>
<td>NiAc$_2$</td>
<td>15±5</td>
</tr>
<tr>
<td>NiC$_2$O$_4$</td>
<td>25±5</td>
</tr>
</tbody>
</table>
Figure 2-9. Temperature (top) and pressure (bottom) curves for three different catalyst materials applied by drop-casting onto silicon wafers of similar size. Ethanol was used as carbon source. a) Fe, b) Co, and c) Ni-based catalyst salts.
Cobalt based catalysts are also frequently used for the synthesis of carbon nanotubes and have also been tested here for their capability to mediate the microwave-assisted synthesis of CNTs (Figure 2-10).

**Figure 2-10.** a), c), and e) SEM micrographs of the carbon nanofibers synthesized on substrates coated with Co-based catalysts; b), d), and f) TEM images of the carbon nanofibers on these catalysts.

The CNTs grown from cobalt based catalyst materials show rather small diameters of 25 to 50 nm, whereby cobalt(II) oxalate resulted in the formation of CNTs showing the most uniform diameters. A comparison of the corresponding temperature and pressure curves during the synthesis process (Figure 2-9c) reveals comparable synthesis conditions like for the experiments performed on the iron catalysts, in particular the pressure values that have been reached. Thus, the catalyst material seems to be a governing factor for the structural properties of the resulting CNT materials.
Chapter 2

Figure 2-11. a), c), and e) SEM micrographs of the carbon nanofibers synthesized on substrates coated with Ni-based catalysts; b), d), and f) TEM images of the carbon nanofibers on these catalysts.

The best results in terms of uniformity and size of the generated CNTs was observed for catalyst materials based on nickel salts. In particular nickel(II) nitrate and nickel(II) acetate resulted in the formation of carbon nanotubes with diameters of 15 to 25 nm (Figure 2-11). Nickel(II) oxalate showed a slightly broader size distribution with significantly larger diameters. The corresponding temperature and pressure curves reveal that the CNTs formed on the nickel(II) nitrate and nickel(II) acetate were synthesized under extreme pressure conditions which were reached already after two minutes irradiation time.

While with iron catalyst particles mainly carbon fibers were produced, and only occasionally hollow nanotubes were generated, significant improvement of the tube quality in terms of smaller diameters could be obtained by using alternative catalysts. Nickel(II) acetate resulted in the formation of tubes with a mean diameter below 20 nm, which were also grown within an irradiation time of 5 min at 200 W microwave power (Figure 2-12).
In the performed TEM investigations it was found that tubes with a diameter smaller than 50 nm are appeared to be hollow, whereas thicker ones appear to be carbon nanofibers.

Also the adjustment of the catalyst layer thickness can further improve the uniformity and diameter of the CNTs. With spin-coated catalyst layers films of CNTs with a mean thickness of 10 nm could be obtained (Figure 2-13).

In general, the type and size of the catalyst determines the diameter of the carbon nanotubes, thus it is important to prepare the catalyst particle in a controlled way with one uniform diameter.
2.6 Influence of the Substrate

Besides the optimization of the catalyst material the substrate plays an important role for the growth of CNTs. The initial studies utilized silicon substrates, however, other substrates are of potential interest as well. These include transparent glass substrates\cite{45,46}, metals\cite{47}, highly insulating mica\cite{48}, but also polymer materials\cite{49}. In particular the latter will be interesting as the selective heating process allows the synthesis of CNTs at relatively low overall temperatures, besides of the elevated temperatures that are generated in close vicinity of the catalyst particles. In the reaction vials microwaves are mainly absorbed by the carbon source as well as by the substrate itself and, thus, different substrates will influence the reaction conditions depending on their ability to contribute to the heat generation. This effect was investigated by the analysis of the corresponding temperature/pressure curves (Figure 2-14) during the heating of different substrate materials. Iron acetate catalyst particles were drop-casted on the silicon wafers for this set of the experiments.

![Figure 2-14. Microwave absorption of the carbon source and silicon substrates. a) Temperature development, b) pressure inside the reaction vial, and c) difference plots extracted from a.](image-url)
First the heating capacity of pure ethanol was investigated. Only at an irradiation power of 300 W an efficient heating up to 150 °C could be obtained, while the overall temperature at 100 and 200 W power is significantly lower. The microwave absorption increases if an additional silicon substrate is inserted into the reaction vial (Figure 2-14a). The higher temperatures have simultaneously an influence on the pressure generated within the vial (Figure 2-14b). The analysis of the efficiency of the heating process reveals the importance of selecting the microwave power. At 100 W irradiation power the energy absorption is sufficient just to maintain the average temperature within the vial at a constant level (Figure 2-14c, left), as heat dissipation effects have to be compensated. These conditions were observed not to be sufficient to initiate the growth of CNTs and carbon nanofibers on the substrate. At higher irradiation powers a clear increase of the temperature and pressure was observed during the irradiation process (Figure 2-14c, middle and right) leading, at simultaneously generated high pressure values, to CNT growth. Substrates which are less favorable to absorb microwave irradiation are in this respect even more critical. This was observed, e.g., for mica and quartz glass substrates, and it was found that even under high power irradiation conditions no tube formation was initiated (Figure 2-15a).
Figure 2-15. CNT growth on insulating substrates. a) SEM image of the substrate irradiated in the standard set-up (conditions); b) temperature and pressure curve comparison obtained without and with an additional silicon substrate; c) SEM investigation of a CNTs layer grown on quartz glass support with additional silicon substrate present in the reaction vial.

However, mounting these substrates onto an additional silicon wafer enhanced the absorption of microwave irradiation and compensated for the limited heating of the substrates (Figure 2-15b) and corresponding heat dissipation effects. These conditions were sufficient to increase the reaction pressure within the microwave vial to the required high values. SEM investigations revealed in this case the formation of dense CNTs films on the quartz glass support (Figure 2-15c).
2.7 Investigation of the Formation of Iron Oxide Particles by Reduction with Hydrazine

As it was highlighted in section 1.5, the role of the catalyst is crucial for the obtainable dimensions of the synthesized carbon materials, and also the preparation of the catalyst layer is influencing the tube growth. Therefore, a detailed study on the formation of iron catalyst particles was performed to investigate the process and to understand the underlying effects. Such particles might find, in particular in combination with patterning techniques, applications with respect to storage devices as well as in initializing the catalyzed growth of nanomaterials and in guiding the initiation of catalytic reactions. Besides the implications in the synthesis of catalyst particles these studies are moreover important with respect to the synthesis of uniform magnetic particles, which represents another active field with respect to their applications. Their broad range of possible applications, in particular the use of magnetic iron nanoparticles in nanoelectronic devices, has attracted considerable interest. These include ferrofluidics,[50] hyperthermal treatment for medical applications,[51] catalysis,[52] active electrode materials,[53] sensor devices,[54] and their application as storage devices.[55] In particular, small iron nanoparticles with a diameter of a few nanometers have attracted significant attention as they show superparamagnetic behavior,[56] meaning that they have no defined magnetic moment in the absence of an external magnetic field. This property is interesting for sensor applications, for tuning the viscosity of ferrofluids, in biomedical imaging, or for the magnetic separation of cells, DNA, and proteins as well as in therapeutic approaches, such as targeted drug delivery and magnetofection.[57,58] Due to the size dependence of the electrical, optical and magnetic properties of the nanoparticles,[59] and also the dependence of the diameter of carbon nanotubes on the catalyst particle size, good control of the particle dimensions is regarded as a key issue for the efficient utilization of such systems.

In the course of these studies iron nanoparticles were obtained by two different preparation processes to obtain the catalyst particles. While common synthetic approaches to form iron-based nanoparticles include the nucleation of nanoparticles in the gas phase,[60] autocatalytic surface growth,[61] seed template growth on gold nanoparticles,[62] thermal decomposition of, for example, iron pentacarbonyl,[63,64] sonochemical decomposition of iron carbonyl,[65,66] and the mechanically based method of milling,[67] iron nanoparticles were synthesized in a
surface-based chemical reaction process in these studies. The particle formation utilizes the reduction of iron(II)acetate with hydrazine vapor,\(^{[29,68]}\) or by liquid hydrazine (\(\text{N}_2\text{H}_4\)) to reduce the iron salts.\(^{[69-72]}\) Alternatively, thermal activation can be used to form the catalyst nanoparticles. The surface-assisted reduction process, however, was observed to result in very homogeneous nanoparticles with uniform particle dimensions and is in the focus of the particle formation process. Different processes were proposed being previously suspected to be responsible for the quite uniform size of the particles, such as limitations of the diffusion of the iron species on the surface, Ostwald ripening,\(^{[73]}\) and others. To better understand the formation mechanism of the particles during the substrate-supported synthesis, SPM as well as TEM measurements were performed. The overall preparation process for the formation of nanoparticles that was followed is schematically depicted in Figure 2-16.

![Figure 2-16](image)

**Figure 2-16.** Schematic representation of the formation of iron oxide nanoparticles by reduction performed a) with hydrazine vapor and b) in a droplet of hydrazine.

First, aqueous or ethanolic solutions with a concentration of \(5 \times 10^{-3}\) mol/L were placed onto the substrate and the solvent was allowed to evaporate. These precursor layers have been investigated by means of SPM and TEM. In the latter case the iron acetate solution was applied onto a carbon-coated TEM grid. In both cases characteristic needle-like structures, formed by the iron acetate, were found both in the SPM and TEM investigations (Figure 2-17).
The size of the needles appears to be rather uniform with a typically length of approximately 250 nm and a needle width of 10 nm. TEM electron diffraction patterns (Figure 2-17d) have been recorded on randomly oriented needles and revealed lattice constants of 1.5 Å and 2.5 Å, respectively. The TEM investigations, moreover, show that the contrast within the individual needles was not uniform. Differences in the density were observed along the needles, which might relate to a higher concentration of iron or a different crystallographic orientation of the material in the dark areas of the needles. Subsequently, the sample was exposed to hydrazine vapor (Figure 2-1a) in a closed reaction vessel. The reduction performed in the vapor phase required significantly longer times in contrast to the times for the direct reduction in hydrazine liquid. In the course of the investigations, the needle-like aggregates were first exposed to hydrazine vapor for 100 min and the TEM grid was transferred back to the TEM. Figure 2-18a reveals that after long exposure times the needle-like crystalline structures are completely converted into small particles as evidenced by the
SPM image. This conversion was investigated in more detail by accompanying TEM studies. Here the overall exposure time was sequentially applied and after different time intervals TEM was used to track changes of the initial structures. After an exposure time of 100 minutes it was found that the needles started to develop into small particles, which are embedded into the needle-like structures.

![TEM images of the partially reduced iron nanoparticles after 100 min treatment with hydrazine vapor.](image)

**Figure 2-18.** TEM images of the partially reduced iron nanoparticles after 100 min treatment with hydrazine vapor.

It is not clear where the particle growth is initiated or if it might be related to the darker structures observed in the original needle-like aggregates. As the reduction process was not completed after the reduction in hydrazine vapor, the substrate was subsequently exposed to hydrazine solution for 10 min to complete the reduction process. The particles formed can be visualized in the TEM micrographs and were further analyzed (Figure 2-19b, c). They have a rather similar structure to the particles that started to form in the early stage of the reduction process within the needle-like structures. Some of the nanoparticles show a brighter contrast in their core area. This might be associated to the oxidation process during the preparation and/or transfer processes; an effect that is frequently observed for highly reactive oxide nanoparticles.\(^{74,75}\) The particles show a typical diameter of approximately 45 nm.
The application of the liquid hydrazine to reduce the iron acetate was observed to be much faster and also the liquid character might have an influence on the particle formation process. However, the structure of the formed particles is rather similar compared to the particle structure in the early stage of the development. This is furthermore supported by the analysis of thermally reduced nanoparticles, which show a similar structure (Figure 2-19a). Moreover, also in Figure 2-19b still a few remaining needles are observed. This is regarded as a hint that the formation of particles is not a process that involves the dissolution of the metal salt and the formation of a new nucleation site.

Besides the structural changes also the underlying chemical changes of the sample were investigated by means of X-ray photoelectron spectroscopy (XPS) to correlate structural and chemical transformations during particle formation. It has to be critically mentioned here that the analysis of iron nanoparticles implies certain difficulties, as the chemical oxidation of the very reactive iron represents inherent problems. The preparation steps have been carried out either in closed vials or in solution (for the reduction with hydrazine). However, the samples were investigated under ambient conditions by SPM. Moreover, the sample handling did not involve the use of a protective environment. Due to the high reactivity and the tendency of iron to undergo a large diversity of oxidation reactions, the formed particles as well as the starting materials might have been oxidized in the course of the preparation process. Thus, XPS data of the materials have to be evaluated under the given, non-ideal preparation conditions. Therefore, a definite conclusion on the underlying chemical processes during the particle formation process cannot be drawn.

Figure 2-19. a) SPM, b) and c) TEM images of the completely reduced iron nanoparticles after exposure to hydrazine solution for 10 min.
Figure 2-20 depicts the Fe2p and the C1s XPS data of different stages of the particle reduction.

![Graphs showing Fe2p and C1s XPS data](image)

**Figure 2-20.** XPS investigation of iron acetate and after 20 min reduction in hydrazine vapor  
*a) Fe2p and b) C1s.*

After a reduction time of 20 min in hydrazine vapor the formation of Fe(0) species was observed. Additionally, the Fe(III) peak increased, most probably due to the fast oxidation of Fe(0) to Fe(III) during the preparation and transfer of the sample. After the reduction, the content of C-O species significantly decreased, which might be related to the reaction of hydrazine with acetate, which indicates the start of the reduction of the acetate to aldehyde. However, after a reduction time of 20 min, a complete conversion had not been reached, in agreement with the TEM investigations, where parts of the needle-like structures were still present. Based on the complementary information derived from the TEM/SPM investigations and the XPS measurements, the following growth model is proposed (Figure 2-21): aqueous solutions of the iron precursor result in the formation of needle-like aggregates when drop-cast onto a substrate and after evaporation of the solvent.
Figure 2-21. Schematic representation of the growth model. a) Iron acetate needle-like aggregates on the substrate, b) formation of particles from the needle-like aggregates.

Upon reduction of the Fe(II) and Fe(III) species, the gradual development of spherical particles is observed, which are located at different places within the needles. It is suggested that the uniform size of the completely reduced particles is a result of the close association of the well-defined needle-like aggregates and the particle formation process itself. Ultimately, the size of the needle, consisting of the iron acetate precursor, defines the material that can be used to form the particle itself. Upon complete reduction, uniformly sized particles were formed. These investigations serve as a first indication of the iron nanoparticle formation, however, more controlled preparation and characterization conditions should be applied to finally prove and to verify the growth model.

The presented investigation on the synthesis of carbon nanotubes by microwave irradiation fuel further research also for direct applications of the carbon nanotubes for the functionalization of SPM tips to obtain ultra-sharp probes for high resolution imaging, improved adhesion measurements, etc. Furthermore, aligned, ordered arrays of perpendicularly oriented CNTs have attracted special interest for their application in field-emitting devices, e.g., in display technology.

In the following section the impact of the microwave-assisted synthesis approach of CNTs will be used to fabricate CNT SPM tips, as well as a suitable concept to fabricate patterned CNT films will be introduced.

### 2.8 Growth of Carbon Nanotubes on SPM Tips

Scanning probe microscopy has developed into a standard tool in material research and represents a frequently used technique in nearly all fields of science, including chemistry, physics, biology and others. The resolution of this technique is, however, strongly related to the quality of the available tip material, which limits not only the lateral resolution,
but implies also limitations with respect to the investigation of, e.g., steep edges. While commercially available SPM tips are fabricated utilizing silicon microfabrication techniques and reach a typical resolution of approximately 10 nm, tailor-made tip layouts have been proposed to improve the tip performance. The tip quality depends mainly on the dimensions and the shape of the probe, the durability of the tip apex, and the nature of interaction between sample and probe. In this respect, in particular, SPM tips functionalized with a CNT have attracted considerable attention. Due to the high Young's modulus of the CNTs and their excellent aspect ratio attempts have been made to use them as probes for SPM. Not only their unique mechanical, but also their chemical and electronic properties open attractive possibilities that can result in improved imaging performance. Due to the high resolution of CNT SPM tips they can be used to image very fine structures in biological as well as molecular materials. Several studies have been performed where CNT SPM tips were used to image biological materials, such as, DNA or proteins. Different methods have been developed to either directly grow CNTs on SPM tips or to place CNTs on tips. For a more detailed overview of the later techniques see Chapter 1. Additionally, placement of the CNT on the SPM tip is usually performed by using SEM manipulators where individual tubes are picked and stabilized on the SPM tip with locally deposited carbon. This method is limited to certain diameters of the nanotube that can be placed on the tip. Moreover, this approach is time consuming and requires a rather expensive experimental infrastructure. This process is also difficult to be used for a scale-up of the manufacturing process. Alternatively, the direct growth of CNTs onto SPM tips can be used. For this purpose different methods can be utilized; e.g., by surface growth or by pore growth. In particular the chemical vapor deposition (CVD) is frequently used and yields thin CNTs directly grown on the tip apex. Besides a relatively fast production time, still dedicated equipment, as well as rather harsh reaction conditions are required utilizing these conventional CVD approaches. Due to the fact that all these methods are also time consuming and costly there is a demand for alternative methods for the fabrication of SPM CNT tips, which make them affordable and allow their use not only for specialized applications.

An alternative approach of utilizing the microwave-assisted growth of CNTs directly on the apex of a commercially available SPM tip is introduced here. The experimental set-up takes previous investigations into account and a modification of the experimental process was developed. In particular mounting the SPM tips to ensure an
effective counter-balance of heat dissipation effects was found to be a crucial step. For this purpose, the commercially available SPM tips were mounted onto pieces (0.5 cm × 1 cm) of silicon wafers by means of a conducting silver paste, which was used to glue the chip, to which the cantilevers and tips are connected. This allowed the efficient control of the heat dissipation from the relatively small area of the tip itself and, moreover, permits a convenient handling of the tips. Another challenge is placement of, in the optimized situation, an individual catalyst particle on the tip apex. Simple immersion of the tip in 5 mM aqueous solution of nickel acetate resulted in the coverage of the entire tip (Figure 2-22a), as indicated by the SEM images, showing the flake-like appearance of the SPM tip. Microwave irradiation resulted in the thermal activation of the precursor material and in the formation of catalyst particles which initiated the growth of CNTs (Figure 2-22b). A complete coverage of the SPM tip with CNTs was observed.

![Figure 2-22. SEM micrographs of the SPM-tip before (a) and after (b) microwave irradiation. (a) The whole SPM tip is covered with nickel(II) acetate catalyst; (b) the CNTs after microwave irradiation.](image)

These investigations demonstrated the effectiveness of the heat dissipation suppression and gave first evidence for the possibility to functionalize the SPM tip with CNTs. In the next step the optimization of the catalyst deposition process was addressed to ultimately be able to grow only one individual CNT on a SPM tip. For this purpose, two different approaches were tested to limit the amount of catalyst deposition. This can be established by simple scanning of the tip over a dried solution of nickel acetate, drop-casted onto a silicon substrate at higher contact forces. In this case a low amount of nickel acetate is deposited onto the tip, which can provide the catalyst seed for the CNT growth. Figure 2-23a depicts the deposited material present on the SPM tip after scanning a small area on the nickel(II) acetate loaded substrate. The presence of material is well visible at the slope of the
tip, indicating that small amounts of the nickel acetate were attached to the tip. The prepared tips were subsequently mounted in the microwave vials and the CNT growth was pursued.

**Figure 2-23. SEM micrographs of an SPM-tip before (a) and after (b) microwave irradiation.**

Figure 2-23b shows the conversion of the nickel(II) acetate material into catalyst particles, which are observed both on the tip apex as well as on the slope of the tip itself. It could be observed that only very few CNTs are grown from the tip and in particular one CNT protrudes vertically away from the tip. This CNT has a length of approximately 600 nm and a diameter of 20 nm. Due to the length a bending of the CNT is observed. This result demonstrates that it is possible to obtain reaction conditions within the pressure vial that permits the growth of individual CNTs due to an effective compensation of the heat dissipation effects. In previous experiments, performed to grow individual CNTs onto solid substrates, it was observed that this represents a challenging task. However, still the amount of catalyst material attached to the tip is not yet well controlled due to the fact that the SPM tip collects considerable amounts of nickel acetate during the scanning process of the dried layer.

SPM force spectroscopy was conducted to further demonstrate the successful functionalization of the SPM tips with carbon nanotubes. Therefore, a set of measurements was performed that included first the recording of an approach and retraction curve with a CNT functionalized SPM tip in the static SPM mode. Figure 2-24a displays a representative curve that clearly demonstrates the bending of the cantilever away from the surface, when (in this particular case) the bundle of CNTs is in contact with the surface and starts to slide away or buckles.
Figure 2-24. Force spectroscopy of CNT functionalized AFM tips. (a) Representative deflection versus distance plot of a CNT modified tip. (b) Measurement with the same tip after the CNT material was removed by applying higher forces. (c) I-V curve of a CNT-modified.
Relatively large adhesion forces suggest in this case that several CNTs are attached to the cantilever, which have a length of approximately 60 nm, as estimated from the z-displacement position of the onset of the bending curve until the typical proportional deflection of the cantilever is observed. These curves are reproducible indicating moreover the stability of the CNTs onto the tip. After this, significantly higher forces were applied onto the tip to remove the CNT material on purpose. The force spectroscopic measurements after this process (Figure 2-24b) indicate the characteristic deviation of the deflection versus distance curves, and a significant decrease of the adhesion forces was observed. Moreover, the characteristic snap-in points are clearly visible, without any indication for a bending of the cantilever prior to the contact of the SPM tip. Additionally, the current-voltage characteristic (Figure 2-24c) was measured on a CNT-modified metal-coated SPM tip, that was gently brought into contact with a graphite substrate. In this case a significantly reduced conductivity could be measured compared to non-modified metal-coated tips.

In general, the microwave-assisted synthesis allows the direct fabrication of CNT SPM tips. The deposition of the catalyst material could be further improved by utilizing particle picking approaches, e.g., by force versus distance curve recording, to further increase the controllability of the presented approach.

2.9 Patterned Growth of Carbon Nanotubes

Interesting possibilities emerge from the use of patterned substrates, as they provide an easy means to localize the catalyst particles and, thus, to define the position of the carbon material. Additional experiments have been performed to fabricate patterned structures. Figure 2-25 depicts an approach to fabricate micro-sized patterns by using a conductive TEM grid to imitate the electro-oxidation process\textsuperscript{[104]} (for details see Figure 2-1 and Chapter 3).
Figure 2-25. Schematic outline of the electro-oxidation approach of the OTS monolayer by the TEM grid.

Figure 2-26a depicts a relatively large structure, resembling a pattern that was generated by the electro-oxidation with a hexagonal TEM grid (Mesh 50, bar diameter 75 µm). The typical black coating is exclusively formed on the hexagonal structures after the catalyst deposition and microwave treatment in the presence of ethanol. However, thinner structures could also be produced by using a fine mesh TEM grid, which results in structures with a typical line width of 6 µm (Figure 2-26b).
Figure 2-26. Fabrication of patterned carbon nano assemblies. a) Patterned carbon nanofibers and tubes arrays on a hexagonal structure electro-oxidized with a TEM grid (Mesh 50, hexagonal grid). b) Smaller bar features (Mesh 400 fine bar grid) after the site-selective growth of nanostructures. Both structures show good selectivity of the grown structures and the presence of a black coating. c) Zoom-in of the structure (b) with special focus on the border of the border of the grown structures to emphasis the selectivity of the growth process. d) The zoom-in on the nanofibers and nanotube films demonstrates the uniform length and diameter of the individual fibers.

Both structures have been investigated by means of SEM and show the presence of carbon nanostructures, where most of the carbon nanostructures appear to stand upright and have a diameter of 40 to 100 nm and a rather uniform length (Figure 2-26c, d). Also here the formation of thinner tubes could be obtained by changing the catalyst material to nickel. It is readily observable that the remaining OTS substrate remains completely free of tube material, and the boundaries of the structures are sharply restricted to the imprinted structure, demonstrating the high selectivity of the process. It was observed that the growth of carbon nanostructures on such patterned substrates requires higher heating power values, as apparently heat dissipation effects play also in this case a crucial role.

Furthermore, nano-sized, patterned catalyst layers have been fabricated according to the approach summarized in Figure 2-1a, b (Chapter 3). Figure 2-27 depicts nanostructures resembling the pattern generated by electro-oxidative lithography by an SPM tip on the OTS monolayer.
Figure 2-27. Fabrication of patterned nanotubes assemblies. a) Patterned carbon nanotubes arrays on line structures electro-oxidized with the SPM tip. b), c) Cross features after the site-selective growth of carbon nanotubes. d) Circle structure of the patterned growth of nanotubes.

Feature sizes ranging from 100 to 500 nm were inscribed by means of a SPM tip on the OTS based monolayer. These could be used to selectively deposit the required catalyst material on the pattern, and resulted in the growth of CNTs exclusively in these positions. It is observed that the rest of the substrates stay free of carbon nanotubes. Such patterned carbon nanotubes films are very important for various applications, where carbon nanotubes are required to be grown site-selectively, e.g., electronic devices, wires and sensors (see details in Chapter 1).

2.10 CONCLUSIONS

A technique for the microwave-assisted synthesis of one-dimensional carbon structures has been developed. It was demonstrated that small iron nanoparticles can be selectively heated by microwave radiation. A major advantage of this approach is the fact that the heat development is limited to the close vicinity of the nanoparticles, while the average overall temperature in the reaction vial remains at relatively low values of 130 to 150 °C.

The approach to synthesize carbon nanofibers and nanotubes was adapted to the special requirements of the microwave set-up and had to be optimized in terms of safety aspects. By using ethanol as a carbon source, provided by a liquid reservoir, which is located beneath the sample, a flux of highly flammable and explosive gas mixtures was avoided. The reaction
conditions for the microwave-assisted synthesis of carbon nanotubes and nanofibers have been investigated in detail. These were observed to have a strong influence on the CNT/CNF formation and on the quality of the obtained materials. The analysis of the temperature and pressure kinetics during the microwave irradiation revealed, in particular, a strong influence of the applied pressure on the formation of the CNTs/CNFs. Further improvement of the quality and size of the synthesized materials was obtained by variation of the catalyst material. Nickel was identified as the most favorable catalyst material to obtain small nanotube diameters down to 15 nm at very short irradiation times of 2 minutes.

Compensation of the heat dissipation, in particular for substrates showing a low absorption of microwave irradiation, resulted in reliable processes that permit the microwave-assisted growth of CNTs on a variety of substrates. Mica and quartz glass substrates could be functionalized by placing them on an additional silicon wafer, which compensated the poor microwave absorption of those substrates and heat dissipation effects. These investigations led to a significant improvement of the developed method and resulted in the controllable synthesis of defined CNTs/CNF systems.

It was demonstrated that the growth of individual CNTs can be achieved and the optimization of the preparation conditions resulting in a promising approach that allows the fabrication of CNT SPM tips utilizing relatively mild synthesis conditions. In particular, the relatively low experimental efforts, as well as the fast fabrication times, are general advantages of the introduced method and provide a promising, cheap technique to fabricate CNT SPM tips. The deposition of the catalyst material can be further improved, e.g., by utilizing particle picking approaches, or by force versus distance curve recording, to further increase the controllability of the presented approach.

Results on patterned OTS/silicon substrates suggest that smaller areas covered with a suitable catalyst layer can be obtained by this method, with important implications for the effective integration of carbon nanomaterials into frameworks of devices. Carbon nanotubes were successfully grown on micro- and nanoscale patterned areas.

These findings are expected to have additionally an impact on the use of the selective heating mechanism, in particular as it provides advantages over conventionally used methods, i.e., the reduced reaction time, the lower overall exposure temperature to the substrates and for the integration of CNTs/CNTs into predefined device frameworks consisting of different materials. It is assumed that the heating efficiency of, other materials, e.g., used in transistor
structures, is significantly lower compared to iron, nickel and cobalt particles, which are generally used as catalyst particles for the growth of carbon nanofibers and nanotubes.

2.11 EXPERIMENTAL

Iron acetate particle preparation.

Iron(II) acetate was dissolved in ethanol \(5 \times 10^{-3}\) M. Afterwards, the iron(II) acetate was drop-casted onto either silicon substrates (UniversityWafer) as well as on carbon coated TEM grids (EMS, 200 mesh, Cu). Finally, the samples were exposed to hydrazine vapor. Alternatively, hydrazine was directly applied to the substrate as a liquid to increase the reduction speed. The sample preparation was performed under ambient conditions. The substrates were investigated by means of SPM in tapping mode (Nanoscope IIIa Multimode, Digital Instruments) using commercially available cantilevers (µMash, NSC35 AlBSC, Estonia). TEM images were acquired on a 200 kV Technai G² Sphera (FEI). XPS was performed on a VG Escalab MKII spectrometer, equipped with a dual Al/Mg Kα X-ray source and a hemispherical analyzer with a five channel-tron detector. Spectra were obtained using a magnesium anode (Mg Kα = 1,253.6 eV) operating at 480 W and a constant pass energy of 20 eV, with a background pressure of \(2 \times 10^{-9}\) mbar. The spectra were referenced to the Si(2p) peak at 103.3 eV of the native SiO₂ layer on the substrate.\(^{105}\)

Preparation of monolayers and patterns.

Silicon wafers were purchased from UniversityWafer and were used as a substrate for the self-assembly of \(n\)-octadecyltrichlorosilane (from ABCR) monolayers (SAMs). Similar substrate sizes were used to enable a comparison of the heating kinetics. Patterning of the substrates was performed either with a conductive SPM (NT-MDT, Solver Pro) tip (µMash, CSC37, Pt coating, −9 V bias voltage, typical oxidation time of 20 ms/dot) or commercially available copper TEM grids (Mesh5 50, bar diameter 75 μm, −30 V bias voltage with a patterning time of ~30 sec). SPM pattering and imaging was performed on a Solver Pro SPM Microscope (NT-MDT).

Various carbon nanotubes catalyst preparation.
Different metal salts (Fe, Ni, Co) purchased from Aldrich were used to prepare 0.2 mol/L solutions in ethanol. These solutions were drop-casted or spin-coated on the Si wafer and dried in the air. Oxidized substrates were immersed in iron acetate solution for 10 minutes. Subsequently, these ions developed into iron oxides upon the exposure to hydrazine vapor (ACROS Organics) and stored at ambient conditions. These substrates were exposed to microwave irradiation (10 min at microwave power of 150 W in an Emrys Liberator single-mode microwave, Biotage) in the presence of an alternative carbon source (Ethanol, Biosolve) in order to observe the selective heating mechanism. Other substrates, loaded with bulk amount of catalyst were exposed to microwave irradiation (5 min at a microwave power of 200 W in an Emrys Liberator single-mode microwave, Biotage) in the presence of different carbon sources (Ethanol (Biosolve), butanol (Merck), 2-propanol (Biosolve) and ethylene glycol (Acror organics)). Moreover, mica (Electron Microscopy Science) and custom-made quartz glass were used as substrates for the CNTs growth.

*Carbon nanotubes characterization.*

Tube and fiber material were characterized by scanning electron microscopy (XL30 ESEM-FEG, Philips) and Raman spectroscopy (RamanStation HTS, Avalon). For TEM investigations, the black coating of the substrates was removed and dispersed in dimethyl formamide (Biosolve) to enable further investigations. Droplets of this solution were applied on silicon surfaces coated with aminopropyltrimethoxysilane (APTMS, Sigma Aldrich) by drop-casting. The typical amount of material that could be synthesized from 50 µL of catalyst solution was found to be approximately 3.0 mg.

### 2.12 References


Synthesis of Carbon Nanotubes and Nanofibers by Microwave Irradiation


Chapter 3. Electro-Oxidative Lithography for Nanofabrication

ABSTRACT

One way of organizing nanomaterials into defined structures is the use of electrochemical oxidation lithography on chemically active surfaces. This technique manipulates and guides the position of, e.g., catalyst particles. This approach can also be used for the post-synthesis organization of carbon nanotubes and, moreover, provides unique possibilities for the fabrication of nanomaterials.

The main advantage that makes this approach highly interesting is the fact that chemically active surface templates can be created, which provide a versatile platform to perform chemical reactions, to selectively bind nanomaterials, i.e., nanoparticles, to utilize self-assembly processes, and to site-selectively form bilayers that consist of molecular building blocks. Due to the fact that, during the electrochemical oxidation, addressable functional groups are created, it is possible to utilize the entire range of molecular interactions to modify the structures. These include electrostatic and van der Waals interactions, hydrogen bonding, complexation reactions, and covalent bonds to selectively bind suitable building blocks.

A comprehensive introduction into the electrochemical oxidation lithography of n-octadecyltrichlorosilane (OTS) monolayers is given here. Aside from the chemical modification process, it highlights the essential parameters of the writing process and the state-of-the art of fabrication strategies that were applied in this thesis to obtain functionalized structures.
3.1 INTRODUCTION TO SPM LITHOGRAPHY

Soon after the invention of scanning probe microscopy (SPM) and the observation of its abilities to modify substrates, the field of scanning probe-base lithography (SPL) was introduced. The application of probe-based techniques for the modification of substrates has widely spread and a large variety of techniques has evolved. These include the movement of atoms (using STM), the production of local deformations in soft substrates (using high contact force SFM), the local application of ‘inks’ (dip-pen lithography), and the local oxidation of suitable substrates (local probe oxidation). In the latter case, the tip is used as an electrode to locally initiate electro-chemical reactions in the vicinity of the tip. These can include oxidation processes, as well as catalytic reactions, etc. Frequently, self-assembled monolayers (SAM), attached to different substrates, are used as surfaces for the pattern creation. The main advantages of utilizing SAMs are their thermal, chemical, and physical stability and the ability to create densely packed layers.

Lithographic techniques based on SAMs frequently utilize silane-based monolayers for the patterning of silicon, glass, activated metal surfaces, and thiol monolayers, which react on gold or silver substrates. Silane-based monolayers demonstrate certain advantages over thiol-based monolayers; notably, the high stability of the monolayer that results from a covalent linkage to the surface. The linkage consists of three bonds between the surface and the silane molecules. One drawback, however, is that the conditions to form well-defined monolayers are more demanding. The silane-based monolayers are more robust and closely packed, which allows them to serve as resist layers for, e.g., etching processes, and also provide insulating properties. Moreover, the high stability allows further modifications to be performed on the monolayers, e.g., post-assembly surface reactions of functional trichlorosilane monolayers.

A special class of SPL utilizes electrochemical reactions, which are initiated by the local application of a bias voltage to the SFM tip. Prominent examples of this technique include the anodization reaction of silicon, charge injection lithography on insulating layers, the oxidation of two-dimensional electron gases, and electrochemical deposition of metals, amongst others. A versatile approach utilizing voltage-driven lithography to locally electro-oxidize a self-assembled monolayer of OTS is described in the following and is,
moreover, used for the post-synthesis assembly of nanometric building blocks, i.e., carbon nanotubes (Chapter 4) and metal nanoparticles (Chapters 2.1.2, 2.1.9. and 5).

### 3.1.1 **Electrochemical Oxidation Lithography**

This approach utilizes a self-assembled monolayer of OTS as a suitable substrate to induce voltage-mediated changes of the chemical properties of the monolayer itself. The versatility of the approach originates from different oxidation modes that can be applied and the fact that the oxidation can be performed on different length scales. For nanometric modifications, a conductive SFM tip can be used; micrometer patterns can be created by means of a conductive stamp (e.g. a TEM grid),\[^{16}\] or oxidation can be performed in a droplet of water to modify large areas of the substrate (Figure 3-1 a-c).\[^{17}\]

![Figure 3-1. Schematic representation of the main oxidation techniques. a) Nanometer scale oxidation by a SFM tip; b) TEM grid mediated micrometer scale electro-chemical oxidation; c) water droplet oxidation on millimeter scale.](image)

The result of the oxidation process critically depends on a number of parameters that can be varied to initiate the different writing modes. Firstly, the process relies on the reliable formation of a water meniscus between the tip (or stamp) and the water film present on the substrate at ambient conditions. This meniscus represents the equivalent of an electrochemical cell\[^{18}\] in which a local electrochemical reaction can be performed due to the very close proximity of the tip/stamp and the surface. It also provides the “electrolyte” for the local anodic oxidation. A negative bias voltage is applied to the tip during the surface
oxidation process. This electrical field is responsible for ionizing the water molecules to form reactive ionic species necessary for the oxidation process.\(^{(19)}\) The applied voltage, as well as the duration of the voltages pulses, plays a crucial role, as does the tip material. The sharpness of the tip limits the obtainable resolution.

Depending on these parameters, different structuring modes can be utilized. At low voltages and short oxidation times, the electrochemical oxidation process results, according to Sagiv \textit{et al.},\(^{(20)}\) in the modification of the OTS monolayer’s top functional –CH\(_3\) groups, creating polar carboxylic acid groups (monolayer oxidation mode). At longer oxidation times and/or higher voltages, the monolayer is locally degraded and the growth of silicon oxide is initiated (silicon oxide generation mode). A schematic representation of both modes is presented in Figure 3-2.

\[\text{CH}_3\text{COOH} \quad \text{COOH} \quad \text{CH}_3\text{COOH} \quad \text{CH}_3\text{COOH}\]

\[\text{SiO}_x\]

\(\text{Silicon oxide generation} \quad \text{Monolayer oxidation}\)

\textbf{Figure 3-2} Schematic representation of the pattern fabrication by electro-oxidative lithography. \(a)\) Silicon oxide growth mode; \(b)\) monolayer oxidation mode.

Potentially, both structuring modes can be used as chemically active templates and can be used to self-assemble nanomaterials in predefined surface areas. A short overview of both oxidation modes, as well as illustrative examples emerging from the techniques, is highlighted in the following sections.
3.1.2 Monolayer Oxidation Mode

The application of mild oxidation conditions results in the chemical conversion of the surface-terminated methyl groups of the \(n\)-octadecyltrichlorosilane (OTS) monolayer into carboxylic acid functions (Figure 3-2b). The electro-oxidation process was first observed on nonadecyltrichlorosilane (NTS) monolayers, but can be also applied on OTS monolayers, which results in a similar functionalization of the surface. It was observed that the monolayers in contact with the negatively biased tip show increased lateral force signals when scanned in contact mode afterwards. The lateral force imaging is dominated by a change of the surface properties from hydrophobic (OTS and NTS monolayers) to hydrophilic (after the application of the bias voltage pulses). The frictional origin of the detected contrast can be seen, if opposite scan directions are applied, which result in the inversion of the lateral force signal. The proposed mechanism of the monolayer oxidation suggests no change of the corresponding height images; however, mostly also a change in the topography is observed. This contrast is also dependent on the scan direction, and, thus, can be related to the influence of lateral forces, which also exert a cross-coupling to the height detection.\(^{21}\) Lateral force imaging represents the only tool to investigate surface properties, e.g. the hydrophilicity, in nanometer dimensions. For this purpose the technique was also used to screen the oxidation conditions of monolayers.\(^{16}\)

The process of electro-chemical oxidation of the OTS monolayer was further investigated by analyzing macroscopic model systems by Fourier Transform Infrared (FT-IR) spectroscopy on macroscopically oxidized surfaces. These experiments confirmed the presence of carboxylic acid groups on the surface after the application of a bias voltage.\(^{22}\) It was, moreover, demonstrated that the quality of the monolayer was not significantly decreased during the electro-oxidation process. While the \(–\text{CH}_2\) vibrations were preserved, the terminal \(–\text{CH}_3\) vibration signal significantly decreased. A further proof for the formation of carboxylic acids was the appearance of an absorption peak for \(–\text{C}=\text{O}\) at 1713 cm\(^{-1}\) in the corresponding FT-IR spectra. The characterization of micrometer-sized features can also be carried out by using XPS to analyze the chemical structures. The group of Andruzzi \textit{et al.}\(^{23}\) investigated micrometer patterns on OTS by XPS. The presence of carboxylic groups after the electro-oxidation step was confirmed by the appearance of a peak at 289 eV in the C(1s) high resolution XPS spectrum from the oxidized structures. Another approach utilized time-of-
flight secondary ion mass spectroscopy (TOF-SIMS) to investigate the chemical transformations on macroscopic structures. In this case, 1-octadecene monolayers were assembled on the hydrogen terminated silicon and electrochemical oxidation lithography was applied.\cite{24,25} The modified areas showed the presence of $C_xH_yO$- and $C_xH_yN$-type peaks, which increased in height with increase of the applied bias voltage during the electro-oxidation step. These peaks were attributed to the formation of organic polar moieties. Additionally, a decrease of the $SiC_xH_y$ signals was observed. The formation process of the polar groups and the growth of silicon oxide can also be observed by the force spectroscopy approach.\cite{26} Here the oxidation process can be observed in a time resolved fashion. While continuously performing force vs. distance curve analysis, the tip is additionally biased with a negative voltage. Only in the period of direct contact the electro-oxidation process can take place, thus creating different oxidation stages of the point structure. Simultaneously, surface properties, i.e., the adhesion to the surface topography can be analyzed.

However, it has to be mentioned here that the overall mechanism for the monolayer oxidation mode is not yet fully understood; additional investigations are required to better understand the underlying chemical processes, as well as the kinetics.

### 3.1.3 Chemically Active Surface Templates Created by Monolayer Oxidation

The carboxylic structures could be used to analyze the oxidation processes, and also as a template for a large variety of post-modification assembly of, e.g., nanoparticles, nanowires, molecules, and of additional monolayers, etc. (Figure 3-3). The placement of different nanomaterials on the oxidized structures represents a promising route towards the nanoscale fabrication of functional devices. Positively charged nanoparticles can be selectively placed on the acid-functionalized surface structures. The assembly of positively charged gold nanoparticles onto –COOH patterns was reported.\cite{27,28} SFM revealed the height increase to be 18 to 20 nm, which corresponded to the size of the Au particles. This approach was also used for the sequential placement of two different sizes of gold nanoparticles. This was done by sequential oxidation steps on OTS with the self-assembly of different nanoparticles after each inscription step.\cite{29} An annealing process at 90 °C for 6 hours was used between the assembly steps to stabilize the particles and to fix them to the surface.
Another approach towards the application of oxidized structures is the in-situ generation of magnetic particles on the inscribed structures.\textsuperscript{[30]} The magnetic properties of the formed particles were studied by magnetic force microscopy, which demonstrated that the particles were superparamagnetic. The oxidized structures can also be directly used to study the wetting behavior of alcohols on nanopatterned lines.\textsuperscript{[31]}

The use of the oxidized areas in the assembly of a second layer on top of the –COOH features, for instance a second reactive layer of trichlorosilane represents another important strategy for the functionalization of the surface templates. The formation of a second layer trichlorosilane is possible due to coupling reaction between the –SiCl\textsubscript{3} groups and the carboxylic acid moieties.\textsuperscript{[32]} For example, the self-assembly of 18-nonadecyltrichlorosilane (NTS), 11-bromoundecyltrichlorosilane, 11-undecyltrichlorosilane (UTS) and others were described.\textsuperscript{[22,32,33]} These different chemical end groups can be used to fabricate two-dimensional arrays of functional groups, which are relevant for a variety of applications, e.g., sensor devices or adhesion layers.\textsuperscript{[34]}

A further application of the oxidized features is the formation of cadmium selenide particles from Cd(II) acetate solution, which were placed on functionalized thiol nanopatterns.\textsuperscript{[35]} The thiol functionalization was also used to fabricate conductive nanometer-scale wire structures that are connected to a macroscopic electrode.\textsuperscript{[36]} An assembly of Au\textsubscript{55}(Ph\textsubscript{2}PC\textsubscript{6}H\textsubscript{4}SO\textsubscript{3}Na)\textsubscript{12}C\textsubscript{6} clusters with a diameter of 1.4 nm was shown.\textsuperscript{[37,38]} These clusters are promising candidates

Figure 3-3. Main strategies to use the chemically active templates created by monolayer oxidation. a) Self-assembly of nanometric building blocks, e.g. nanoparticles or b) additional assembly of a monolayer for surface chemistry reactions and rendering the charge of the structures.
for single-electron devices. Moreover, silver nanoparticles have also been placed on such substrates by the treatment of thiolated templates. Subsequent use of a silver enhancer solution resulted in the amplification of the particle size. It was shown that the addition of elemental gold from the spontaneous reduction reaction of HAuCl₄ on the eicosanethiol promoted the silver deposition from a silver enhancer solution.[39]

As a potentially important functional group that shows promising abilities to guide the assembly of negatively charged nanomaterials, e.g. nanoparticles[40] or DNA, etc., amine functionalities can be implemented by two different approaches.[41] The first method employs a vapor-phase self-assembly process of aminopropyltrimethoxysilane (APTMS) to create amine (–NH₂) moieties on the electro-oxidized surface areas. The second method of amine monolayer placement consists of a sequence of several reaction steps. First, an 11-bromoundecyltrichlorosilane is assembled onto oxidized structures. This is followed by the reaction of the bromo unit with sodium azide via a nucleophilic substitution reaction and the subsequent reduction of the formed azide functionalities with lithium aluminum hydride. This leads to the formation of the amine functions. Another attractive and versatile monolayer is based on 11-bromoundecyltrichlorosilane. This bromo functionalized layer can be, e.g., used to initiate a controlled atom transfer radical polymerization, which begins on the patterns of bromo functionalized structures and proceeds with the formation of polymer brushes.[42] After conversion into azide structures, bromo functionalized monolayers can be used for the cyclo-addition reactions with alkynes.[43] This allows the arrangement of a broad variety of functional groups,[44,45] molecules, and dyes.[46] The formation of molecular overlayer structures gives rise to numerous possibilities to construct functional building blocks.

An overview of the different possibilities for post-modification of the oxidized monolayers is shown in Figure 3-4.
As described in Chapter 2, carboxylic acid functionalized surface templates can be used to self-assemble iron oxide particles, which can be used as catalyst particles for the growth of carbon nanotubes. The particles assembled from iron(II) acetate solution onto oxidized patterns served as the catalyst in the indirect measurements of the selective heating by microwave irradiation. Oxidized patterns were, furthermore, used as templates to assemble silver nanoparticles (Chapter 5), as well as carbon nanotubes from surfactant solution (Chapter 4).
3.1.4 Silicon Oxide Growth Mode

The growth of silicon oxide by anodization lithography, as introduced by Dagata et al.,\cite{48} is well-studied. Investigations of the kinetics\cite{49,50} and characterization of the chemical nature of the created silicon\cite{51} have been performed. The oxidation takes place at the anode, which is the surface in this case.\cite{52,53} The tip acts as the cathode, which consists of a SFM tip coated with a noble metal (i.e. Pt or Au) with a redox potential higher than water. Here, the reactive species required to initiate the anodization are formed.

In addition to studies of the oxidation process itself, the use of monolayer-coated substrates was introduced. Sugimura et al. extended the approach to the local probe oxidation of self-assembled monolayers that consist of trimethylsilyl and octadecyltrimethoxysilanes on a silicon substrate.\cite{54,55} The use of the additional monolayer provides significant advantages because it can be used, for example, as a passivation layer or as a means to control subsequent etching processes.\cite{56} The electric field generated between the tip and the sample locally destroys the monolayer and the anodization of the released silicon surface proceeds upon prolonged application of the bias voltage on the tip, which results in the formation of SiO\textsubscript{x} features. For instance, a (3-aminopropyl)triethoxysilane (APTES) monolayer could be exclusively deposited on the SiO\textsubscript{x} structures.

Additionally, reversible patterning can be performed, as shown by Sugimura et al.\cite{57} This can be obtained by switching the polarity of the voltage applied to the SFM tip. The investigation was performed on a p-aminophenyltrimethoxysilane monolayer and it was shown that the oxidation/reduction cycles can be repeated several times. The oxidation process depends on various parameters, e.g., relative humidity, tip-substrate distance, applied voltage, tip geometry, oxidation times, etc. Several groups have described a linear relationship between the thickness of the oxide layer and the applied voltage at the onset of the anodization.\cite{58,59} The oxidation rate, on the other hand, decreases rapidly with the increase of the oxide layer thickness.\cite{60,61} The observed behavior was explained by the self-limiting influence of a decreasing strength of the applied field and a build-up of stress.

Kim et al. investigated the influence of the length of the alkyl chain on the anodization process for the creation of line patterns and the diameters of the dot patterns.\cite{62} This was investigated on monolayers prepared from hexyl-, octyl-, dodecyl- and
octadecyltrichlorosilane. Higher oxidation voltages resulted in the formation of broader features on each of the monolayers. At the same applied voltage, longer alkyl chains could be patterned with narrower lines, and the rate of the line variation decreased as the alkyl chain length of the monolayer increased. Even though the wetting properties of the monolayers were comparable, the differences in the resulting line width were evident. It was suggested that the alkyl chain length of the monolayer has an influence on the water meniscus area and its resistivity against degradation. Significant variations in the required threshold voltages, which have to be applied to initiate the silicon anodization of monolayer-coated substrates, were observed. The threshold voltage increased with increasing alkyl chain length of the SAM. This was attributed to the required electric energies that are required to degrade the monolayers and the organization of the monolayer itself, which depends on the alkyl chain length of the precursor molecules.

As previously mentioned, the application of higher voltages and/or oxidation times on OTS monolayers results in the degradation of the monolayer, which is followed by the growth of silicon oxide at the interface with the substrate. The process is schematically outlined in Figure 3-2a and represents the second mode of pattern inscription.

Relatively few investigations have been performed addressing the use of additional self-assembled monolayers, whereas there have been a number of investigations performed on the oxidation conditions of silicon oxide patterns. Hoeppener et al. investigated the surface properties during the oxidation process, as well as the monolayer degradation.[63] The oxidation process depends on various parameters, while the choice of the tip and its geometry has an influence on the size of the oxidation patterns. Only recently, Herzer et al.[17] showed that anodization lithography on OTS-functionalized surfaces results in structures that appear to grow silicon oxide in the core area, while, in the periphery of the core, a small region of electro-oxidized OTS monolayers is found. The corresponding investigations were conducted by lateral force microscopy, selective water vapor condensation, and FT-IR mapping on model systems, oxidized within a droplet of water.

Functionalized silicon oxide structures can be used to bind additional molecules, in particular DNA, proteins, etc.[64,65,66] Amine-functionalized SAMs provide a good binding for negatively charged colloidal particles.[67] Placing the structures in the colloidal nanoparticle
solution results in an electrostatic interaction of the negatively charged gold particles and the positively charged amine-terminated patterns, which was demonstrated, e.g., by Li et al.\textsuperscript{[68]} Recently, Martínez et al. introduced a different approach where the authors used an APTES functionalized surface.\textsuperscript{[69]} They demonstrated that the local probe oxidation can also be applied and the APTES locally degrades upon the application of a sufficient bias voltage. In contrast to others, the authors utilized the electrostatic repulsion between positively charged $[\text{Mn}_{13}\text{O}_{12}(\text{bet})_{16}(\text{EtOH})_{4}]^{14+}$ single molecule magnets and the amine-terminated, unmodified APTES areas and, guided by this means, the assembly of the magnets on the oxide structures. Another application of silicon oxide features was described by Graaf et al. Here, Rhodamin 6G particles were self-assembled on the oxide structures via electrostatic interactions. Selective growth of SWCNTs on silicon oxide nanodomains was demonstrated by He et al.\textsuperscript{[70]} Some examples, highlighting different aspects of the approach, are summarized in Figure 3-5 to provide an overview of the state-of-the-art.

**Figure 3-5.** Examples of the silicon oxide growth mode: (a) Au nanoparticle placement on APTMS/SiOx array (reprinted from ref. 67); (b) placement of colloidal nanoparticles (reprinted from ref. 67); (c) stretched DNA on an array of APTMS/SiOx (reprinted from ref. 64); (d) Schematic representation of the assembly of a second monolayer on SiOx patterns, and (e) SFM-tip induced Si oxidation lines on Si substrate (reprinted from ref. 60); (f)
selective SWCNTs growth and (g) \textit{Mn}_{12} single-molecule magnets on SiO_x patterns (reprinted from ref. 69).

The combination of both methods, the silicon growth and the oxidation of self-assembled monolayer for the fabrication of nanomaterials, is demonstrated in Chapter 5.

3.2 Conclusion

Electro-oxidative lithography represents an extremely versatile technique for the nanofabrication of functional patterns. It combines high resolution, simplicity of the process, and the chemical concepts of self-assembly, specific interaction, and reactivity. The chemical stability and versatile nature of self-assembled monolayers are the key features of this process. The integration of binding sites allows the utilization of highly selective self-assembly strategies to construct device frameworks from nanomaterials.

This technique includes two main pathways. The first pathway consists of applying a sufficient bias voltage to destroy the SAM locally and to cause the growth of silicon oxide. The second consists of utilizing a lower bias voltage, such that the functional end groups on the SAM are modified. These pathways result in patterned structures that have substantially different properties, which are useful for various applications. Selected examples for each pathway were discussed in this chapter.

In the following chapter, selected strategies will be used to guide the post-synthesis assembly of CNTs into predefined structures, utilizing the monolayer oxidation regime of the electro-oxidative process. In addition, a more detailed investigation of the oxidation characteristics will demonstrate additional possibilities to improve the patterning abilities of electrochemical oxidation lithography on OTS monolayers and will introduce new strategies for advanced nanofabrication.
3.3 REFERENCES

Chapter 4. **CONTROLLED HIERARCHICAL LATERAL PLACEMENT OF CARBON NANOTUBES**

**ABSTRACT**

Besides of the organization of carbon nanotubes (CNTs) during the synthesis process, e.g., by utilizing patterned catalysts, the lateral post-synthesis assembly of CNT by suitable techniques has developed into one of the most frequently used tools to assemble architectures of CNTs, e.g., for transistor applications. Major issues that have to be addressed to implement efficient strategies include the solubility of the CNT suspensions, the suppression of bundle formation, and the separation of the tubes according to their physical properties. While the separation of the tubes is up to now only addressable by processing of the CNT raw material, the utilization of surfactants can contribute to the avoidance of bundling and improves the stability of the resulting solutions. For this purpose implementation of these techniques into a conceivable fabrication approach is targeted in this chapter. Moreover, the utilization of electrochemical oxidation lithography for the sequential lateral placement of ‘pre-selected’ CNTs onto chemically active surface templates will be introduced. This approach provides important advantages compared to conventional lithographic tools, i.e. photo-, e-beam and focused ion beam lithography, as such techniques only generate topographical features.
4.1 INTRODUCTION

The use of carbon nanotubes in electronic devices has been identified as a promising field of applications.[1-3] Carbon nanotubes are in the focus of interest as they are, e.g., capable to withstand relatively high current densities, thus providing advantages over conventional thin metallic conductor structures being implemented into electronic circuits. Smaller structures inherently imply demanding requirements on the used materials, as heat generation is regarded as an important issue that diminishes the performance and life-time of nanoscale electronic device structures.[4-8] Therefore, a number of attempts have been reported in literature, where carbon nanotubes are replacing, e.g., conductor structures or are used to build transistor structures with convincing results with respect to their performance.[9]

However, the efficient integration of CNTs is seen as a critical step into the routine utilization of such materials. Up to now the fabrication of devices relies on a statistical process, which utilizes large arrays of device layouts and CNTs are integrated ‘by chance’ into such devices. Thus, the number of properly assembled structures usually remains very low. A number of major problems have to be addressed to allow the general use of carbon nanotubes as alternative building blocks for electronic circuits. The first problem is the purity of the crude carbon nanotube material, which generally is a mixture of tubes with different electronic properties.[10,11] Purification routes, applied mainly subsequently to the synthesis, have been developed to obtain carbon nanotubes with well-defined properties.[12,13] Other problems associated with the utilization of CNTs are related to their poor solubility and their tendency to form bundles in suspensions and solutions, making it difficult to integrate individual CNTs into devices.

Finally, another limitation deals with the arrangement of carbon nanotubes within the device layout. As the tubes are highly flexible and are difficult to orientate several procedures have been developed to obtain an organisation of the carbon nanotube systems (see Chapter 1.4.1). Few attempts also use scanning probe and e-beam lithographic methods to organize carbon nanotubes, however, the reported approaches use conventional photoresists, which make the sequential build-up of the device structures difficult, as the tube material, which was placed in the first step, might be affected in a second structuring process.[14-17]

In this chapter different strategies are presented to overcome these common problems. These include the improvement of the solubility and the tailor-made functionalization of chemically
active surface structures, that can guide the selective assembly of CNTs. Finally, a sequential fabrication scheme is introduced that allows the controlled self-assembly guided fabrication of basic transistor structures, i.e., the step-by-step assembly of crossed CNT structures.

### 4.2 Lateral Placement of CNTs by Electrochemical Oxidation Lithography

As a suitable tool to guide the self-assembly of CNTs electrochemical oxidation lithography was identified. This allows the site-selective placement of CNTs into predefined configurations. The approach combines the advantages of chemical addressability, good control over the device dimensions, in terms of lateral resolution, as well as the possibility to hierarchically define assembly sites by utilization of sequential oxidation steps. A possible selective placement strategy is highlighted in Figure 4-1.

![Figure 4-1. Assembly of CNTs onto functionalized patterns generated by means of electro-oxidative lithography. a) Electro-oxidation of an OTS monolayer. b) Functionalization of the acid groups by an amine terminated precursor molecule (APTMS). c) Site-selective assembly of CNTs onto the amine functions due to electrostatic interaction.](image)

After inscription of an acid functionalized line the structures were functionalized with APTMS to provide an amine termination of the line feature, following a standard approach for the assembly of CNTs.\[^{18-22}\] The self-assembly of the amine terminated precursor molecules was performed in a chemical vapor deposition approach, where the APTMS is slowly evaporated and self-assembles exclusively on the inscribed line feature. The positively charged amine groups provide an excellent binding behavior to CNTs which are applied in a solution based subsequent self-assembly step. Figure 4-2 depicts representative SFM tapping mode images documenting the successful assembly of CNTs on amine functionalized line...
features. It is clearly observed that the self-assembled tubes exclusively are located on the inscribed line, whereas the OTS covered surface remains free of CNTs.

**Figure 4-2.** a,b) Tapping mode images of the CNT functionalized line.

While the selective assembly of the CNTs on the line feature is evident, the excessive bundling of the assembled tubes represents a limitation. The formation of bundles is a frequently observed problem that is usually present already in solution. The bundling and strong entanglement of the CNTs represents an obvious drawback for the fabrication of device features consisting of individual tubes. Besides the problem of bundling CNT solutions are also frequently not stable, and CNTs tend to quickly precipitate. This limitation can be addressed by adding suitable surfactants to the suspension.

Different cationic, anionic and neutral surfactants are available, which render CNTs highly soluble. The use of the surfactants to disperse CNTs is a standard approach and has advantages compared to the chemical functionalization of CNTs, which can be performed only at the tube’s ends or requires defects in the tubes. In some cases the surfactant molecules form ordered layers on the surface of the nanotubes. When higher surfactant concentrations are used the surfactant forms a micellar structure around the CNTs, forming a hydrophobic core. Although the interaction between the surfactant molecules and carbon nanotubes were intensively studied, the way in which the surfactant molecules are organized around the CNTs is still unclear. There are three main organization methods: random absorption of the surfactant molecules without any preferential arrangement, hemispherical absorption on the nanotubes, and encapsulation of the carbon nanotubes in a
cylindrical micelle.\textsuperscript{[30]} The majority of theoretical and experimental investigations, however, supports the random orientation of the surfactant molecules.\textsuperscript{[31-33]}

In the course of the studies performed here tetrade cyltrimethylammonium bromide (TTAB) was used as surfactant and a detailed investigation of the improvement of the solubility was carried out. Major goal of these investigations was to de-bundle CNTs in suspension\textsuperscript{[34]} and to be finally able to selectively place individual CNTs onto chemically active surface templates. An investigation on the solubility properties was performed by UV-vis absorption measurements.\textsuperscript{[35-37]}

4.2.1 Absorption Spectra of Multi-Wall CNTs in TTAB Surfactant Solution

A series of the absorption spectra of MWCNT dispersed in aqueous TTAB solutions are summarized in Figure 4-3. Individual spectra were recorded at different dilutions of the CNT stock solution with 100 mM TTAB.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4-3.png}
\caption{Absorption spectra of Bayer MWCNTs dispersed in 100 mM aqueous TTAB solution. Spectra from bottom to top are shown for the following dilutions (C/C\textsubscript{S}): 301, 134, 87, 64, 46, 36, 30, 25, and 21; respectively. The inset shows the optical density at a wavelength of 500 nm as a function of the relative MWCNT concentration C/C\textsubscript{S}. Bottom: SEM image of MWCNT dispersed in 100 mM aqueous TTAB solution diluted 21 times.}
\end{figure}
In these spectra, the optical density gradually increases with decreasing wavelength, reaching a maximum in the short UV range at 262 nm, which was assigned to absorption maximum of dispersed MWCNTs by difference groups.$^{[38-41]}$

TTAB stabilized CNT dispersions are observed to be very stable and no precipitation of the CNTs could be observed over long periods of time. Deposition of the CNTs onto silicon wafers (Figure 4-3b) and investigations of the CNTs by SEM imaging furthermore demonstrates that individual tubes rather than bundles are present in solution.

### 4.2.2 Site-selective Placement of CNTs from Surfactant Solutions

The prepared suspensions have been utilized in the following to improve the assembly of individual CNTs on lithographically fabricated chemically active surface templates. Due to the fact that TTAB is a surfactant that introduces positive charges to the CNTs, a modified assembly strategy had to be used. In contrast to the conventional approach to utilize APTMS as a binding promoter, the direct assembly of the CNTs onto structures fabricated by electrochemical oxidation lithography can be targeted. To optimize the preparation conditions first screening attempts have been performed on microscopically structured OTS monolayers, utilizing the TEM grid mediated monolayer oxidation approach (for details see Chapter 3). The selective self-assembly was promoted by the electrostatic interaction between the negatively charged acid groups of the surface pattern and the positive charge of the stabilized CNTs.

For the TTAB stabilized CNTs (Figure 4-4) good selectivity of the CNT binding, as well as the preferential absorption of individual tubes rather than bundles is observed. The degree of entanglement of the tubes is also greatly reduced, as compared to Figure 4-2.
These results stimulated the further use of the surfactant stabilized CNT suspensions to be able to self-assemble individual CNTs on smaller surface templates. In this case finer line features were inscribed by means of a conductive SFM tip with the goal to control the site-selective assembly of individual CNTs.

4.3 Hierarchical Template-Guided Assembly of CNTs

After achieving good control of the assembly of CNTs on chemically active patterns by the utilization of a suitable surfactant, the controlled assembly of complex structures that consist of individual tubes can be performed. Taking into account the requirements for a reliable fabrication process, additional challenges have to be addressed in this context. These include, aside from the pre-selection of suitable materials, which is to date only possible by separation of the raw materials prior to the assembly, also the possibility to sequentially guide the assembly the pre-selected materials. Electro-oxidative lithography represents here a favourable tool, as the OTS-based monolayer can be facilitated with new structural features after any modification and/or assembly step. A schematic outline of the proposed fabrication sequence is presented in Figure 4-5.
Based on this selective assembly process a procedure was developed that permits the sequential oxidation of an OTS monolayer with the subsequent placement of nanotubes, that allows the combination of pre-selected nanotubes in a controlled fashion, thus providing control over the self-assembly process of a structure that resembles a basic carbon nanotube transistor layout.

First step of the fabrication process is the formation of thin line features that can be utilized to self-assemble the first CNT. Figure 4-6a,b depicts typical SFM images of the oxidized structures, which are characterized by a strong contrast in the lateral force image (Figure 4-6b), reflecting the fact that the surface modification is mainly a chemical transformation of the monolayer into acid functions, whereas no significant contrast is observed in the corresponding topography image (Figure 4-6a).

The substrates were subsequently immersed in a TTAB-stabilized carbon nanotube solution for 24 hours (C = 48 mg/mL). The substrates were taken out, rinsed with water, and dried in a stream of N₂. Inspection of the line structures by tapping mode SFM (Figure 4-7a, b) revealed the selective assembly of individual multiwall carbon nanotube assemblies exclusively on the patterned areas, whereas no tube material was found on the surrounding OTS monolayer.
**Figure 4-7.** Site-selective assembly of multiwall carbon nanotubes on the oxidized line structures. a, c) Topography and b, d) phase image.

Frequently, the rinsing process with water does not remove the entire surfactant and, thus, contamination of the structures by the surfactant is observed. A representative example of this contamination is the drop-like features observed on the CNTs in Figure 4-7a.

Typically large line structures tend to host a higher number of individual CNTs. Thus, control of the number of tubes requires the inscription of small line features, which can potentially host only a very limited number of CNTs (Figure 4-7). A reliable assembly of individual CNTs was observed for line features smaller than 200 nm.

After placement of an individual tube on the inscribed structure, additional features can be generated on the non-modified OTS substrate by conducting an additional oxidation step. However, attention has to be placed on the conservation of the assembled nanotube. This targets in particular the fact that the electro-oxidation process can affect also the already assembled nanotubes. It was *e.g.* observed that oxidation conditions, which are used to initiate the functionalization of the OTS monolayer, are sufficient also to cut carbon nanotubes. This is in particular the case, if the oxidation process is carried out in contact mode. In this case, a combination of the applied bias voltage and the shear forces, exhibited by the scanning tip, can result in a cutting of the tube material as illustrated by the SFM images depicted in Figure 4-8.
Another possible problem of the sequential oxidation process is the possibility of physical movement of the CNTs by the tip motion. By dragging the cantilever along a predefined path, the CNT can be moved across the surface as illustrated by the image sequence depicted in Figure 4-9.

**Figure 4-9.** Physical movement of CNT during the sequential oxidation. a) Topography and b) phase images of individual CNT selectively placed on an oxidized line structure. A segment of the CNT is moved along the oxidation line. c) Topography image and d) phase are shown. The white line indicates the path of the scanning tip.

It is clearly seen that the assembled CNT (Figure 4-9a, b) was partially moved out of the structure by the moving SFM tip (indicated by the white line in Figure 4-9c, d).

Due to these effects a modified oxidation approach had to be developed. Since contact mode and voltage applications are sufficient to destroy or dislocate the self-assembled CNTs, advantage is taken of the close-loop set-up of the SFM, which compensates drift effects of the scanner and allows for an accurate positioning of the SFM tip on the substrates with a
precision in the nanometer range. Thus, a careful tuning of the inscription process allows switching off the bias voltage in close vicinity of the pre-patterned CNTs and, moreover, ensures that the tip is lifted up, while crossing the CNT. Thus damage and movement of the previously assembled CNT can be avoided.

The subsequent placement of the CNT on the surface template is carried out following the same approach as for the previously inscribed line structure. Instead of the multiwall carbon nanotubes used after the first oxidation step, another type of multiwall carbon nanotube (Nanocyl MWCNTs) suspended in TTAB aqueous solution was used for the placement on the second line feature. These tubes have a slightly thinner mean diameter compared to the MWCNTs from Bayer, which were used in the first fabrication step. This demonstrates the usefulness of this technique for the controlled deposition of different types of CNTs with different properties. The resulting structures are investigated by tapping mode SFM and representative images are depicted in Figure 4-10a, b. Overlapping CNTs can clearly be seen, both of which follow the oxidation line, whereas the rest of the substrate is bare of CNTs.

**Figure 4-10.** Height (a) and phase (b) images of the second selective placement of a CNT on the oxidized structure.

Although slightly thinner tubes were used for the second self-assembly the variation of the thickness within the CNTs suspensions themselves does not allow the quantitative analysis of the CNTs thickness in the structure. However, evidently also different tubes (i.e. SWCNTs or nanowires) can be utilized for the second assembly step, thus, a completely controllable fabrication process was developed that provides full control over the lateral arrangement of the individual building blocks. Moreover, a pre-selection of the materials by previously carried out separation techniques is possible, e.g., to engineer the band gap properties of CNT
transistors. This will also allow to combine either semiconducting CNTs, or to utilize nanowires of different materials, e.g., silver or metal oxide nanowires. These possibilities certainly represent a step forward to the controlled bottom-up fabrication of even more complex, functional devices in a reliable fashion. Major drawback of the fabrication approach is the fact that not always the entire CNT assembles on the inscribed features, but part of the tube is protruding over the edges of the structure. Here the intentional application of the cutting process, introduced in Figure 4-8, might be used to correct for the improper assembly of the CNT.

4.4 CONCLUSIONS

A number of investigations resulted into a well-controllable fabrication scheme for basic CNT transistor layouts, which are sequentially fabricated by surface template inscription and guided self-assembly processes. As important research targets, the use of surfactants as well as an optimization of the surface templating process were introduced, that allow for an improved hierarchical fabrication scheme potentially opening new possibilities to realize even more complex structures.

As major advantages of this approach the good control over the lateral placement, the availability of addressable chemical functional surface templates, the possibility to pre-select the self-assembled building blocks, as well as the sequential nature of the patterning process can be summarized, which are hardly accessible by conventional lithographic tools, i.e., photo- and e-beam lithography.

4.5 EXPERIMENTAL SECTION

Suspension preparation.

Aqueous stock suspensions of carbon nanotubes in 100 mM tetradecyltrimethylammonium bromide (TTAB; Aldrich, >99%) or sodium dodecyl sulfate (SDS, Aldrich, >99%) were prepared by 60 min sonication (Sonic Vibracell VC750, tip 5 mm diameter) at 20 W of output power with 13 to 14 mg of CNT material in 12 mL water, followed by centrifugation (Eppendorf Minispin) for 10 min at a G-Factor of 600 (3000 rpm) to remove the undispersed material.\textsuperscript{[42,43]} After that the stock suspension was diluted up to 246 times to keep the optical density of the solutions below 5 and absorption spectra were measured with a UV-VIS-NIR
absorption spectrometer (Cary 500, Varian) in the wavelength range from 1300 to 200 nm with an optical path length of 1 cm. Absorption spectra are presented as absorbance per unit of path length. The measurements were carried out with multi-wall carbon nanotubes from Bayer (Germany), NanoLab (USA) and Nanocyl (Belgium). All measurements were done at room temperature (22 °C).

**Monolayer preparation.**

*n*-Octadecyltrichlorosilane monolayers have been prepared on clean silicon substrates (Silicon Quest, International, p-doped, double-side polished, 1 to 10 Ωcm⁻¹). Cleaning was performed in a plasma cleaner (Diner) for 1 min. Self-assembled monolayers were prepared from Bicyclohexyl (BCH, Sigma Aldrich) solution which was dried over sodium and distilled. 5 µL OTS in 1 mL BCH were used to perform the self-assembly process. Wafers were immersed in the solution for approximately 1 min, were dried in a stream of nitrogen and sonicated in toluene to remove access material. After that the samples were dried again in a stream of nitrogen. Final cleaning prior to use was performed with Scotch tape, by attaching and detaching it from the surface.

**Electrochemical oxidation and SFM imaging.**

The structuring of the substrate utilized a NT-MDT NTegra Aura system. Voltages were applied to a conductive SPM tip (Pt/Ti-coated, soft, tapping mode cantilevers (NSC35) from μ-Mash). Pulse duration and voltage were optimized to obtain features with different line-width. Imaging was initially performed in lateral force mode, but in tapping mode (NSC36, μ-Mash) after the tube was placed to avoid tip-tube interactions. Sequential oxidation was performed with the close-loop system on and the oxidation process was stopped in the vicinity of the existing line containing the attached CNT. This is an important step to avoid the displacement of, or damage to, the carbon nanotube. The oxidation step was performed in contact mode. The second tube was attached to the newly oxidized line structure and the imaging was performed in tapping mode.

### 4.6 REFERENCES


Chapter 5. **Electro-Oxidative Lithography for Nanometer Gaps and Ring Fabrication**

**Abstract**

Electro-oxidative lithography represents a versatile tool for the direct manipulation of selected properties of substrates with nanometer precision. In this chapter two new concepts were introduced which enable the construction of nanometer gaps and metallic circles. For this purpose, the electro-chemical oxidation of monolayers and bilayers consisting of n-octadecyltrichlorosilane (OTS) was investigated in detail. Based on these investigations new fabrication concepts could be developed, adding directly to the accessible structures for electrochemical oxidation lithography. Thus, a new rational design to generate well-defined gap-structures was established. In particular, customized solutions for all electro-lithographically fabricated device layouts of complex arrangements could be introduced. This concept increases the applicability of scanning probe microscopy (SPM) mediated electro-chemical oxidation lithography of self-assembled mono- and bilayer systems in the area of nanofabrication. The second concept introduces a new fabrication method to obtain ring structures with nanometer dimensions. This method takes advantages of both, the anodization and electrochemical oxidation lithography by the SPM tip on a self-assembled monolayer of OTS. The oxidation conditions, as well as the scaling options of this lithographic process, were investigated and revealed good controllability of the feature dimensions. These structures were further functionalized with silver particles, thus, converting the structure into mesoscopic ring structures with potential applications in optics and photonics.

Parts of this chapter have been published:

5.1 INTRODUCTION

The integration of nanoscale building blocks into device frameworks represents currently a research area where several fundamental strategies have been proposed towards the fabrication of functional devices. However, up to now only a few reliable integration concepts could be realized.\(^{[1,2]}\) Self-organization processes, guided by chemical driving forces, are among the most promising approaches that might solve the problem of integrating nanomaterials, \(e.g.,\) nanoparticles, nanotubes, etc., into electronic device structures.\(^{[3,4]}\) Not only the challenge how to guide the integration but also the strict requirements to match the device dimensions to the nanometric dimensions of the building blocks are central problems that has to be addressed in this context.

An approach that permits the reliable and well-controlled fabrication of nanometric gap structures based on an electro-chemical oxidation process of a self-assembled monolayer was developed by Sagiv \textit{et al.}\(^{[5]}\) Such structures were previously used in a number of studies as a platform to site-selectively apply wet chemical modification routines, \(e.g.,\) to obtain metallic features, or to guide the self-assembly of nanometer-sized building blocks, \(i.e.,\) nanoparticles.\(^{[6,7]}\) More details of this approach are given in Chapter 3. We introduce here considerable extensions of the possibilities to use the electrochemical oxidation lithography for nanofabrication, which are mainly based on a detailed investigation of the differences between the oxidation kinetics on monolayer and bilayer systems, as well as on a study of the kinetics of the monolayer transformation.

The first concept is based on a combination of the oxidation of monolayer and bilayer systems of \(n\)-octadecyltrichlorosilane (OTS). It was used as a promising possibility to easily generate, \(e.g.,\) well-defined gap structures with nanometer dimensions and, furthermore, to reliably integrate nanoparticles in the device framework. The second concept, on the other hand, combines the silicon oxide growth and monolayer oxidation mode of electro-chemical lithography on OTS monolayers. This method results in the formation of mesoscopic ring structures, which can subsequently be metallized. In the following sections the experimental results are summarized for both of these concepts.
5.2 GAP FORMATION

The formation of the nano-scale gaps can be performed by utilization of monolayer and bilayer systems. Detailed investigations of the oxidation conditions, which occur on OTS monolayers and bilayers, are a prerequisite for this approach. The oxidation of monolayers has been investigated by different research groups in the past,[8-12] whereas the possibility to also oxidize bilayers was only recently reported. However, no detailed investigation of the oxidation conditions were described.[13] Therefore, an in-depth study was performed that allows the determination of the oxidation conditions of a bilayer of OTS, and to compare the oxidation characteristics with a monolayer oxidation procedure.

5.2.1 INVESTIGATION OF MONO- AND BILAYER OXIDATIONS

Line features were inscribed next to a boundary that separates a bilayer area from the surrounding base monolayer (Figure 5-1). The formation of the bilayer was performed by an electro-chemical oxidation of 20 µm line features performed with a conductive, biased stamp (in this case a TEM grid).[14] The electro-oxidation of the monolayer underneath the bar features resulted in the formation of acid groups that can be used to self-assemble a second OTS layer,[5] exclusively in these areas due to the formation of hydrogen bond interactions between the polar acid groups and the silanol functions of the OTS (for further details see Chapter 3). The formation of silanol is triggered by small amounts of water being present in the solution and/or on the polar structured features inscribed during the electrochemical oxidation process with the TEM grid. The resulting transition area between the non-modified monolayer and the bilayer structures on the electro-oxidized structure reveals a characteristic step in height due to the formation of the bilayer structure (Figure 5-1a).
Figure 5-1. a) 3-D representation of a SPM height image, depicting the step created by the formation of a second OTS layer on an electrochemically oxidized grid pattern, which was formed on top of an OTS monolayer. b) Contact mode height and c) lateral force images of line features that have been inscribed at different oxidation times. Repetition rates for individual measurements are indicated in (b). The individual pulse duration was 25 ms. d) Analysis of the inscribed features on the monolayer (repetition rate: once) and e) on the corresponding bilayer system (repetition rate: once (black), 5 times (red), 10 times (green)).

To provide identical oxidation conditions (i.e. humidity and tip quality) a set of oxidations was performed with bias voltages of −10 V with respect to the SPM tip close to the boundary of the monolayer/bilayer structure (Figure 5-1b). Line features were inscribed at different oxidation times. It was observed that long oxidation times on the monolayer resulted in the formation of silicon oxide structures due to the degradation of the monolayer and subsequent anodization of the underlying silicon substrate (not shown here). Therefore, only for mild oxidation conditions features were inscribed across the boundary, whereas for longer oxidation times the inscription was just started on top of the bilayer utilizing a close-loop
positioning system. The maximum voltage application time was limited to 35 ms. However, even longer oxidation times could be realized by repeating the oxidation process in one surface spot for several times by the lithography mode of the SPM. Measurements were performed with one, five and ten repeating steps. It was taken care that all inscriptions were performed at the same overall scan size, thus the density of measurement points does not contribute to the width of the line features. Figure 5-1 depicts the height (b) and lateral force images (c) of a set of oxidations that were performed with an oxidation time of 25, 125 ms, and 250 ms, respectively. The line feature inscribed with the 25 ms time was oxidized across the boundary structure. The formation of thicker lines was observed on this monolayer compared to the structures inscribed on the bilayer under the same oxidation conditions. Also on the bilayer an increase of the line thickness with longer oxidation times could be observed. These oxidations were performed for a number of different oxidation times, which were analyzed by plotting the resulting line width (measured in the lateral force images) versus the oxidation time. The results are shown in Figure 5-1d (monolayer) and Figure 5-1e (bilayer). The overall shape of the diagrams is comparable; however, it is observed that oxidations on the bilayer level require approximately 5 times longer to obtain the same line width. A comparison of the individual values also demonstrates that the multiple application of oxidation voltages does not have an influence on the oxidation characteristics and, e.g., oxidations performed once at 25 ms result in comparable line widths than oxidations which were performed at 5 times applying 5 ms voltage pulses.

Experiments with lower oxidation voltages required significantly longer oxidation times to obtain reasonable patterns and it was more difficult to create them on the bilayers than monolayers. Therefore, the present study was limited to bias voltages of –10 V. The tendency to observe a plateau region in the oxidation characteristic is observed in the monolayer as well as in the bilayer region. This effect needs to be further investigated by more detailed investigations and might provide deeper insight into the dynamics of the oxidation process, however, this effect is not yet understood.

5.2.2 Fabrication of Well-defined Nanometric Gap Structures

The observed characteristic differences in the oxidation conditions can be practically used to obtain a layer-selective oxidation process. This is of interest for a number of applications, i.e. for sensor-systems or single-electron transistors, etc.\textsuperscript{[15-18]} To demonstrate the advantages to
utilize patterns consisting of a combination of OTS monolayers and bilayers for nanofabrication processes a practical fabrication concept to generate well-defined gap structures and later also to create functional anchor sites within the gap structure was developed. An outline of the fabrication process is schematically depicted in Figure 5-2.

Figure 5-2. Schematic outline of the fabrication process of gap structures and selective placement of an individual particle in between the electrodes. a) SPM tip mediated electrochemical oxidation of a line feature on an OTS monolayer (red line). b) Selective self-assembly of OTS on the line feature, resulting in the formation of a bilayer line (blue line on top of the red line). c) SPM mediated electrochemical inscription of a line, crossing the bilayer, and attached electrode pads (additional red line). d) Metallization of the newly inscribed structures (yellow). e) SPM mediated oxidation of a point structure in between the electrodes (red dot). f) Self-assembly of gold nanoparticles, driven by electrostatic interactions, to incorporate them into the gaps (yellow).

The fabrication process consists of several steps and starts with the inscription of a thin line. In this way line features with a line width from 10 to several 100 nm can be generated, depending on the applied oxidation conditions (see, e.g., Figure 5-2a and Chapter 3 for a detailed introduction to the oxidation and bilayer formation process). This line can serve as a
scaffold for a bilayer structure, where selectively a second OTS layer can self-assemble; in analogy to the TEM grid oxidation utilized in the oxidation study described above. Such a bilayer line is depicted in Figure 5-2a, and the typical height of the bilayer is approximately 1 nm. This value is rather small compared to the calculated thickness of an OTS layer (~2.6 nm); however, measurements were performed in contact mode, which might result in a reduced height due to the compression of the layer under these imaging conditions. Perpendicular to this line feature a new electrochemical oxidation of the monolayer system can be performed (Figure 5-2c). The tip starts to oxidize the monolayer and it is observed that the oxidation automatically stops when the tip reaches the bilayer line (under the prerequisite that the oxidation conditions are chosen not to permit oxidation of the bilayer structure, see Figure 5-1e).

![Figure 5-3. a) 3D representation of the bilayer line. b) Lateral force images acquired in opposite scan directions. c) Zoom into the crossing area.](image)

The corresponding lateral force images (Figure 5-3b) illustrate this fact, as the oxidized line exhibits polar acid groups, which are well detectable in the corresponding lateral force signals due to their higher hydrophilicity. This causes preferential absorption of water on the oxidized structures compared to the hydrophobic –CH$_3$ terminated non-modified monolayer and the OTS bilayer line, and thus, an increase in the lateral force contrast on the polar line. The frictional nature of the inscription can be visualized if different scan directions are applied; in this case a complete reversal of the contrast is observed (Figure 5-3b). It is, moreover, clearly seen that the oxidation of the monolayer perfectly stops at the boundary of the bilayer line and no oxidation is performed on top of the line feature (Figure 5-3c). Conveniently, the oxidation re-starts immediately after the tip reaches again the monolayer level. No apparent initiation time is required and, thus, very sharp boundaries can be created. Therefore, no sophisticated methods to control the applied bias voltages are required, which increases the speed of fabrication tremendously. Moreover, it is obvious that the dimensions
of the gap feature directly scale with the line-width of the bilayer line, thus a very controlled fabrication of gap features is possible, which can be already determined by choosing the oxidation conditions of the first inscribed line. The newly inscribed line feature was moreover facilitated with a sort of electrode pads at the end, which could potentially be used to connect the device.

The chemical reactivity of the second line feature, due to the generated polar acid groups, can be used to metalize the structure by a wet-chemical development process that utilizes the self-assembly of metal salts on the hydrophilic acid features in combination with a subsequently applied reduction step. The small sizes of the created particles can be further improved applying an electroless metal deposition process to enlarge the metal seeds, and to develop the inscribed features into a metal structure consisting of two electrodes connected by wires, which are separated by the bilayer gap where no particles are formed.

![Figure 5-4. SPM tapping mode images of the structures after the metallization step. The topographical (a,c) as well as the phase images (b,d) clearly indicate the selectivity of the metallization process and (c) demonstrates the formation of very sharp boundaries, which are defined by the bilayer line.](image)
Figure 5-4a,b depicts the overall structure as well as a close-up of the gap region (Figure 5-4c,d) and supports a well-defined boundary. The sharpness of the gap structure is additionally a result of the complementary surface properties of the oxidized line (hydrophilic), the hydrophobic OTS bilayer feature and the surrounding OTS monolayer. This hydrophobicity prevents the spreading of the metal salts, which are prepared from aqueous solutions. The distinct difference in the surface properties, which can be created by electro-chemical oxidation lithography, is regarded as one of the most important advantages of the approach.

As it derives from the oxidation characteristic of the bilayers (Figure 5-1e) it is still possible to activate also the bilayer structure, e.g., within the gap region, by the application of suitable bias voltage pulses of longer pulse duration. This permits the site-selective placement, e.g., of individual metal particles within the gap structures, due to the introduction of a new, chemically active binding site. This can be achieved by placing the tip within the gap feature and a subsequent application of a bias voltage of $-10 \text{ V}$ for 45 ms, which resulted in the formation of an anchor point functionalized with carboxylic groups. No investigation of this process step was performed due to the required application of lateral force imaging techniques; these need to be performed in the contact mode and inherently pose the danger that nanoparticles also from the metalized contact features are moved mechanically. Nonetheless, it is possible to actively use the newly created chemical bonding site on the bilayer level to immobilize a 40 nm positively charged silver nanoparticle by utilizing its electrostatic interactions with the negative surface charges of the acid functions. The immobilization was performed by immersing the substrate into an aqueous solution of ligand stabilized silver nanoparticles. The successful binding of an individual silver particle can be directly visualized by means of tapping mode SPM microscopy as depicted in Figure 5-5 which shows a comparison of the structure prior (a) and after (b) the self-assembly process of the silver particle.
Based on these results a new concept for the formation of nanometer size gaps structures was developed. The selectivity of the oxidation process on monolayer and bilayer systems introduces new possibilities to the electro-chemical oxidation approach and provides more promising tools to create complex structural features.

Additional possibilities emerge if the structuring is not limited to the electro-oxidation of the monolayer itself, but a combination of the anodization approach is utilized. This results in an inherently heterogeneous structure that can be used for the fabrication of mesoscopic rings.

5.3 Mesoscopic Ring Structures

Mesoscopic ring structures represent an area of research with receives increasing attention. Theoretical predictions as well as experimental work has been conducted and a large variety of physical effects can be observed in closed ring systems, consisting of metals, or semiconductors. These range from quantum coherence phenomena\textsuperscript{[20,21]} to the influence of external fields\textsuperscript{[22]} and form flux closure effects in magnetic ring structures\textsuperscript{[23,24]} to (nonlinear) optical effects\textsuperscript{[25,26]} Magnetic fields, \textit{e.g.}, can induce persistent currents in conducting rings\textsuperscript{[27-29]} and plasmon resonances can be utilized to enhance or to polarize electric fields in the ring structures\textsuperscript{[30,31]} The mesoscale has attracted here significant interest, as phenomena driven by visible light require ring dimensions down to the submicrometer range\textsuperscript{[32,33]}

For all potential applications the design parameters, \textit{i.e.}, the diameter of the ring, the width of the rim, and the material of the ring, play an important role and contribute to the structure’s properties. The fabrication of ring systems utilizes frequently standard photo- and electron
beam lithographic tools. However, the required equipment is not always readily available; also changes in the design of the rings require expensive new masks. Thus, a straightforward tool to fabricate ring structures with a moderate experimental effort is highly desirable. In the last years different methods to fabricate mesoscopic ring structures have been proposed, which are partially based on lithographic techniques (e.g., dip-pen lithography, soft-lithography, and shadow evaporation techniques utilizing masks), but also the utilization of self-organization methods was reported. These include, e.g., the use of higher evaporation rates at the contact line between the fluid of a droplet containing metal nanocrystals, and the substrate at pinning centers, which results in a preferential deposition of nanoparticles in the perimeter of the droplet and, thus, in the formation of ring structures. Moreover, phenomena such as ‘breath figures’ on prepatterned substrates, templating nanorods from water droplets that condense on the surface of nonpolar solvents from humid air, and thermodynamically controlled evaporation processes have been utilized. Furthermore, etch-spreading lithography approaches on particle arrays with alkanethiol monolayers and silane monolayers have been reported. The concept to utilize particle arrays is frequently used in different fabrication concepts, which include, e.g., the particle imprinting method or nanosphere molds and a hot embossing approach. Other processes utilize ordered phase separated block copolymers as templates for the formation of nanorings.

In this thesis a SPM tip-mediated electrochemical oxidation lithography approach was used to fabricate such structures. This method utilizes a combination of both oxidation modes, accessible by electrochemical oxidation of a silicon substrate, covered by a n-octadecyltrichlorosilane (OTS) self-assembled monolayer providing good control over the size, shape and thickness of the fabricated ring templates. The principles of both techniques are summarized in Chapter 3.

5.3.1 Fabrication of Ring Structures by Electro-oxidative Lithography

The key step of this process is the electrochemical oxidation process that is initiated by a negatively biased SPM tip, which is brought into contact with the OTS monolayer (Figure 5-6).
Figure 5-6. (a) Tip mediated electrochemical oxidation/anodization reaction on OTS monolayers. (b) The local application of negative bias voltage pulses results into the formation of circular oxidation patterns, which consist of a core area, where the monolayer degraded and silicon oxide is formed. In the periphery of the oxide structures the advancing meniscus results in the oxidation of the monolayer and the formation of acid groups in a rim around the SiOx core.

The electrochemical oxidation process proceeds in two oxidation steps: the chemical functionalization of the monolayer itself, which results in the formation of polar acid groups – if moderate voltages are applied for relative short periods of time – and the anodization of the silicon substrates – when higher voltages and long pulse durations result in a degradation of the monolayer and allow the growth of silicon oxide. Both oxidation regimes are intensively studied and have been utilized in a large number of approaches to create functional nanostructures (see Chapter 3 for a detailed overview).

The new aspect of the approach developed here is to combine both oxidation modes and to use it for the fabrication of metallic ring structure systems. Certainly, electro-oxidation and anodization lithography could be also used to directly inscribe the circular structures by moving the tip along the circle line, however, a significant drawback of this method is the relatively long time that is required to inscribe the individual structures. Combination of the silicon oxide growth mode and the monolayer oxidation allows the creation of ring structures in a single oxidation step, thus only a point contact of the tip in the center of the planned ring structure is required.

### 5.3.2 Investigation of the Oxidation Parameters

The rim thickness as well as its diameter is depending on the choice of the oxidation conditions. The inscription of ring structures was performed at high oxidation voltages of up
to 10 V to be able to perform the anodization process, which follows the degradation of the OTS monolayer. The pulse duration was set to oxidation times longer than 1 second. Recently, these oxidation conditions were investigated by Fourier-Transform Infrared (FT-IR) spectroscopy measurements on macroscopic anodization patterns produced by performing the oxidation in a droplet of water that was placed on the OTS monolayer.\cite{51} It could be demonstrated that the anodization process on OTS monolayers is associated with the formation of a rim area, which is formed by the movement of the perimeter of the water meniscus on the surface due to the changes of the surface properties in the meniscus area. Consequently, the increased contact area during the oxidation process due to spreading of the water forms circles with a rim area. The resulting rim area is not degraded but the electro-oxidation of the monolayer takes place, which results in the formation of chemically active, polar functional carboxyl groups. Thus, three different areas could be defined. Namely, the non-modified hydrophobic OTS monolayer, a nano-scale rim of significantly higher hydrophilicity, and the very hydrophilic silicon oxide core of the circles. Control of the dimensions of the individual features requires a careful adjustment of the oxidation time. In particular, for high resolution features with small line-width the oxidation conditions need to be carefully matched. The formation of the rim area can be investigated by means of lateral force microscopy, even though the obtainable contrast of the different oxidation regimes remains small due to the small differences in the topological structure (nanoscale roughness) and, more importantly, due to the only slightly different wettability properties of the hydrophilic silicon oxide features and the rim area. Moreover, a cross-talk between the torsion of the SPM tip and the height signal is observed, which allows, however, distinguishing between real topographical features, \textit{i.e.}, the silicon oxide core region of the structure, and height contrasts, which are an artifact of higher lateral forces.\cite{52} Even though the interpretation of lateral force measurements is not straightforward it has to be mentioned that it currently represents the only direct tool to investigate the formation of the two oxidation states of the OTS monolayer in submicrometer dimensions; as a consequence this method is used as the routine method of investigation.

Figure 5-7 depicts a typical example of anodizations that were created at \(-10\) V and a pulse duration of 10 seconds.
Figure 5-7. Typical SPM contact mode images of an inscribed anodization/oxidation pattern, formed by the application of a $-10$ V bias voltage pulse during the point contact of the conductive SPM tip and the OTS monolayer (duration 10 sec). a) The height image reveals the presence of an elevated core region. This core region is surrounded by a darker rim area. b) Also the lateral force signal resolves the two different oxidation regimes. A dark core area is surrounded by an even darker rim area.

The SPM height measurement (Figure 5-7a) revealed the formation of an elevated area in the center of the structures, which originates from the formation of silicon oxide. Moreover, a dark rim area is clearly visible around the central area. This dark rim is not an artifact of imaging processing, *i.e.*, plane fitting etc., and the rim area appears independently on the scan direction. Moreover, a closed circle is always observed, which is regarded as good indication that the features originate from a real contrast. A corresponding darker rim feature is also observed in the corresponding lateral force images as depicted in Figure 5-7b.

The dimensions of the individual areas, *i.e.*, the diameters of the silicon oxide core and the chemically functional rim area, are strongly dependent on the oxidation conditions (oxidation time, applied bias voltage, number of voltage pulses per spot, humidity). These parameters can be used to tune the ring diameter, as well as the thickness of the ring structures itself. Figure 5-8 depicts results of a study on the dependence of the ring dimensions on the applied oxidation conditions, demonstrating the tunability of the approach and the possibility to manipulate the dimensions of the anodization patterns.
In each of the oxidations the clear separation of the resulting structures into a core and a rim region are visible in the height image. The corresponding lateral force image showed, however, only a weak contrast, due to the chosen scan direction\textsuperscript{[52]} Thus, quantitative analysis of the ring features was performed on the height images. A linear dependence of the overall ring structures with the oxidation time was observed. Also the dimensions of the core and the rim region follow this scaling, thus allowing a direct control of the resulting structural feature sizes. Additional possibilities in manipulating the core diameter to rim thickness ratio emerge from controlling the humidity. Thus, several parameters are in hand to manipulate the ring structure geometries, which opens a promising and a rather fast access to tailor-made ring structures.

5.4 **SELECTIVE METALLIZATION OF THE RIM FEATURES**

Metallization\textsuperscript{[53]} or deposition of semiconductor materials\textsuperscript{[54]} is still required to convert the ring features into functional device layouts. Besides the possibility to prove in this case the
chemical nature of the rim area, silver particles can also be used to metalize the rim region and, thus, to convert the structures into mesoscopic ring features. A straightforward protocol to metalize the acid functionalized rim region is to immerse the substrate into an aqueous solution of metal salt (e.g. iron acetate, nickel acetate, or silver acetate according to the previously discussed method earlier in this chapter as well as in Chapter 2) and to subsequently reduce the metal ion in an additional step to metal seed particles. The chemical differences of the core and the rim region can be directly used to selectively bind, e.g., silver acetate, only to the acid groups that are located in the rim region and to subsequently reduce the silver salt to form small silver nanoparticles. The particle size and the particle coverage after this step were, however, not sufficient to form continuous ring structures, thus an additional metal staining process had to be applied (similar to the process that was used for the metallization of the gap structures described in Section 5.2.2 of this Chapter), which resulted in the formation of a metallic circle.

Figure 5-9 depicts representative examples of such ring structures, demonstrating that after the development process silver is only located in the rim areas, whereas the surrounding, non-modified OTS background, as well as the central area of the oxidized features, remains mainly free of silver particles (Figure 5-9a-d).
Figure 5-9. SPM tapping mode image of silver ring structures fabricated by electrochemical oxidation/anodization lithography, silver deposition and subsequent silver enhancement. a) Array of 9 ring structures fabricated with identical oxidation conditions. The tip was brought in a 3 by 3 pattern in contact with the surface. b) Magnification of an individual ring structure. c) Individual ring structure fabricated by application of a shorter voltage pulse, resulting in a thin metalized rim area. d) 3D plot of c).

Only few particles are located within the core region of the oxidized feature, which can be explained by the hydrophilic surface properties of the grown silicon oxide, as well as its porous appearance, which can result in an unspecific deposition of silver ions in this area. In this case potentially few seed particles are formed also in this region of the oxidized structure. However, the silver content inside the structures is much lower than in the rim region. Figure 5-9a depicts an array of uniform ring structures that have been fabricated by inscribing several oxidation patterns in a grid-like fashion with identical oxidation conditions (~10 V, 10 s). The resulting features show a comparable size and a rather good uniformity of the structural characteristics, i.e., the rim thickness.

The utilization of a combination of electrochemical oxidation lithography and anodization of the underlying silicon substrates provides new possibilities to generate chemically heterogeneous ring patterns that can be developed into mesoscopic ring structures. The
dimensions of the ring are widely tunable by the application of different oxidation conditions to the SPM tip. The structures were successfully loaded with the metallic silver nanoparticles, resulting in selective and uniform assembly. This new concept opens a wide range of possibilities for the fabrication of different nanometer scale building blocks, *i.e.* mesoscopic superconducting quantum interference devices (SQUID)\(^{[55-57]}\) or photonic resonator structures.\(^{[58-60]}\)

**5.5 CONCLUSIONS**

Based on the presented investigations promising and rather straightforward approaches to fabricate gap and ring structures were developed. Both approaches utilize characteristic features of the oxidation process. These include the different oxidation times that are required to perform the electrochemical oxidation on OTS monolayer and bilayer systems. This process is well controllable and allows a complete scaling and control of the obtained device features. As illustrative examples, how these oxidation properties can be practically used, the fabrication of a nanometric gap structure was demonstrated and an approach to assemble a nanoelectronic device layout based on self-assembly and electrochemical structuring techniques was introduced.

Moreover, the combination of the electrochemical silicon oxide growth and oxidation of an OTS monolayer was investigated. The growth of silicon oxide on an OTS monolayer leads to the generation of an activated, acid functionalized rim in the periphery of the water meniscus. Chemically well-defined regions were created that could be tuned regarding their dimensions by a simple variation of the oxidation parameters. Utilizing wet-chemical modification schemes it could be demonstrated that the resulting features can be converted into metallic ring structures with high uniformity and reproducible quality.

The use of chemical modification approaches to functionalize the structures opens moreover several possibilities to fabricate a large diversity of nano-scale building blocks, consisting of various metals, semiconducting particles and other materials. In this case special advantage is taken from the chemical addressability of the acid functionalized areas, which represents the main advantage of the introduced approach.
5.6 Experimental Section

Monolayer preparation

$n$-Octadecyltrichlorosilane monolayers have been prepared on clean silicon substrates (Silicon Quest, International, p-doped, double-side polished, 1-10 $\Omega \text{cm}^{-1}$). Cleaning was performed in a plasma cleaner (Diner) for 1 min. Self-assembled monolayers were prepared from Bicyclohexyl (BCH, Sigma Aldrich) solution which was dried over sodium and distilled. 5 $\mu$L OTS in 1 mL BCH were used to perform the self-assembly process. Wafers were immersed in the solution for approximately 1 min, were dried in a stream of nitrogen and sonicated in toluene to remove access material. After that the samples were dried again in a stream of nitrogen. Final cleaning prior to use was performed with Scotch tape, by attaching and detaching it from the surface.

Bilayer preparation

Bilayers on oxidized surface features were prepared following the approach used also for the monolayer formation. To obtain large bilayer areas with a transition to the monolayer level, OTS monolayers were structured by the electro-oxidative printing approach. Oxidations were initiated by a conductive stamp (TEM grid, EMS 200 Mesch), or with a conductive SPM tip (NSC36/TiPt $\mu$Masch) for the line and electrode features.

Electrochemical oxidation and SPM imaging

The structuring of the substrate utilized a NT-MDT NTegra Aura system. Voltages were applied to a conductive SPM tip (Pt-Ti coated soft tapping mode cantilevers (NSC35) from $\mu$-Mash). Pulse duration and voltage were optimized to obtain features with different line-width. Imaging was performed in lateral force mode, or after particle placement in tapping mode (NSC36, $\mu$-Mash).

Oxidations of the bilayer structure

Oxidations were performed as described for the monolayer oxidation. Oxidation times were adjusted to the results of the investigation of the oxidation characteristic. For the mesoscopic ring formation the relative humidity was regulated to ~60%. Lateral force measurements were performed with soft cantilevers in contact mode (CSC35, $\mu$Mash).
Bilayer preparation with the TEM grid oxidation mask

Templates for the formation of a bilayer step to investigate the oxidation conditions on monolayer/bilayer systems have been performed with a 200 Mesh copper TEM grid, used as a conductive stamp. Oxidation voltages of 30 V (grid negatively biased) have been applied to electro-oxidize the OTS monolayer. The same procedure as for the monolayer preparation was utilized.

Metallization of the structures

Acid functionalities, generated during the electrochemical oxidation process were used to selectively assemble silver acetate (Sigma Aldrich) onto the inscribed structures. The surrounding, non-modified OTS monolayer, served as a protection to prevent the non-specific deposition of silver salt. Reduction of the silver acetate was initiated by hydrazine vapor (Sigma Aldrich). Subsequently, the silver seed particles were enlarged by an electroless metal deposition process (Silver enhancer kit, Sigma Aldrich) which was applied for 2 min.

Particle placement

After oxidation of the bilayer in between the electrodes silver particles (British Biocell) with a diameter of 40 nm and a cationic stabilizing layer was self-assembled from dilute solutions ($10^{-3}$ M). The substrates were rinsed with ethanol and investigated by means of tapping mode SPM.
5.7 REFERENCES


SUMMARY

The field of nanotechnology has experienced constantly increasing interest over the past decades both from industry and academy. Commonly used nanomaterials include: nanoparticles, nanowires, quantum dots, fullerenes, and carbon nanotubes. Carbon nanotubes, in particular, are promising building blocks for a large variety of potential applications. Because of their structure and high aspect ratio, nanotubes have unique electronic, chemical and mechanical properties. These properties attract much interest to the investigation of carbon nanotubes for potential applications in electronics devices, batteries, solar cells, gas storage technologies, and other fields. Topics addressed in this dissertation relate to the synthesis of carbon nanotubes and their integration into different structures, with particular focus on the basic problems of nanofabrication.

Chapter 1 discusses the recent developments of the research activity in the field of post-synthesis placement of carbon nanotubes (CNTs) on substrates. This includes alignment guided by physical forces, external fields and chemical interactions. The usefulness of any given technique strongly depends on the desired application, while additional innovations for the further expansion of the post-synthesis alignment field need to be introduced.

Chapter 2 introduces the microwave-assisted synthesis of one-dimensional carbon nanostructures. Selective heating of small iron nanoparticles under microwave irradiation was investigated. An important advantage of this approach is the fact that the heat development is limited to the close vicinity of the nanoparticles, while the average overall temperature in the reaction vial remains low, allowing the utilization of a diverse range of substrate materials. The approach to synthesize carbon nanofibers (CNFs) and nanotubes was adapted to the special requirements of the microwave apparatus and had to be optimized for safety. By using ethanol as a carbon source, provided by a liquid reservoir located beneath the sample, a flux of highly flammable and explosive gas mixtures was avoided. The reaction conditions for the microwave-assisted synthesis of carbon nanotubes and nanofibers were investigated in detail. These were observed to have a strong influence on the CNT/CNF formation and on the quality of the obtained materials. Further improvement of the quality and size of the synthesized materials was obtained by variation of the catalyst material. Nickel was identified as the most favorable catalyst material to obtain small nanotube diameters down to 15 nm using very short irradiation times of two minutes. Compensation of the heat dissipation, for
substrates showing a low absorption of microwave irradiation (mica and quartz glass), resulted in reliable processes that enable the microwave-assisted growth of CNTs on a variety of substrates. It was demonstrated that the growth of individual CNTs can be achieved. In particular, the relatively low experimental effort, as well as the fast fabrication times, are general advantages of this method and provide a promising, cheap technique to fabricate CNT-modified SPM tips. The deposition of the catalyst material can be further improved by, e.g., utilizing particle picking approaches or by force versus distance curve recording, to further increase the controllability of the presented approach. Results on patterned n-octadecyltrichlorosilane (OTS) substrates suggest that smaller areas covered with a suitable catalyst layer can be obtained with this method, with important implications for the effective integration of carbon nanomaterials into the framework of devices. Carbon nanotubes were successfully grown on micro- and nanoscale patterned areas. These findings are expected to have an additional impact on the use of the selective heating mechanism, as it provides advantages over conventional methods, i.e., the reduced reaction time, the lower overall exposure temperature to the substrates and for the integration of CNTs/CNTs into predefined device frameworks consisting of different materials.

Chapter 3 gives a comprehensive overview of the electro-oxidation lithography on chemically active surfaces. This powerful technique can be used to organize nanomaterials into defined structures. The main advantage of this technique is the fact that it can manipulate and guide the position of catalyst particles, nanowires or other nanometer-scale objects that are required for the desired structures. Due to the fact that addressable functional groups are created during the electrochemical oxidation, it is possible to utilize the entire range of intermolecular interactions to modify the structures. These include electrostatic and van der Waals interactions, hydrogen bonding, covalent bonding and complexation reactions to selectively bind suitable building blocks. This approach can also be used for the post-synthesis organization of carbon nanotubes and, moreover, provides unique possibilities for the fabrication of nanomaterials.

Chapter 4 discusses the post-synthesis assembly of carbon nanotubes of the pre-patterned structures. Stable suspensions of carbon nanotubes were prepared via several different approaches, including agitation in organic solvents or the use of surfactants. The latter yielded in stable suspensions of carbon nanotubes. Electro-chemical oxidation lithography was utilized for the placement of individual carbon nanotubes. The structuring of the OTS monolayer was repeated and, in a second oxidation process, new active binding sites were
generated. This was followed by the sequential placement of CNTs onto chemically active surface templates created in the vicinity of the existing tube. Major advantages of this approach include good control over the lateral placement of the CNTs and the availability of addressable chemical functional surface templates. Furthermore, the possibility to preselect the self-assembling building blocks as well as the sequential nature of the patterning process are discussed, which are not easily accessible by conventional lithographic tools, i.e., photo- and e-beam lithography. This process provides the possibility to carefully select the tube material and to combine pre-defined building blocks, e.g. in transistor layouts. Thus, a powerful approach has been developed that allows control over the device layout at several length scales.

Chapter 5 demonstrates two new concepts for the use of electro-oxidative lithography for the formation of nanoscale building blocks, e.g., nanometer gaps and metallic circles as shown in this work. The electro-chemical oxidation of monolayers and bilayers consisting of OTS was investigated in detail, including the different oxidation times required to perform the electrochemical oxidation on monolayer and bilayer systems. Thus, a new rational design to generate well-defined gap-structures was established. In particular, the fabrication of a nanometric gap structure and an approach to assemble a nanoelectronic-based device layout was developed. The second concept introduces a new fabrication method to obtain ring structures with nanometer dimensions. This method combines the silicon growth mode and the monolayer oxidation mode from the available electro-oxidation lithography techniques. The oxidation conditions, as well as the scaling options of this lithographic process were investigated and revealed good controllability of the feature dimensions. These structures were further functionalized with silver particles, thus, converting the structure into mesoscopic ring structures with sufficiently high uniformity and reproducible quality. These concepts can be used for the formation of nano-scale functional devices.

In conclusion, new concepts have been developed to target different, challenging aspects of nanofabrication. This combines alternative synthesis strategies for carbon nanotubes and the implementation of these nanotubes into nanostructures. Electro-oxidative lithography was utilized as a chemical structuring tool to guide self-assembly processes of nanotubes and nanoparticles. Fundamental investigations on the oxidation conditions allowed a significant expansion of the applicability of this structuring technique and demonstrated the possibility to target different aspects of modern nanofabrication.
SAMENVATTING
CURRICULUM VITAE

Tamara Druzhinina was born January 20th, 1980, in Moscow (Russia). After finishing the secondary education in 1997, she started her study in physics at the Moscow Engineering Physics Institute (Russia). In 2003 she obtained her master degree under supervision of Prof. V.V. Dmitrenko. After that, she spent a year as a researcher in the group of Prof. F. Mugele in the University of Ulm (Germany). Accepting the invitation to join the group relocation to the Netherlands, she continued her research on the physics of complex fluids at the University of Twente (the Netherlands). In 2006 she started her PhD work in the group of Prof. U.S. Schubert at the Eindhoven University of Technology in the research field of nanotechnology. The most important results of this research are described in this thesis.
LIST OF PUBLICATIONS

Refereed Publications


Refereed Publications (not part of this thesis)


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