Doctoral Thesis

Functionalization and characterization of multiwalled carbon nanotubes for nanorobotic applications

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Functionalization and Characterization of Multiwalled Carbon Nanotubes for Nanorobotic Applications

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Zusammenfassung


Ein weiterer Teil der Dissertation beschäftigt sich mit der Synthese und Charakterisierung von ferromagnetisch gefüllten Kohlenstoffnanoröhren (FFCNT) für biomedizinische Anwendungen. Die Technologie der Chemischen Gasphasenabscheidung wurde adaptiert um in Formvorlagen aus Aluminiumoxid CNTs um einen Kern von Nickel-
Abstract

Nanorobotics satisfies the increasing demand of exploring the world of very small. It covers many nanotechnology engineering disciplines and can mainly be defined in two aspects: 1) the technology of creating machines at or close to nanometer scale. 2) the manipulation of nanoscale objects within nanometer resolution. Recent developments in nanorobotics not only accelerate progress on examining physical or biological phenomena in low dimensional realm by providing new scientific tools, but also open newer industrial and medical applications which have been previously impossible, such as controllable drug delivery, intra-cellular operations, chip-level integrated circuit repairing and positional nanoassembly. In this work, carbon nanotubes (CNTs) have been chosen as basic functional material to study nanorobotics.

The first part of this thesis focuses on nanomanipulation systems and operation procedures that are required for characterizing and fabricating multi-walled carbon nanotubes (MWNTs). Different picking-up and soldering strategies have been developed for nanomanipulations inside scanning electron microscopes and transmission electron microscopes. These strategies were employed to study the electromechanical coupling of MWNTs and to modify their structures by mechanical peeling. Based on these nanomanipulation techniques, individual MWNTs are employed to make ultra-compact protruding force sensors. This pioneer work presents a new NEMS architecture named NEMS-on-a-tip which consists of a one-dimensional nanostructure integrated on a protruding device carrier. NEMS-on-a-tip devices can be integrated into micro- to nano-sized independent systems towards sensing and manipulating objects in a narrow space.

Another part of the work relates to synthesize and characterize ferromagnetic filled carbon nanotubes (FFCNTs) for biomedical applications. Chemical vapor deposition technology is adapted to grow CNTs filled with nickel and iron nanowires inside anodic aluminum oxide templates. The method provides the possibility to produce FFCNTs with uniform geometry and high filling rate. The structural, electrical and mechanical properties of resulting Ni filled CNTs are intensively studied by various technologies, such as electron microscopy and nanomanipulation. Results show that Ni filled CNTs have a disordered carbon structure and thus, possess low electrical conductivity and small Young’s modulus.
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1 INTRODUCTION

1.1 Motivation

As a new scientific branch of robotics, nanorobotics helps satisfy the increasingly demand of exploring the world of very small. It covers many nanotechnology engineering disciplines and can be mainly defined in two aspects [1-3]: 1) the technology of creating machines at or close to the nanometer range, typically from 0.1 to 100 micrometers. 2) Rules of robot design and operating that allow precision interactions with nanoscale objects, or the manipulation of small objects with nanoscale resolution (nanomanipulation). Recent developments in nanorobotics can not only accelerate progress for examining physical or biological phenomenon in a low dimensional realm by providing new scientific tools, but can also open newer industrial and medical applications that have been previously impossible [4, 5], such as controllable drug delivery, intra-cellular operations, chip-level integrated circuit repairing and nanoassembly. However, although these potential applications have been promised by numbers of researchers, nanorobotics is still in the research and development phase and faced with many technical challenges.

Currently, there are three major challenges that confront nanorobotics over last decade. First, various nanoscale structures, such as carbon nanotubes, semiconductor nanowires and nanobeads, had been proposed as fundamental building blocks that can be used to make nano/micro size robots[6, 7]. However, physical properties of these small materials have not been fully understood. Nanostructures usually possess different chemical and physical properties from their bulk companions [5]. Exploring these unique properties requires sophisticated measuring systems and the ability to interact with such small structures with no perturbation. Second of all, although standard silicon-based micro fabrication techniques have been successfully utilized in microelectronics and the MEMS industry, they are limited by their fundamental physical resolution and two-dimensional fabrication ability [8]. Therefore, new strategies have been pursued for nanoscale device fabrication and integration. Finally, nanoscale objects cannot be easily manipulated by traditional robotic manipulation methods due to their small size and the complex interaction forces between the objects and manipulator. For example, to pick up a nanostructure from a substrate becomes a difficult task due to the strong adhesion forces between the substrate and the structure and unexpected electrostatic forces between the manipulator and the structure. Thus, new robotic manipulation strategies
have to be developed in order to operate nanostructures. These challenges can be found in variant forms in every nanorobotic applications.

In this dissertation, I use carbon nanotubes (CNTs) as a basic material to study nanorobotics. On the one hand, nanorobotic systems have been integrated into electron microscopes to experimentally investigate the basic physical properties of CNTs, especially their electromechanical coupling. On the other hand, new functionalization, fabrication and integration methods have been developed to build CNT-based nanorobots.

1.2 Carbon Nanotubes and Their Properties

1.2.1 Structure of Carbon Nanotubes

Figure 1.1.1: High resolution images of CNTs (a) Scanning tunneling microscope (STM) image of carbon nanotube deposited on HOPG substrate (from Prof. V. K. Nevolin, Russia). (b) High resolution transmission electron microscope (HRTEM) image of a multiwalled carbon nanotube. (c) HRTEM image of a single-walled carbon nanotube (from IBM website).

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991 [9], significant progress has been achieved for both understanding their fundamental properties and exploring possible engineering applications. This novel nanomaterial presents outstanding mechanical and electrical properties [10, 11] and, therefore, becomes one of the most promising building blocks for nanodevices. Carbon nanotubes are thin, hollow cylinders of covalently bonded carbon atoms, as shown in Figure 1.1.1. They come in two different flavors: single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) which consist of
concentric SWNTs (or shells) stacked together. SWNTs are typically 1–2 nm in diameter and several μm to mm in length. MWNTs typically have diameters in the range of 5–50 nm and are typically several tens of μm in length. CNTs can be created by either catalytic [12], arc-discharge [9] or laser-ablation methods [13]. The work in this thesis has been done on MWNTs created by catalytic or arc-discharge methods.

![Diagram of SWNT formation](https://ipn2.epfl.ch/CHBU/NTbasics1.htm)

**Figure 1.2:** Forming a SWNT by wrapping a graphene sheet. Two black arrows show the basic lattice vectors and the purple arrow identifies the direction of wrapping. The angle between the direction of wrapping and the lattice is called the “chiral” angle. Red, blue and green lines are indicated the three main chirality groups. (from http://ipn2.epfl.ch/CHBU/NTbasics1.htm)

The carbon atoms in the walls of a nanotube are arranged in a honeycomb lattice just as in a single sheet of graphene. In fact, a SWNT can be thought of as a single rolled graphene sheet wrapped at different angles (seen in Figure 1.2). The properties of a CNT then derive from the properties of graphene. Depending on the “rolling” angle with respect to the lattice, the relative arrangement of the atoms in the walls of the CNT with respect to the CNT axis is different. The angle between the orientation of the lattice and the CNT’s axis is known as the “chirality” of the CNT, which determines its diameter and electrical properties [10]. As shown in Figure 1.2, the chiral vector \((n, m)\) is used to describe the chirality of a tube, and the three resulting types of SWNTs, commonly referred as ‘armchair’, ‘zigzag’ and ‘chiral’
tubes, are schematically illustrated in Figure 1.3. For a given chiral vector, tube diameter $d$ and chiral angle $\theta$ can be expressed by:

\[ d = \frac{a\sqrt{m^2+mn+n^2}}{\pi} \]  

(1.1)

\[ \theta = \cos^{-1}\left(\frac{2n+m}{2\sqrt{n^2+nm+m^2}}\right) \]  

(1.2)

Figure 1.3: Three chiralities of CNTs. (a) Schematic drawing of the ‘armchair’, ‘zigzag’ and ‘chiral’ SWNTs. (b) STM images of chiral and zigzag CNTs (from Wildoer et al. 1998).

A MWNT consists of several nested carbon shells. The individual carbon shells within a MWNT are suspended using inter-atomic van der Waals force. The number of MWNT shells varies between 2 to a few tens and its outer diameter usually occurs in the range of a few to tens of nm depending on the growth process. There are two models that can be used to describe the structures of multi-walled nanotubes. In the Russian Doll model, sheets of graphite are arranged in concentric cylinders, e.g. a (0, 8) single-walled nanotube (SWNT) within a larger (0, 17) single-walled nanotube. In the Parchment model, a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled newspaper. The interlayer distance in multi-walled nanotubes is close to the distance between graphene layers in graphite, approximately 3.4 Å. In this work, we mainly use the Russian Doll model to describe a MWNT, especially in the simulation part.
1.2.2 Mechanical Properties of Carbon Nanotubes

Both MWNT and SWNT have anisotropic mechanical properties. CNTs can tolerate an extremely high axial load because of the strong sp² hybridized C-C bonds within the shells. They can be easily bent due to the one dimensional geometry and, for MWNTs, weak interlayer interactions (mainly van der Waals force) occur. The two most important parameters characterizing the mechanical properties of a material are the elastic modulus and the tensile strength. Theoretical calculations for the elastic modulus and the tensile strength of a SWNT predicted values ranging from 0.5 TPa to 5 TPa for the elastic modulus [14-19] and 10 GPa to 40 GPa for the tensile strength [20].

Experimentally, Atomic Force Microscopy (AFM) and Electron Microscopy (EM) based observation and nanomanipulation have been intensively used to investigate mechanical properties of CNTs. Figure 1.4 shows two examples. Early work mostly concentrated on the properties of MWNT and CNT bundles. Thermal and electrostatic excited MWNT vibrations were imaged by transmission electron microscope (TEM) and scanning electron microscope (SEM) at different temperatures and then extracted the elastic modulus by fitting the shape of resonance [21-24]. They found the elastic modulus of MWNTs ranging from 1TPa to 1.4 TPa. Similar methods were also applied on individual SWNTs but the results varied from 18 GPa to 2.5TPa [25]. Wong et al. used an AFM cantilever to bend singly clamped MWNTs and directly measure their elasticity and strength [26]. They found values of elastic modulus around 1.3TPa. This was the first nanomanipulation experiment with regard to characterization of the mechanical properties of CNTs. Later many other groups used this
method to study the elastic properties of doubly clamped ropes of SWNTs and individual SWNTs [27-30]. They found the elastic modulus for arc-discharge grown SWNTs was about 1 TPa and was an order of magnitude lower for tubes grown by catalytic methods. Meanwhile, a similar experiment also determined that the upper bound of the tensile strength was around 40GPa [28]. The elastic properties of SWNT ropes had also been studied by attaching them to two AFM cantilevers inside a SEM [31]. The measurements showed elastic modulus values around 1TPa and tensile strength of 40GPa. Furthermore, the shear modulus of MWNTs was measured by fabricating a metallic paddle on top of the nanotube to which a twisting force could be applied using an AFM cantilever [32]. The measured values of 400GPa were in rough agreement with theory. To date, nanomanipulation based mechanical characterization methods have been widely used on many nanostructures due to their flexibility and reliability.

![Symmetric van der Waals forces](image)

**Figure 1.5: Schematic drawing of sliding movement of inner shell regarding outer shell in a perfect MWNT. Symmetric interlayer van der Waals forces results in the ultra-low interlayer friction. (Adapted from Ref. 35)**

Interlayer interactions are unique mechanical properties of MWNTs. Theoretical analysis predicted a small interlayer axial load transfer and a vanishingly interlayer friction in defect free MWNTs. These interesting properties are due to the suppression of collective stick-slip motion in commensurate tube pairs[33], as shown in Figure 1.5. Recent experimental results have proven the prediction is true by sliding and rotation of the exposed inner part of MWNTs with respect to their outer housing using ultra small force inside TEM and AFM [34-36]. They also proposed that defects were created on CNTs during the sliding or rotation, and that the innate ability of nanotubes to self healing could rapidly fix defecting atomic structures and restore smooth motion. However, most of the current studies still believe that the interlayer interactions in a MWNT depend on the concentration of its native interlayer defects (especially self-interstitials) and, therefore, would be different from tube to tube. My experimental results also confirmed the latter assumption. The low friction can only be
presented between two neighbor shells when they do not have many interlayer defects. For most of layers, the interlayer interactions are strong due to the high density of defects. Therefore, among many interlayer spaces in a MWNT, there may be only a few with low friction. We will discuss this in details in chapter 2.

1.2.3 Electric Properties of Carbon Nanotubes

The unique electronic band structure of graphene provides remarkable electrical properties for CNTs, as shown in Figure 1.6. Depending on its chirality, SWNTs can be either metal, semiconductor [37, 38], or small band gap semiconductor [19]. Theoretically, it is believed that the cylindrical structure of a SWNT applies periodic boundary conditions on the electron wave function around the circumferential direction of a tube, which limits the electron transport in this direction. Therefore, electrons in a SWNT can only move along the axis of the tube. Based on this assumption, the Landauer-Buttiker model [39] is utilized to express the theoretical conductance $C$ of a SWNT. A SWNT has four degenerate one-dimensional conduct channels, two due to spin degeneracy, and two due to the degeneracy arising from clockwise/counter-clockwise “handedness” of the electron wave function. The conductance of each channel can be expressed by:

$$C = \left(\frac{e^2}{h}\right) \sum_{i=1}^{4} T_i$$

(1.3)
where $T_i$ denotes the transmission probability through the $i$-th channel and approximate to 1, and $e^2/h$ equals $3.87 \times 10^{-5}$ $\Omega^{-1}$ which is half the value of quantum of conductance.

Based on this model, short SWNTs (less than 200nm) present ballistic transport properties at a low bias voltage (no electron scattering caused by acoustic phonon). Several experiments have been done to verify this, both in metallic tubes [40, 41] and in semiconducting tubes in an ‘on’ state [42, 43]. For longer SWNTs, the main origin of resistivity is believed to be due to scattering by acoustic phonons. At low biases, the scattering is weak and the measured mean free paths at room temperature is in the range of hundreds nanometers to a micron [38]. At high biases, the scattering effect becomes stronger due to the high energy absorbed by electrons and stronger phonon vibration caused by higher dispersed energy. Therefore, the conductivity of long SWNTs changes nonlinearily at a high bias condition.

Semiconducting SWNTs have a band gap $E_g = 0.7eV/D[\text{nm}]$, where $D$ is the CNT diameter[11]. That this formula is only valid for SWNT with small diameters (less than 5nm) [10]. For thicker tubes, the band gap is almost the same as graphene. Small-band semiconducting tubes have gaps on the order 100meV that originate from mechanical perturbations such as twist, curvature, or local strain in an otherwise metallic tube [19, 44, 45]. An electrostatic field can also couple to the potential of the tube and shift its Fermi energy from the valence band, into the gap and further into the conduction band, modifying the CNT conductance [37]. This field-effect transistor (FET) behavior is useful for circuit-type applications and sensors [46].

The electric properties of MWNTs are different from SWNTs. Although it has been known that most of MWNTs are metallic, the conductivity of a MWNT cannot be expressed by a simple equation [47]. Regarding the conductivity of defect-free MWNTs, there are two essential questions must be answered. 1) How to determine the mean free paths and electron-phonon scattering rate in a MWNT? 2) How many layers contribute to electron transport in a MWNT? For the first question, theoretical and experimental work has shown the mean free paths are in the range of 0.8 to 4 $\mu$m in a MWNT depending on the applied bias [48, 49].When the applied bias is about 0.1v, the highest mean free paths can be achieved. For the second question, there is no clear answer. Results differ dramatically depending on the model used for their investigation. Zero intershell transport was predicted for an infinite long and defect free MWNT, because the energy and Bloch wave vector must be conserved [50]. That means the innershells have no contribution to the overall conductance of the tube. In contrast, large intershell transmission was expected when electrons could be injected as a local wave.
package [51]. Experimentally, some indirectly local/non-local resistance measurements have been performed, but the results varied significantly [52, 53]. This question will be discussed in detail in the following chapters.

So far, we only considered the electrical properties of defect-free CNTs. In reality, most CNTs have impurities or defects. Some defects, for example the Stone-Wales defect, can simply reduce the conductance of the layer on which they are located by resonant backscattering effect. Other defects can change the interactions of two neighbor layers, which can either increase the conductivity by adding a conduction bond into the interlayer space or decrease the conductivity by mismatching the energy level of electrons in the two neighbor layers [11]. Since there is no efficient way to control the type and the concentration of defects in a CNT, the electrical properties of each individual CNT are quite different. This fact may require us to characterize each CNT before using it to build electrical devices.

Besides the intrinsic conductivity of CNTs, the nanotube–metal contact resistance is another important parameter that strongly affects the performance of CNT based electronics. Unlike the near-ohmic behavior of metal-metal contacts and interconnects, contact resistance at the metal–CNT junction is considered a Schottky barrier due to the weak Fermi level pinning at the metal nanotube interface [46]. Therefore, the contact resistance is relatively large and strongly depends on physical design and process parameters such as electrical contact area, electrode materials used, and the structure of the concentric shells within the tube [54-56]. We believe that gold and palladium are currently the best electrode materials for CNT-based electrical devices because their work functions are similar to CNT’s. Moreover, MWNT-metal junctions usually have smaller contact resistance than SWNT-metal junctions [46].

1.2.4 Electromechanical Coupling of Carbon Nanotubes

In additional to the exceptional electrical and mechanical properties, electromechanical coupling is an interesting characteristic of CNTs. Some researchers assert that these remarkable properties do not come about merely by coincidence, but arise from the fact that in CNTs the electronic and mechanical degrees of freedom are tightly coupled, and that it is this strong coupling that gives rise to the superior electronic, thermal and mechanical properties observed [57]. For examples, strong piezoresistive behavior has been found for SWNT. Theoretical and experimental observations have shown that the band gap of a
semiconducting nanotube can be modulated by changing its axial strain [58-60]. This relationship is given by

\[
\frac{dE_p(\varepsilon)}{d\varepsilon} = \text{sign}(2p + 1)3t_1(1 + \theta)\cos 3\theta \tag{1.4}
\]

where \(\varepsilon, \nu, \theta\) and \(t_1\) represent the axial strain, Poisson’s ratio, chiral angle of the tube and the tight-binding hopping integral (\(\sim 2.6\text{eV}\)), respectively. The index \(p\) assumes values of 0 and \(\pm 1\) and is defined as \(m - n = 3k + p\) where \((m,n)\) represents the chiral vector of the NT and \(k\) is an integer. Any change in the band gap of a semiconducting nanotube has a direct effect on its conductivity, which explains its piezoresistive behavior. From Equation (1.4), it is evident that the piezoresistance is strongly dependent on the chirality of the nanotube. However, the electromechanical coupling of MWNTs remains an opening issue. Since MWNTs are mainly metallic tubes, band gap theory cannot be applied. Furthermore, MWNTs cannot be simply treated as a 1D conductor because of the possible interlayer electrical coupling. When a tube suffers from a mechanical strain which causes the increasing of backscattering effect on the outermost shell, the electron can move in radius direction by high local fields and electron hopping. Although a few theoretical and experimental results have been reported, the evidence is rather weak to achieve a clear conclusion [61, 62]. In this thesis, we will clarify this problem through experimental observation in later chapters.

From the above discussion, it is evident that the electrical and mechanical properties of a CNT highly depend on its atomic structures, such as chirality and concentration of nature defects. Thus, the ability to construct CNT-based devices is determined by the ability to synthesize or select CNTs with desired atomic structures. However, obtaining CNTs with a specific chiral vector and controlled defects level is a significant technological challenge is currently not possible. However, this must be addressed to realize CNT-based devices in industrial products.
1.3 Functionalization of Carbon Nanotubes for Nanoelectromechanical Systems (NEMS)

Figure 1.7: Schematic view and TEM image of MWNTs attached by Ferritin-CNx using chemical functionalization (Adapted from Ref. 67).

Although there are limitations, CNTs are believed to be one of the best building blocks for NEMS devices. In order to extend their applications, various functionalization methods have been developed to enhance or modify the intrinsic properties of CNTs. To date, chemical functionalization, structure modification and materials filling are the three major methods to provide additional functions to an original CNT. Chemical functionalization is the most common approach to change the chemical and physical properties of a tube [63]. OH or COOH functional groups are often attached on the surface of CNT by thermal activity or acid treatment [64, 65]. Figure 1.7 shows an example of chemical functionalization of MWNTs [66]. This method changes the surface properties and electron configuration of a CNT but also induces structural defects in the tube. Functionalized CNTs are usually sensitive to certain chemical agents and can then be coated with different molecules. These nanotubes can be used for chemical sensing [65, 67] and medical applications, such as cancer cell labeling and targeted drug delivery [64, 68, 69].

Structure modification changes the layer or interlayer structure of CNTs, by which new electromechanical properties can be pursued. The first effort at changing CNT structure was to open its caps [34]. Open-ended CNTs can be produced by introducing external energy to break weaker bonds in pentagonal carbon rings while keeping the bonds in hexagonal carbon rings. Thermal oxidation and electrical vaporization have been used for this propose [34, 70]. Open-ended CNT offers the best candidate for nanofluidics research and applications [71].
Recently, different methods have been developed to controllably engineer shell structures on MWNTs, so called shell-engineering [72, 73]. Mechanical shell engineering removes parts of the outermost shell from a MWNT to create telescoping CNTs or sharp CNTs. These materials are ideal building blocks for nanoscale mechanical sensors, actuators and field emission devices [74, 75]. Figure 1.8 (c) shows an example where a nanoscale linear actuator was built from a telescoping MWNT [74]. Electrical shell-engineering etches the middle part of the outer shells by saturation current. Resulting CNTs have a suspended inner tube which is clamped by two end caps. Nano-bearing, nanoswitches and mechanical nanotransistors have been developed using these CNTs. Figure 1.8 (a) and (b) show two examples of these devices [75, 76]. Shell engineered CNTs have different properties from original ones. For example, the bending strength of a telescoping CNT is determined by the weaker interlayer interactions and, then, interlayer electron hopping becomes a decisive factor in determining the electrical conductance of such a tube. These new properties extend the application of CNTs and will be discussed in following chapters.

Figure 1.8 NEMS devices based on shell engineered MWNTs. (a) Rotational nanoactuator using a MWNT engineered by electrical breakdown (Adapted from Ref. 76). (b) NEMS bi-directional bearings based on shell engineered MWNTs (Adapted from Ref. 78). (c) Linear nanoactuator based on a telescoping MWNT (Adapted from Ref. 75).

Because of the hollow structures of CNTs, filling CNTs with other materials has been an interesting topic since the first CNT was discovered. These composite materials were believed to possess the physical and chemical properties of the original CNTs and filled materials [77-79]. Ferromagnetic materials are often used materials for CNT filling due to their magnetic properties. Various methods to fill the CNTs with ferromagnetic materials include arc-discharge capillary infiltration, electrolysis of molten salt and chemical vapor deposition (CVD) technique [79, 80]. Figure 1.9 shows two TEM images of CNT filled with Fe (a) and Ni (b). CNTs filled with ferromagnetic materials, such as Ni, Fe or Co, can be used as nano-
magnets and may find their potential applications in magnetic force microscopy, high density magnetic recording media, biology, microwave absorption, molecular spintronics, nanoelectromagnetic inductors, nanopipettes, nanowelding and electrochemical energy storage [81]. Although many efforts have been published with regard to these new materials and applications, two opening issues still exist. 1) How to control the geometry and filling ratio in a ferromagnetic filled CNT (FFCNT)? 2) What are the new physical and chemical properties of FFCNTs? Today, these questions dominate research in the field.

![Figure 1.9 TEM images of MWNTs filled with ferromagnetic materials (a) MWNT filled with Fe (Adapted from Ref. 79) (b) CNT filled with Ni Nanowire (Adapted from Ref. 81)](image)

In summary, functionalized carbon nanotubes provide additional properties and extend the utilization of CNTs in fundamental research and market driven applications. However, significant improvements are required to optimize the synthesis protocol for different functionalized CNTs in order to produce reliable tubes with stable structures. Theoretical and experimental investigations must be performed to characterize the physical and chemical properties of these new CNTs for their applications.

### 1.4 Research and Technological Contributions

This thesis presents a series of strategies to synthesize, functionalize and characterize MWNTs for NEMS and nanorobotic applications. The development of NEMS and nanorobotics are synergistic. Nanorobotics provides efficient tools for concept verification, fabrication and characterization of new NEMS devices, while NEMS devices enhance the capability of nanorobots. The primary contributions of this effort are in the following areas: (1) Developing three-dimensional nanomanipulation protocols for characterization and
construction of one-dimensional nanostructures inside electron microscopes. (2) Developing new concept, architectures and fabrication processes for protruding NEMS devices, which we call NEMS-on-a-tip. (3) Realizing and characterizing prototypes of CNT-based NEMS-on-a-tip force sensors. (4) Developing and optimizing the synthesis approach for producing ferromagnetic filled CNTs with controlled geometry and high filling ratios. (5) Characterizing the mechanical and electrical properties of nickel filled CNTs.

In-situ SEM/TEM based nanomanipulation has been approved to be one of the most efficient methods to characterize nanostructures. Recently, this technique also demonstrated its ability to modify shell structures in MWNTs and build prototypes of NEMS devices for scientific purposes [73]. However, the development of nanomanipulation is ongoing. New paradigms have been shown in this thesis for manipulating one-dimensional nanostructures/devices. Different picking and releasing strategies have been developed, optimized and tested on various nanostructures. Standard operation sequences have been presented and customized for manipulating CNTs inside SEM and TEM. In order to achieve this, contact mechanisms between nanostructures have been investigated.

In order to understand and use electromechanical properties of MWNTs, a series of experimental results have been presented to clarify the piezo-like behaviors of individual MWNTs. Moreover, telescoping MWNTs were fabricated using mechanical shell-breaking in SEMs. To control this process, the tensile strength and the breaking mechanism of carbon shells in MWNTs have been quantitatively studied as well. These telescoping MWNTs present a strong and repeatable electromechanical coupling property which is distinguished from original MWNTs. This property makes them ideal building blocks for many novel NEMS devices and will be highlighted in this thesis.

In the area of NEMS design and fabrication, new device architectures have been proposed. In contrast to NEMS-on-a-chip architectures shared by most current NEMS devices, new architectures allow us to integrate an ultra-compact NEMS device into a one-dimensional carrier, which is also utilized for energy and information exchange between NEMS and external systems. The architecture is called NEMS-on-a-tip. NEMS-on-a-tip devices possess a one-dimensional protruding geometry. This feature makes them good candidates for in-situ sensing and operation tasks in a limited small space, such as living cells and capillaries. We have demonstrated the concept, design rules, fabrication and integration principles through the first NEMS-on-a-tip device: protruding NEMS force sensors based on shell engineered MWNTs.
One of the most important issues for NEMS-on-a-tip device is the development of a small protruding carrier which can provide support to nanoscale functional elements integrated on it. In order to fully take advantage of size and electromechanical properties of a functional element, the overall dimensions of the carrier should be smaller than one micron, while its electrical and mechanical properties should be tunable for different applications. To make such a carrier by standard microfabrication processes is a great technical challenge due to the physical resolution limitations in these processes. Previously, several novel fabrication methods have been proposed to make these types of structures, such as focused ion beam based nanostructuring and electron beam construction of CNTs [82, 83]. However, these methods are time consuming and the physical properties of the resulting carriers are not well controlled. In this effort, we present an efficient fabrication paradigm to microfabricate protruding nanoscale functional structures. As an example, variant protruding nanoelectrode pairs have been fabricated. Their applications have also been described in the thesis.

Another aspect of this doctoral work relates to the development of high-yield synthesis of carbon nanotubes filled with ferromagnetic materials, such as nickel, iron and cobalt. Though in-situ methods and growth mechanisms have been proposed for synthesizing metal filled CNTs by chemical vapor deposition (CVD), the current approaches are not sufficient to completely describe the formation of in-situ filled carbon nanotubes. The properties of resulting CNTs are strongly influenced by the reaction conditions and different mechanisms may be involved in their formation. Moreover, even the CNTs from the same reaction run can have different properties. In-situ methods, in particular, cannot control the volume of the filling metal inside each CNT. Another problem relates to the lack of CNT shape control. Resulting CNTs could have different curvatures and, therefore, present completely different mechanical properties. To overcome these problems, we have proposed a simple but efficient template based approach to produce CNTs filled with various ferromagnetic materials. This method combines the electrochemical deposition and CVD techniques, and, by optimizing the process parameters, it can successfully achieved straight FFCNTs with uniform size and a high metal filling ratio.

We also investigated the electric and mechanical properties of resulting CNTs. Past results have shown that the incorporation of foreign material into CNTs’ cavities may modify the original mechanical properties of the nanotubes [84]. Other work predicts that the properties of metal filled nanotubes will be dominated by the intrinsic mechanical properties of the CNT [85]. However, no experimental result has been reported on this problem. In this work, we
experimentally studied the electrical and mechanical properties of Ni filled CNTs grown by the template method.

1.5 Organization of the Thesis

Chapter 2 presents an overview of the three-dimensional nanomanipulation technology. In this work, nanomanipulation has been performed inside electron microscopes in order to obtain the real-time visual feedback. SEM and TEM have been utilized for this purpose. Various manipulation tools have been introduced in the chapter and different manipulation setups have been described for different applications. Several challenges in SEM/TEM based manipulation, such as picking strategy and reduction of charging effects, have been solved in order to optimize the manipulation process. To demonstrate these improvements, a series of experimental results have been shown with regard to characterization and mechanical shell engineering of MWNTs.

The material presented in Chapter 3 focuses on the NEMS-on-a-tip architecture. Using ultra-compact NEMS-on-a-tip force sensors as an example, we present the key technologies related to this new architecture. Theoretical and experimental results have been reported regarding the enhanced piezoresistive property of MWNT by shell engineering. A telescoping CNT has been used as the functional element in a NEMS-on-a-tip force sensor. Silicon based nanofabrication processes which can efficiently produce protruding nanoscale electrode pairs (PNEP) as nanodevice carrier has been described. Moreover, proposed PNEP has also been used to facilitate the nanomanipulation process so that the multishell transport property of individual MWNTs can be directly investigated.

A technique to produce carbon nanotubes filled with ferromagnetic materials is presented in Chapter 4. This technique includes three main processes: making anodic aluminum oxide (AAO) templates on silicon substrates, growth ferromagnetic nanowires inside AAO template by electroplating, and growth of CNTs filled with these nanowires by the CVD technique. The structural and physical properties of resulting tubes have been reported as well.

Finally, Chapter 5 summarizes the results of this effort and highlights the key research conclusions. An outlook for future directions of this research is also presented.
2 Nanomanipulation inside Electron Microscopes

In his famous speech "There is plenty of room at the bottom" in 1959 [86], Richard Feynman discussed how to manipulate and control things on a molecular scale in order to achieve electronic and mechanical systems with atomic sized components. Since then, efficient assembly strategies for nanostructures have been pursued by many scientists. However, progress was slow until nanotechnology emerged and rapidly developed in the last two decades. The major challenge in this field is to develop a reliable method to integrate nanoscale structures into micro/macrosystems. Recently, various top-down or bottom-up approaches have been developed in order to fabricate devices with integrated nanostructures [87-91]. Charged particle beam patterning processes, such as electron beam lithography (EBL) [92], focus ion beam lithography (FIB) [83, 92] and duel laser beam 3D nanolithography [93, 94], are the predominant top-down methods to create or integrate nanostructures into a larger system. Although these methods provide a systematic way to produce devices, they are time consuming due to their directly writing principle. Moreover, they can bring unexpected damages, such as crystallography defects, into the target nanostructures and thus, affect the performance of final devices.

In-situ growth and self-assembling methods are typical bottom-up strategies. Directly growing SWNTs from patterned catalytic particles on MEMS devices [95] and dielectrophoretic nanoassembly of MWNTs [76] are two good examples for these kinds of methods. The biggest advantage of these methods is the ability to achieve batch fabrication of devices integrated with nanostructures as functional elements. However, these methods are sensitive to many parameters and, therefore, difficult to be controlled in scaling-up production. Thus, the yield of devices made by the bottom-up method is generally low. Hybrid fabrication methods which combine the top-down and bottom-up strategies have been developed to solve these problems [2].

Robotic manipulation is the most straightforward ideas for integrating nanoscale building blocks into large systems due to their successful applications in macrostructure assembly. Although many scientific challenges arise when the objects scales to nanometer range [96], nanomanipulation is believed to be one of the most promising methods to build nanostructure based systems in the future. In the last decade, a series of theoretical and experimental studies had been done to perform nanomanipulation on different nanomaterials[3, 97-99], such as CNTs [100] and silicon nanowires [101]. Though nanomanipulation is still a slow and
inefficient operation, it has shown its power for future nanoassembly applications. With the development of novel precision manipulation systems and grasping tools, nanomanipulation will become an important method for future industry.

2.1 State-of-the-art Nanomanipulation

To date, most nanomanipulation experiments have been preformed using scanning probe microscopes (SPM), especially atomic force microscope (AFM) [91, 92]. Comparing to optical microscopes by which the samples can only be observed or optically excited, AFM techniques allow users to interact with the sample by intermolecular forces, and they provide higher observation resolution. It is this feature that makes them good candidates for nanomanipulation. Using AFM based manipulation system, researchers successfully patterned Xenon atoms at IBM Rueschlikon and many new electrical and mechanical properties of various nanomaterials, such as CNTs [102, 103], nanowires [104] and graphene [97], have been discovered by this technique. The main restrictions with SPM and AFM based manipulation are 1) Samples must lie on a planar surface. It is not possible to manipulate samples that are vertically aligned on the substrate. 2) Manipulation and integrated of nanoscale objects are mainly done by pushing. It is difficult to perform picking and releasing operations. 3) Observation and manipulating cannot to be done simultaneously. These restrictions limit the applications of SPM/AFM based manipulation.

To overcome these problems, in-situ SEM or TEM manipulation is often preferable. SEM offers a possibility of imaging three dimensional objects with a relatively high frame rate and high resolution (2nm). SEMs have a large chamber volume and a large range of working distance, which provides sufficient working spaces for 3D nanomanipulation. Another big advantage of in-situ SEM based manipulation is the possibility of utilizing different picking and releasing methods and tools, such as MEMS gripper [98], CNT nanotweezers [105, 106] and electron beam induced deposition [107], to integrated nanoscale building blocks into a predefined device. TEM has sub-nanometer resolution and the interaction between the transmitted electron and the sample provides various information on the sample, from the material composition in an alloy to the atomic structure in a crystal. However, the chamber size of a TEM is relatively small, which makes the design; installation and operation of a TEM compatible manipulator difficult. Thus, TEM based manipulation is only a useful tool to study the intrinsic electrical and mechanical properties of nanomaterials, especially, to
investigate the mechanical response of the target nanostructure under different loads; but it is not a convenient method to assemble nanostructures into devices. Although in-situ SEM/TEM based nanomanipulation has many advantages over the SPM/AFM methods, it also has some disadvantages. The major problem is the required high vacuum environment. This requires the sample and manipulator to be vacuum compatible. Another disadvantage relates to the high energy electron beams inside SEM/TEM which can destroy the intrinsic structure of the sample when it is an organic or bring strong charge effect during the manipulation if the sample is an insulator.

2.2 Nanomanipulation Systems and Strategies

2.2.1 SEM based Nanomanipulation Systems

Scanning electron microscope uses a high energy electron beam to scan the sample surface in a raster pattern while a raster pattern while the secondary electron (SE) or back scattering electron (BSE) signal is recorded to form an image. A standard SEM includes a column chamber and a sample chamber which are connected chamber which are connected to a two level vacuum system. The column chamber is relatively small and maintained relatively small and maintained under a high vacuum (10^-9 to 10^-10 mbar). The filament, electromagnetic lens, electromagnetic lens, aperture system, scanning coils and some special detectors (InLens and energy selected back energy selected back scattering electron (ESB)) are mounted in the chamber. The sample chamber is larger chamber larger chamber furnished with a three degree of freedom stage motor, SE and BSE detectors. The basic detectors. The basic structure of an SEM is shown in Figure 2.1. Since the volume of an SEM chamber is up to 30 liters, it is convenient to install a complex manipulation system into it.

Figure 2.1. An SEM based manipulation system contains a precision actuation system and end effectors. A good actuation system should have high precision movement (with nanometer to subnanometer resolution) and large actuation range (a few centimeters). The system must be SEM compatible. Therefore, no magnetic parts or outgassing parts should be in the system. These requirements can be fulfilled by piezoactuatedated stick-slip drivers. The working principle of such drivers is shown in Figure 2.2. It is based on stick-slip phenomenon which is caused by the surfaces alternating between sticking to each other and sliding over each other, with a corresponding change in friction force. When a DC voltage is slowly applied to the piezoelement, the driven force is

27
smaller than the static friction between the piezoelement and the moving unit of the actuator. The moving unit sticks on the piezoelement and moves according to the deformation of it. When the voltage suddenly turns off, the instant driven force is large enough to overcome the static friction, and then the reduction of the friction to kinetic friction can cause a sliding movement between the moving unit and the piezoelement.

Figure 2.1: Schematic diagram of an SEM
Figure 2.2: Schematic diagram of the working principle of stick-slip piezoactuator

For a standard industrial robot, its end effectors can be any machine tools or electromechanical elements, depending on applications. There are only a few tools that can be mounted on an SEM mounted on an SEM based manipulator due to its small load capability (less than 20 gram) and limited mounting and limited mounting space. Conductive probes and AFM cantilevers are the most commonly used tools for manipulation inside an SEM. Combined with proper picking and soldering methods, these tools have been utilized for the manipulation of diverse 1D nanostructures, such as CNTs, nanowires, and nanocoils. The tools also can be used to drive mechanical actuators on MEMS devices. Picking is a major challenge for probe based manipulation, and we will discuss it in the following section. Microfabricated grippers and tweezers are other options. However, the size of current microgrippers is in the range of 20 to 100 microns [98]. More work has to done to develop a reliable and repeatable fabrication process to produce grippers with the comparable size of individual nanostructures. Additionally, in order to use a microgripper inside an
microgripper inside an SEM, its driving units must be SEM compatible. In this doctoral work, etched tungsten probes and AFM cantilevers are the main manipulating tools.

Figure 2.3 shows two examples of these tools: (a) AFM cantilever with 130μm length and 5nm tip radius (b) 10μm thick tungsten probe with tip radius of approximately 100nm (Picoprobe, T-4-10-1mm).

Figure 2.3 End effectors for SEM based nanomanipulation. (a) AFM cantilever with 5nm tip radius (from nanoworld). (b) Tungsten probe with 100nm tip radius (from picoprobe)

In order to integrate a manipulation system into an SEM, there are two basic configurations. The first one is to mount the manipulator separately from the SEM sample stage. The advantage of this configuration is the ability of providing additional degrees of freedom (DOF) to operators. The total DOF is the sum of the DOF of the manipulator and the DOF of the sample motor stage. This configuration includes two sources of mechanical vibration and drifting, which makes the manipulation more difficult. Another configuration is to directly mount the manipulator on the SEM sample stage, which is more convenient for our work. This configuration is shown in the Figure 2.4.
An image of the manipulator/SEM integration setup which was used in this work is shown in Figure 2.5. This setup includes two manipulators with different end effectors and can provide enough flexibility to perform various tasks, from characterization of CNTs to integration of nanostructures into NEMS devices. The setup was built inside a Zeiss Ultra55 field emission scanning electron microscope (FESEM) which operates at $1 \times 10^{-5}$ to $1 \times 10^{-6}$ mbar and at room temperature (25°C). The manipulating targets, e.g. CNT samples or NEMS devices, were attached on the SEM sample stage using conductive silver tape. Two 3DOF manipulators (Kleindiek MM3A) were mounted onto the stage as well. For mechanical shell engineering of MWNTs, integration of CNTs into NEMS devices, and NEMS device calibration, one Picoprobe was mounted on a manipulator for such tasks. For electrical breakdown based shell engineering and electrical transport measurement, two probes served as electrodes. One of
them was fixed but insulated from the SEM sample stage. Another probe was held by a manipulator. When we characterize the mechanical properties of CNTs, an AFM cantilever served as a force sensor and was vertically attached on the sample stage of one manipulator.

Figure 2.5 A typical SEM based nanomanipulation system including two manipulators with different effectors.

2.2.2 Picking strategies of SEM based nanomanipulation

Picking specimens is the most important and fundamental process for 3D nanomanipulation and nanoassembly, and in most cases, also the most difficult process. The essential procedures include: 1) alignment of a tool, typically a probe, with an object and 2) exertion of a force between the probe and the object larger than between the object and the substrate supporting it. In an SEM, van der Waals forces and electron-beam-induced deposition (EBID) have been shown to be effective. In order to develop a proper picking method for nanostructures, the contact force between the end effector and target structures, in our case CNTs, first needs to
be investigated. When a tungsten probe contacts a CNT, the contact force is mainly the van der Waals force. If the CNT is modeled as a rigid cylindrical rod, the van der Waals force can be expressed by [100]:

\[
f_{vdw} = -\frac{AL\sqrt{r_0}}{8\sqrt{2}D^2}
\]  

(2.1)

Where, A is Hamaker constant, which is usually $0.8 \times 10^{-19}$ J for CNTs. L and $r_0$ are the length and radius of the tube, respectively. D is the interface distance. For the CNT/metal interface, the typical Lennard-Jones distance of about 0.2 nm can be used [100]. Using this equation, we can calculate that the van der Waals force between a solid CNT (1 µm length, 10nm diameter) and silicon substrate is 0.875 µN.

However, the actual case is much more complex. A real CNT can be treated as either a rigid rod or an elastic rod depending on the shell structure of the tube. Suppose that a CNT consists of n shells. When n is smaller than 8, it should be treated as an elastic rod. Otherwise, it can be treated as a rigid rod [103]. Elastic rods can be deformed in their radial direction by surface ver der Waals forces when they contact a surface. Therefore, based on Johnson-Kendall-Roberts theory, the

Figure 2.6 Two cylinders in contact (a) with perpendicular axes. (b) with parallel axes.
Roberts theory, the expression of the van der Waals force should be modified with the effective radius instead of the effective radius instead of the radius of the original tube [108]. Since we use tungsten probes to pick up CNTs, the van der Waals force can be calculated as two elastic cylinders in contact with each other. In the case of contact between two cylinders with parallel axes, shown in Figure 2.6(b) the efficient radius is:

\[
 r_{eff} = \frac{r_{cnt}r_{probe}}{r_{cnt}+r_{probe}} \quad (2.2)
\]

In the case of the contact between two cylinders with perpendicular axes, shown in Figure 2.6 (a), the efficient radius is:

\[
 r_{eff} = \sqrt{r_{cnt}r_{probe}} \quad (2.3)
\]

Using these equations, we can quantitatively estimate the maximal van der Waals forces between a CNT and a tungsten probe when the tube is treated as an elastic rod. Given that the diameter of the probe is 100nm and that the tube/probe contact with parallel axes, the force is 0.84 µN for a 10nm thick tube and 1.13 µN for a 20nm thick tube. When these objects contact with perpendicular axes, the force is 47nN for a 10nm thick tube and 81 nN for a 20nm thick tube. If a tube has a large number of shells, we can also calculate the van der Waals force by (2.1).

The MWNTs used in this work have the diameters ranging from 20nm to 30nm. Using high resolution TEM investigation, we found the number of shells of those tubes were usually more than 10. Therefore, these tubes can be treated as rigid rods. Based on the above calculation, the van der Waals forces are in the range of 1 µN to 2 µN. Compared to the adhesion force between tube and the substrate, the van der Waals force was quite low. An enhanced soldering method was required to guaranty a successful picking operation.
Compared to picking using van der Waals forces, electron beam induced deposition is a more powerful picking method for SEM based nanomanipulation. EBID can also be used for soldering existing nanostructures, such as carbon nanotubes, to other micro- and nanostructures [100, 107, 109]. The basic principle of the deposition method can be shown in Figure 2.7. The EBID is a process that can be readily performed inside SEMs with residual hydrocarbon containments or with precursors induced close to the deposition site. Precursor molecules adsorbed on the substrate surface are decomposed into non-volatile and volatile particles by a focused high energy electron beam, e.g. the primary beam of an SEM. The non-volatile particles attach to the substrate and form the deposit, while the volatile particles are drawn away by the vacuum system. Depending on the precursor and chamber condition, the deposited material consists of metal atoms, carbon atoms and nanoscale diamond-like-carbon embedded in amorphous carbon [110]. The EBID deposition rate depends on the energy of electrons in the primary beam, which is equal to the accelerating voltage of the SEM. It is known that low accelerating voltages favor a higher yield of secondary electrons that have a larger cross section for molecular decomposition and, thus, EBID deposit growth [110, 111].

In our laboratory, tungsten peroxide powder was used as a solid precursor to fabricate high aspect ratio ultra-sharp tungsten nanowires on a pre-etched tungsten probe by EBID.
deposited nanowires are shown in Figure 2.8. The wire was 1 µm in length with a few nm tip radius. The measured deposition rate was 25 to 30 nm per minute. Compared to silicon based AFM tips; the resulting nanowires have not only an ultra-sharp tip but also better mechanical properties (higher aspect ratio and less brittle). Therefore, they are able to be used as end effectors to push or pick up objects a few nanometers size. However, due to the appearance of carbon impurities inside the nanowires, their intrinsic resistivity is much higher than the original bulk material. For instance, the electrical resistivity of tungsten is 52.8 nΩ·m at room temperature while the resistivity of the EBID deposited tungsten nanowire is about 740 nΩ·m. This causes that deposited nanostructure cannot be directly used for nanoelectronic applications or manipulation tasks which are aimed at characterizing the electrical properties of nanoscale objects. For our soldering purposes, EBID appears to be a useful tool. In our experiments, we used residual hydrocarbon gas inside the SEM chamber for soldering. Using hydrocarbon gas, EBID became a low rate deposition process and could be easily controlled by chamber pressure, acceleration voltage and deposition time. To optimize the soldering process, a series of tensile experiments have been done to test the strength of EBID connections between a CNT and AFM tip with different deposition conditions.

Figure 2.8 A SEM image of ultra-sharp tungsten nanowires deposited on a tungsten probe by EBID.
Figure 2.9 In-situ SEM tensile test of EBID connection between CNT and AFM tip. (a) Single MWNT connected with a tip and a tungsten probe during the test. (b) broken tube after the test.

The experimental setup included a manipulator and an AFM cantilever, as shown in Figure 2.9. The cantilever served as a force sensor to measure the force applied on the EBID connection. During the experiment, a MWNT was aligned and fixed on a tungsten probe using a long term EBID process. A layer of amorphous carbon coated the tube and increased its strength. This tube was then moved to touch to the tip of the AFM cantilever, and a one minute EBID deposition was executed under different vacuum and high voltage conditions to make a connection between the tube and tip, as shown in Figure 2.9 (a). Then, the SEM chamber was further pumped down for 1 hour without any high voltage. This step minimized unwanted EBID during the tensile test. After this, a pulling force was exerted on the EBID connection through the tube by the nanomanipulator. The force slowly increased until the target EBID connection was broken or the tube was broken. The force was measured by the deformation of the AFM cantilever. In these experiments, the spring constants of cantilevers were in the range of 4.13N/M to 5.321N/M. The results are shown in the table 2.2.

Table 2.2 Tensile strength of EBID deposited connection between a CNT and an AFM tip

<table>
<thead>
<tr>
<th></th>
<th>2KV</th>
<th>5KV</th>
<th>10KV</th>
<th>20KV</th>
<th>30KV</th>
</tr>
</thead>
<tbody>
<tr>
<td>5×10⁻⁵mbar</td>
<td>2.1µN</td>
<td>11.3µN</td>
<td>7.8µN</td>
<td>1.3µN</td>
<td>0.7µN</td>
</tr>
<tr>
<td>1×10⁻⁶mbar</td>
<td>0.8µN</td>
<td>10.1µN</td>
<td>8.1µN</td>
<td>1.8µN</td>
<td>0.2µN</td>
</tr>
<tr>
<td>1×10⁻⁷mbar</td>
<td>0.7µN</td>
<td>4.1µN</td>
<td>3.9µN</td>
<td>0.5µN</td>
<td>0.2µN</td>
</tr>
</tbody>
</table>
These results show that under a constant acceleration voltage, the strength of the connection was reduced with the chamber pressure. But for acceleration voltages lower than 2kV or higher than 20kV, the strength of connections was significantly weaker even though the pressures were quite high. The reason is that for 2 kV, the primary electron beam did not have enough energy to decompose enough molecules for deposition. For 20 to 30kV, although there were enough decomposed molecules, there were not enough secondary electrons to form a strong deposition. Therefore, the optimal EBID soldiering process is achieved at 5kV with a chamber pressure of $6\times10^{-6}$ mbar. A higher chamber pressure was preferred. Practically, however, this is problematic for nanomanipulation work due to the long pumping time required.

### 2.2.3 TEM based Nanomanipulation System

TEMs can be used to achieve high resolution images for ultrathin samples (typically thinner than 20nm), such as the image shown in Figure 2.10 (b) where the shell structure of a MWNT is visible. Since the detected electrons are transmitted through samples with energy higher than 100 keV, the resolution of TEMs can be very high. However, in order to achieve optimal imaging conditions for the thin TEM samples, the working distance has been made short. This means the distance between condenser lens and objective lens must be very short (only about 5 mm) and the sample must be located in this narrow space.

Figure 2.10 (a) shows the basic construction of a TEM. One TEM image can be acquired from different signals, such as standard transmission electron and high angle scattering electrons. Moreover, by using the interference of the electron wave after it has passed through the sample, a phase contrast image of the sample can be formed. This image shows the atomic structure of the sample with 0.2 nm resolution [112]. For TEM based manipulation, we only use transmission electrons to construct phase contrast images.

The TEM based manipulator used is a ST1000 STM–TEM holder (Nanofactory) which is based on the stick-slip principle. It has an STM unit built in a TEM sample holder [Figure 2.11 (a)]. The specimen area of the sample holder is shown in Figure 2.11 (b). The sample is conductively glued to a piece of gold wire (0.35 mm diameter) in a specimen holder, while the gold wire (0.25 mm diameter) STM tip is mounted in a tip holder hemisphere with
six elastic legs connected to a piezoscanner via a sapphire ball, which allows both millimeter-scale coarse sliding and subnanometer fine movement in all three dimensions [X-, Y-, and Z-directions, as shown in Figure 2.11 (a)]. In the coarse-motion mode, the tip holder is actuated in a stick-slip inertial sliding way, whereas in the fine-motion mode, the tip holder is positioned by the solid deformation of the piezoactuators from the same manipulator. The superposition of the coarse and fine motions in the same mechanism makes the manipulator compact enough to be contained in a TEM holder. To get subnanometer resolution for both manipulation and in situ observation, the holder is mounted inside a Phillips CM30 TEM equipped with a goniometer [Figure 2.11(c)].

Figure 2.10 Transmission electron microscope and its high resolution imaging ability. (a) Schematic diagram of a TEM. (b) HRTEM image of a MWNT with catalyst tip. The shell structure of the tube can be easily observed.

Compared with the end effectors used for SEM manipulation, only a few simple tools can be used inside a TEM. Besides the standard 0.25-mm-etched golden wire probes, we have developed a set of special tools developed a set of special tools for different purposes. Tungsten probes [Figure 2.12 (a) and (b)] are prepared by attaching the 10 μm tip of a commercially available tungsten probe onto a golden wire with silver cement. These probes have a higher hardness and are more suitable for manipulation than the
for manipulation than the golden wires designed for STM imaging. Dipping these probes into a double-sided silver conductive tape (Ted Pella, Inc.) for SEM, “sticky” probes are prepared.

Figure 2.12 (c) and (d), which are suitable for picking up relatively large objects. Hooks [Figure 2.12 (e) and (f)] are formed by controlled “tip-crash” of the thin tungsten probes onto a substrate. These special tools greatly extend the applicable range of the STM–TEM holder. They can also be shared with different manipulators in an SEM and a TEM, making it possible to investigate the same sample in different environments. In this report, we show the application of the tungsten probes and “sticky” probes.

Figure 2.11 Nanorobotic manipulation system in a TEM. (a) ST1000 STM–TEM holder (Nanofactory). (b) STM unit. (c) Installation of the STM–TEM holder in a Philips CM30 TEM.

Figure 2.12 Special tools for TEM base nanomanipulation. (a) and (b) TEM and SEM images of tungsten probes [inset of (a) shows the tip]. (c) and (d) TEM and SEM images of “sticky” tungsten probes. (e) and (f) TEM and SEM images of nanohooks.
2.2.4 Pick#ing Strategies of TEM Based Nanomanipulation

In the section 2.2.2, we showed the basic principles of using van der Waals force and electron-beam-induced deposition to align and pick up a nanostructure by a probe inside an SEM. However, in a TEM different challenges exist. First of all, because of the nature of transmission imaging, it is more difficult to know the relative position between the probe and the sample along the electron beam direction. For example, it is difficult to judge if two 1D nanostructures are in the sample horizontal plane or not until they contact each other. When a dense, nontransparent probe is adopted, the situation is even worse. For tackling this new challenge, we have to first bring the sample into the eucentric height. Then, we use “wobble” focusing to position the probe relatively far from the sample. The amplitude of the wobbling has to be minimized by moving the probe up and down so that the probe can be brought to the same focusing plan with the sample. We then approach the sample with the probe from the same side until a contact is established. The probe is biased with a low voltage (typically 100 mV) so that the contact can be detected from the current readout of an ampere meter. Another strategy is based on the instant deformation of a nanotube at the moment of a contact.

Attaching a nanostructure onto a probe in TEM is more difficult than the same operation in an SEM. Using a CNT as an example, the fixation of a nanotube onto a probe inside a TEM can be realized with van der Waals forces, EBID or sticky materials. Attachment and subsequent picking up using van der Waals forces is reversible, hence, multiple attempts are possible with the same probe. Figure 2.13 shows the process to pick up a MWNT using van der Waals force. However, as we discussed in section 2.2.2, van der Waals interactions between the probe and the tube are not necessarily sufficient for picking up a nonfreestanding nanotube. To enhance the attachment between nanotube and probe of manipulator, EBID is an option. However, it differs from SEM. A TEM usually operates under an ultrahigh vacuum with extremely high acceleration voltages (120kv to 300kv). These conditions decrease possible chamber contamination and keep the surfaces of probes and nanotubes clean for a longer time, which enhances the van der Waals interaction between them. Based on our EBID strength test in the SEM, we know the TEM cannot provide an optimal deposition condition for EBID. There are fewer precursor molecules and fewer second electrons generated for EBID. Additionally, a TEM is generally equipped with apparatus to protect the samples from typical contaminants such as pump oil, which further reduces the deposition rate of EBID. These facts make EBID-based picking methods are difficult. In our work, a few trials have been performed to attach individual MWNTs to a probe using EBID. Results are shown in Fig.
2.14. It shows that a tube has been being fixed to a probe after a 30 min exposure to the electron beam (HT: 300 kV), which is typically more than ten times slower than in an SEM.

Figure 2.13 Picking up a nanotube using van der Waals force and moving it downward from the position shown in (a) to (b). Inset shows the contact part with higher magnification. The contact point is hidden by the probe.
Figure 2.14 Picking up a nanotube using long time EBID inside TEM.

Compared to EBID, using a “sticky” probe is a more efficient way to attach a tube onto a probe. Fig. 6 shows a Cu-filled nanotube fixed to a “sticky” probe and picked up by mechanical pulling. However, it has been found that in the environment of a TEM, the “sticky” probe loses its stickiness very quickly, which might be caused by the high-energy electronbeam bombardment and/or the high vacuum. Moreover, EBID is irreversible and “sticky” probes cannot be reused. New approaches are needed if the purpose is to handle or assemble the tube onto other places rather than fix it onto the probe. Microgrippers are promising tools for reversible handling, as has been shown inside SEMs [98], but the design of the gripper remains a challenge due to the narrow space inside a TEM holder. Here we demonstrate a new strategy using electrical breakdown for CNT picking up.

The basic idea of the electrical breakdown picking method is to break the target CNT or the connection between the CNT and the substrate so that the van der Waals force between the tube and the probe is high enough to pick up the tube. Here, we show how electrical breakdown can achieve this aim. Figure 2.15(a) shows a section of a bamboo-structured CNT in contact with a probe while a 10 V bias is applied to probe and substrate (not shown). For a
uniform tube, the breaking site can be at any position along the tube. The selection of a breaking point can be realized by preparing an artificial defect such as a kink on the tube. A kink can be introduced by buckling and/or pushing the tube against a substrate. This process will be shown in the subsequent text. Figure 2.15(b) shows a pre-kinked tube being broken at the kink site by the application of a 10 V bias.

![Figure 2.15](image)

**Figure 2.15 Picking up a bamboo-structured nanotube using van der Waals force in combination with the electric breakdown** (a) a uniformed bamboo-structured tube and (b) a pre-kinked tube (inset shows the preparation of a kink by pushing the tube against the probe before moving it to the final position and performing electrical breakdown).

Figure 2.16 shows the same procedures on a standard nanotube while monitoring the current change during the process. A bias voltage is applied to the tube starting from 0 mV with a step size of 200 mV. No obvious change in either the structure or the electric properties of the tube occurred until a bias voltage of 2500 mV was reached. A typical \(I-V\) curve is shown in Figure 2.16 (d). At 2500 mV, the current reaches up to ca. 1 mA, and the tube starts breaking down at the kink site into two sharpened remaining tubes. Figure 2.16(e) shows the change of the current and the voltage as the current approaches the saturated value. In the first 6.25 s, the voltage increases from 2400 to 2500 mV, and the current increases from 926 to 937 \(\mu\)A (3.25 s) then a sharp drop in current occurred until it reached a stable value around 374 \(\mu\)A, and the tube peeled accordingly. At 309.75 s, the tube broke completely and the current dropped to zero. In Figure 2.16(b) and (c), we can clearly observe the broken sharp tip of the target tube, which turns a MWNT into a sharp needle with a few nanometer tip diameter.
2.3 Modification and Characterization of MWNTs using Nanomanipulation

As mentioned in the introduction, nanomanipulation is a powerful and convenient tool for modification, characterization and integration of MWNTs in NEMS applications. In this section, we describe the manipulation principles and process to achieve these aims.

2.3.1 Shell Engineering of MWNTs by Mechanical Pulling inside SEM

Three methods can be used for shell engineering of MWNTs, chemical etching, mechanical pulling and electrical breakdown. The shell of CNTs is mainly constructed by hexagon C-C rings. However, pentagon or heptagon C-C rings also exist on the cap and defect regions of a
tube. Since the C-C bonds in pentagon rings are weaker than bonds in hexagon rings, chemical or thermal oxidation first break C-C bonds on the cap and defect sites in the outermost shell of a tube [10, 70]. Although it is the most efficient method to change the shell structure, we cannot precisely control the process. Since defects can be located on any position along the CNT, the resulting tube could have an unexpected geometry and a dramatic change in intrinsic properties. Current driven shell etching is more promising since it is simpler, provides better control over breakdown location and can realize fundamental architectures suited for diverse nanoscale devices [72, 113]. In this method, electrically induced joule heating causes high CNT temperatures, estimated to be as high as 2000K [113]. The concentration of native defects on a CNT can change due to high temperature. Thus the nature of the tube changes as well [114-116].

Figure 2.17 Molecular dynamic simulation result of defects created by tensile stress (Adapted from Ref. 119)
Mechanical pulling is an important method to remove the outer-shells of a targeted tube. Each shell of a MWNT is a single layer of carbon atoms with various defects. When one end of the tube is fixed, we are able to exert a pulling force on the rest of the tube along its axial direction. When the force is large enough, C-C bonds on the outer-shells start to be broken and the inner-shells are exposed. During this process, only tube’s strain energy continually increases. When the strain energy is large enough to break the first C-C bond, any further increase will immediately break the tube at the first broken position. Therefore, no random defects are introduced into the tube.

To mechanically change the shell structure of a MWNT, the first question is to estimate how much force is needed in order to break the outer shells of a target tube. Then, we are able to create a significantly strong bond between the tip of a manipulator and a selected MWNT so that enough pulling force can be exerted on the tube to break its shells. In order to answer this question, we first calculate the force needed to break a carbon-carbon sp² bond. The length of such a bond is 0.144nm and the bond dissociation energy is 9.16×10⁻¹⁰ nJ per bond [7]. Therefore, the force needed to break a single bond is 6.36nN.

For a zig-zug CNT with a 6.4nm diameter, the number of bonds on the radius direction is 91. If the axial load can be distributed uniformly on the tube, 579 nN is needed to break the shell. This result is quite similar to the experimental result of breaking force for MWNTs [109]. However, in most cases this theoretical calculation does not match experimental observation, especially for multiwalled carbon nanotubes. Several factors affect the amplitude of the force. 1) The theoretical calculation is only valid for perfect CNTs. The breaking force will be dramatically reduced when the required breaking force. 2) The chiral angle between C-C bonds varies depending on the chirality of the tube, which changes the total bond strength of the tube. 3) The axial load distribution on the tube changes dynamically under a tensile stress [117]. For instance, molecular dynamic simulation shows Stone-Wales bond rotation defects are created in the outermost shell under tensile stress [118], as shown in Figure 2.17. These defects change the uniformity of the load distribution and first break the C-C bond at the defect sites. 4) Interlayer defects could bond several shells together which extremely increases the required breaking force [114]. In summary, we found the practical broken forces of CNT shells are always much larger than the force expected by theoretical calculation.
To find out the range of actual breaking forces, we experimentally test the necessary peeling forces of commercial available MWNTs purchased from MER crop. The tube diameter is in

![Figure 2.18 SEM images of mechanical peeling of shells on a MWNT. Each image shows a peeling process while the peeling force is measured.](image)

```mermaid
pie
  label "" value 70
  label "" value 30
end pie
```
the range of 20 to 40nm and length is in the range of 1 to 5µm. The experiments are performed by nanomanipulation inside an SEM. A freestanding MWNT was selected and the probe was driven to approach it. The tube should be perpendicularly aligned to the probe. When the probe contacted with the root of MWNT, a long EBID process was executed. To realize this, we focused the 5kv electron beam on the contact point between the MWNT and the probe. After 15 minutes, enough amorphous carbon was deposited to make a strong bond. The tube was removed from the substrate using axial pulling and moved to a vertical aligned AFM cantilever. The tube was then connected to the tip of the cantilever by the same EBID process, as shown in Figure 2.18 (a). An axial pulling force was exerted on the tube by the manipulator. A continual imaging process was executed to record the deformation of the cantilever, thus the pulling force was extracted from the deformation. The maximum recorded force was treated as the peeling force. This process was repeated for several times on an individual MWNT in order to quantitatively compare the peeling forces for different number of shells, shown in Figure 2.18 (b)-(d). After each peeling process, a SEM image was taken to record the modified tube, as shown in Figure 2.19. A post imaging process was utilized to analyze the number of shells removed by each peeling.
Eight nanotubes were investigated. The peeling forces were in the range of 1.8µN to 7.4 µN, which is much smaller than the theoretical prediction. For example, in the experiment shown in Figure 2.18 and Figure 2.19, the first peeling operation broke four outermost shells with diameters from 38.92 and 37.73nm. They should contain about 2130 C-C bonds and, therefore, the predicted breaking force was 13.5µN. But the measured broken force was 2.4 nN. For the second peeling, the breaking force was 5.1 µN while the calculation showed 45.6 µN. It was also interesting to find that each peeling operation usually broke more than two shells. This differs from the existing theoretical and experimental observations of ultra-low sliding friction between two neighbor shells. Their measurement showed that the intershell sliding friction was 3-5nN for 5nm diameter tubes and can be up to 120nN for thick tubes, which is much less than the force needed to peel our tubes [36]. Since EBID can only provide the connection between the outermost shell and the probe, only one shell should be broken if the intershell friction is so low for all the intershell interactions. Moreover, if the interactions between two
neighboring shells were always small, the second peeling operation would not be successful. After the first four shells were broken the carbon atoms located on the interface were not stable and would create new bonds. Since the carbon atoms on the next inner shell were in a stable state in term of their electron configuration, the ones on the interface could only bond each other or bond with molecules inside the atmosphere [119]. The latter case would rarely happen since the SEM was running under a high vacuum condition. This implies that the force which caused the second peeling mainly came from the intershell interaction. Our experimental results indicted a different mechanics dominated by the intershell interactions inside MWNTs. It appears likely that defects, especially the self-interstitials, create strong intershell interactions. This type of defect significantly increases the transfer of the axial stress from outer shells to inner ones.

Figure 2.20 Shell engineering of a MWNT by mechanical pulling with location control. (a) The pulling force is applied on the lower region of the tube and (b) outer-shells are broken at the root region.
The second question we want to answer is how to control the location of the breaking site on a tube. We could control the location by controlling the position where the pulling force is exerted. Figure 2.20 shows this process. By contacting a probe to the lower part of a freestanding MWNT, we were able to break the outer shells at the root of the tube. However, we can only roughly control the location by this method due to the large probe size. Alternatively, since we know that the concentration of native defects dominates the mechanical peeling process of a tube, breaking always starts from high defect site where the bonding force is relatively weak. Therefore, we have developed a method to introduce defects on the location we want to break. In Figure 2.21, we demonstrated this method by a series of manipulation operations. A MWNT was fixed on two probes and a large kink was induced at

Figure 2.21 Multiple shell-engineering of a MWNT by mechanical pulling. (a) Buckling a MWNT to create defects on desired position. (b) Pulling the tube to remove the outer-shells on the desired position. (c) Multiple peeling at the same site.
the site we want to break, as shown in the Figure 2.21(a) (red circle). Pulling was then preformed by moving the probe against the tube. It is clearly shown in Figure 2.21(b) and (c), the outer shells of the tube were broken at this site.

2.3.2 Shell Engineering of MWNTs by Electrical Breakdown inside TEM

![Controlled peeling of an MWNT.](image)

**Figure 2.22** Controlled peeling of an MWNT. (a) Original tube. (b) One layer (see inset) is peeled under a 2-V bias. (c) Multiple layers are peeled under a 2.4-V bias. (d) Tube is broken under a 2.5-V bias.

Electrical breakdown is another important method to change the shell structure of a MWNT [72, 113]. This method provides the possibility to control the number of layers removed from the target tube. In order to investigate this feature, we performed a series of electrical breakdown experiments on MWNTs inside a TEM while relevant $I$–$V$ properties were
measured. For shell engineering using electrical breakdown, the target MWNT was bridged between two electrodes using a TEM based nanomanipulation system (seen section 2.2.3). Figure 2.22 shows the procedure of gradually electric breakdown of a selected nanotube. The changes of the structure and the electric properties of the tube were monitored using TEM images and a multimeter, simultaneously. Figure 2.22 (a) and (b) shows the peeling of a single layer of the MWNT. The relevant $I$–$V$ properties have been depicted in Fig. 2.23(a) and (b). Due to the exposure of an innerlayer, the transport properties of the MWNT have clearly been changed. At 1-V bias, the resistance of the tube is 21.89 kΩ, while it was originally 31.09 kΩ before being peeled. So, under this bias the coupling resistance is 9.2 kΩ. More layers can be peeled by applying higher voltages between the two ends of the nanotube. The resulting tubes are shown in Figure 2.22 (c) and (d). The current versus time changes were monitored with a multimeter, as shown in Fig.2.23 (c) and (d).

Figure 2.23 $I$–$V$ and $I$–$t$ curves for controlled peeling of a MWNT. It can be seen from (a) and (b) that the $I$–$V$ curve changed shape after one layer is broken. The curvature may reflect changes in the interlayer coupling. The plots (c) and (d) show the change of current as the nanotubes peeled as shown in Figure 2.22 (b) to (c), and (c) to (d), respectively.
2.3.3 Characterization of Electromechanical Coupling Property of MWNTs

TEM based nanomanipulation was also utilized to investigate electromechanical coupling properties of individual MWNTs. In Ref. 122, it is suggested that the remarkable electromechanical properties of CNTs do not come about merely by coincidence, but arise from the fact that in this system the electronic and mechanical degrees of freedom are tightly coupled [121]. Thus, electromechanical coupling is present in all CNTs. For SWNTs, it is true since they present an obvious piezoresistive property (seen Chapter one). However, different results have been reported regarding the electromechanical coupling of MWNTs [61, 62, 122]. In order to clarify this problem, we performed in-situ TEM based manipulation on individual MWNTs.

![TEM images of continually buckled individual MWNT](image)

**Figure 2.24 TEM images of continually buckled individual MWNT for electromechanical coupling measurement**

During this work, an individual MWNT was bridged between two probes which were mounted on manipulators. By moving one of the probes, the tube could be compressed or bent depending on the probe’s movement. During this operation, the changes of the structure and
the electric properties of the tube were monitored using TEM images and a multimeter, simultaneously. As shown in Figure 2.24 (a)-(d), one tube continually buckled when the compressing force increased. Meanwhile, the resistance of the tube decreased with the bucking deformation, as shown in Fig.2 .25. This result seems appears with the results published in Ref. 123, where the authors found similar electromechanical coupling behavior and explained that the changing of contact resistance between the tube and electrodes attributed to this behavior. This result can also be explained by Ref. 122 where Ramen spectroscopy was used to monitor the electromechanical coupling.

![Figure 2.25 I–V for each buckling state shown in Figure 2.24](image)

However, in a different measurement, we found a different result. Figure 2.26 shows the resistance of a tube increased with the bucking deformation. This result consists with the results in Ref 62 and 63, where the authors suggested the increasing of electron scattering under mechanical deformation caused the decrease in conductivity.

We can explain these different results from a new point of view. In contrast to SWMTs, MWNTs are not an ideal one dimensional conductor. Instead, they should be treated as a two-dimensional transport system. Electrons transport not only along the axis direction of the tube but also in the radius direction of the tube. Therefore, when mechanical deformation is
applied to a tube, it can enhance the electron transport in one direction while reducing it in another direction. The final result can be varied depending on which one dominates the overall transport property. In order to have a definite electromechanical coupling property, we have to artificially define a dominated transport direction for a tube. We will see in the next chapter that a telescoping MWNT can have a definite electromechanical coupling property.

Figure 2.26 $I-V$ for a electromechanical coupling measurement with different behavior

2.4 Summary

SEM/TEM based nanomanipulation systems have been presented in this chapter. Different picking strategies are described for different applications. Several fundamental technical questions, such as the tensile strength of EBID deposited connections and practical peeling force for MWNT shell engineering, have been experimentally investigated in order to optimize the procedure of SEM based CNT nanomanipulation. Moreover, electromechanical coupling of MWNTs has been measured by TEM based nanomanipulation.
3 Carbon Nanotube Based NEMS-on-a-Tip

Nanoelectromechanical systems [123, 124] have been designed for measuring mass in femtogram ranges, sensing forces at piconewton scales, generating motions with gigahertz frequency, probing objects of nanometer sizes, and delivering mass at attogram level [125-129]. The architecture is a key issue for designing NEMS. Most previously demonstrated prototypes of NEMS have taken an on chip architecture, which can be called NEMS-on-a-
chip. Current efforts are focused on the batch fabrication of functional elements [46, 76] and large scale integration of separate elements [130]. NEMS-on-a-chip is especially suitable for mass or pressure sensing [58, 129]. However, for such functions as force sensing or mass delivery, NEMS with a protruding element will be more convenient for in-situ operations. Moreover, the requirement of integration of NEMS devices into micro/nanosize robots can also be fulfilled using the same configuration. In our work, this special architecture is called NEMS-on-a-tip. In general, NEMS-on-a-tip resembles piezoresistive atomic force microscope (AFM) cantilevers [131] in structures but with nanometer dimensions. In order to successfully make a NEMS-on-a-tip device, three major challenges have to be overcome. 1) Design and fabrication of functional elements using one to several nanostructures so that the overall size of the device can be small enough to fit its applications. 2) Development of new fabrication process which can efficiently produce small protruding carriers that can provide enough support to the nanoscale functional element integrated on it. The overall dimensions of the carrier should be similar size as the functional part while its electrical and mechanical properties should be tunable for different applications. 3) Integration of functional elements and protruding carrier together.

In order to overcome these challenges, we present a solution that combines microfabrication and nanomanipulation technologies. A NEMS-on-tip force sensor based on individual shell engineered MWNT has been demonstrated to verify our solution. In addition, a series of new experimental results have been reported with regard to the multilayer conductance in MWNTs and electromechanical coupling properties of telescoping MWNTs.

### 3.1 NEMS-on-a-tip: CNT based Protruding Force Sensor

#### 3.1.1 Concept

The well-defined geometry, exceptional mechanical properties, and extraordinary electrical characteristics of carbon nanotubes qualify them for structuring NEMS. Individual CNTs have been used as AFM cantilever tips for avoiding tip crash and detecting deep topology features [132, 133]. However, the force sensing elements have been the original detectors of a conventional AFM cantilever, typically a laser-level mechanism. The deformation of the CNT itself has been ignored. By replacing the laser-lever detectors with piezocantilevers, it is possible to achieve a smaller system, but integrating sensing elements into the CNTs is a
better solution for achieving even smaller structures without ignoring the deflection of the CNT itself.

With NEMS-on-a-tip architectures (Figure 3.1), we show design fabrication and characterization of ultra-compact force sensors based on the electromechanical coupling property of a multi-walled carbon nanotube. In the section 2.3.3, we discussed different changes in electrical properties of CNTs under mechanical load. These phenomena offer the practical potential of CNTs in NEMS for high sensitive position/force measurement by taking the architecture of either NEMS on a chip or NEMS-on-a-Tip. While chip-type NEMS force sensors have been explored with individual single-walled carbon nanotubes [58] or multi-walled carbon nanotubes [134] bridging and fixing onto electrodes, NEMS-on-a-Tip with an individual CNT attached on a probe while sensing to a sample is much less explored. In the latter case, the change of the contact resistance between the CNT and the sample (see Figure 3.1 (a)) during the measurement will be a problem. Furthermore, only conductive samples are able to be explored by this method, which limits its applications in many fields. To resolve these problems, several new designs with the NEMS-on-a-tip architecture are shown schematically in parts b-d of Figure 3.1. The common idea of these designs is to assemble an individual MWNT or telescoping MWNT on two electrodes while leaving one of the tube ends freely suspended. When a required force is exerted on the free end, a mechanical deformation/displacement of the tube is induced. According to the electromechanical coupling property of MWNTs discussed in the chapter 2, the conductivity changes of the tube which are measured between two electrodes are able to quantitatively reflect the force. Because of their self-closed circuit, the influence of contact resistance between the CNT and the sample in the new designs is minimized. Furthermore, these designs can be used for both conductive and non-conductive samples. Utilizing these tip-type force sensors as a tip of scanning probe microscopes, the final device is able to provide in-situ measurement of spatial and force profiles of nanostructures, simultaneously.
Figure 3.1 Different configurations of NEMS-on–a-tip force sensor. (a) CNT-based force sensors as a probe tip. (b) Type I: An entire MWNT is assembled onto a probe with two electrodes (c) Type II: A telescoping MWNT is connected to two electrodes by the outermost and the exposed inner layer respectively. (d) Type III: A telescoping MWNT is fixed on its outermost shell by two electrodes.

3.1.2 Theoretical and Experimental Verification of the Concept

Because of the extremely complex electronic structure of MWNTs, the transport mechanism of MWNTs has been inconclusive [47, 135, 136]. Specially, the contribution of the intershell
interaction of MWNTs to their conductivity is still not fully understood. Although many researchers have tried to investigate the multishell conductance problem, the answer is still not clear [53, 137] [50]. On the experiential side, the major barrier is due to the difficulty in measuring the conductance change of an individual MWNT before and after removing its innershells without changing the electrical contact state. At the end of the chapter, we will provide a solution to overcome this barrier.

As previously mentioned, the electromechanical coupling property of MWNTs is not entirely clear. Different electromechanical coupling behaviors have been experimentally observed for different tube. In section 2.3.3, we proposed a 2D electron transport assumption which could explain this phenomenon. There are two factors that affect the transport property of a MWNT: intershell conductance and electron scattering on each shell. The latter one will be increased when the tube suffers from a mechanical deformation, which will reduce the overall conductivity of the tube. Meanwhile, the former one could increase the overall conductivity of the tube under the mechanical deformation due to the reduction of interlay gaps and increased of conductive bridges. Therefore, we cannot quantitatively conclude which factor dominates electromechanical coupling property of the unbroken tube. However, when two electrodes connect to the two different shells of the MWNT, the interlayer conductance would play a decisive role in carrier transport, and thus determines the electromechanical coupling behavior [136].

3.1.3 Theoretical Calculation of Intershell Interactions in a Telescoping MWNT

In this section, two fundamental simulation studies are present towards understanding the electromechanical coupling property of telescoping MWNTs. In the first simulation, the static quasicontinuum method developed in Ref 139 and 140 [138, 139] was utilized to calculate the change of intershell distance in a telescoping MWNT under certain mechanical load. The structure model of the nanotube was divided into a coarse meshed regime and a fine meshed regime. The fine regime only included the carbon atoms which are located or closed to the broken site. In this regime, the mesh elements were defined as the real carbon lattice. The other parts of the tube were treated as a coarse regime where triangular elements with the Hermite type interpolation function were used to define the meshes. The meshed CNT is shown in Figure 3.2. In this work, the coordinates of carbon atoms were obtained by the software Nanotube Modeler.
Figure 3.2 Quasicontinuum model of a telescoping DWNT

Figure 3.3 The relationship between bending angle and intershell distance (a) strain energy vs bending-angle curve (b) Intershell distance vs strain energy curve.

The interactions between neighboring atoms were expressed by Berner’ equation and the interactions between neighboring layers were expressed by the Lennard-Johns’ function. The tube was bent by fixing one end and applying a displacement on another end. The strain energy was calculated for each mesh nodes and the total strain energy was minimized to find the optimal position for each mesh note. For a 100nm long (20 20) (15 15) DWNT, the total strain energy vs bending angle curve is shown in Figure 3.3 and the corresponding shell spacing was calculated. As a result, we found the intershell distance decreased under a mechanical bending. The change of the distance was not uniform along the tube. The
maximum change happened at the interface between inner and outer shells. For instance, for 30 degree bending, the maximum gap reduction was 7.9% at the broken site.

Figure 3.4 An illustration of ab initio and semi-empirical atomistic models will be combined in a multi-scale description of a carbon nanotube electronic device

The second effort was to study the transport property of telescoping MWNTs by self-consistently solving the Poisson and Schrödinger equations using the non-equilibrium Green’s function (NEGF) formalism which was development in Ref. 40 and 141 [39, 140, 141]. The NEGF transport equation was solved at two levels: i) a semi-empirical atomistic level using the $P_z$ orbital of carbon atoms as the basis and ii) an atomistic mode space approach, which only treats a few subbands in the tube’s circumferential direction while retaining an atomistic grid along the carrier transport direction. As shown in Figure 3.4, a shell engineered DWNT (20, 20) (15, 15) contacting a pair of electrodes is used for analysis. The crucial parts of the tube, i.e. metal/nanotube contacts (1nm) and the interface between broken outer shell and inner shell (0.34 nm) were treated by a rigorous ab-initio method [136], while the rest part of
the tube was modeled by a simpler $P_z$ orbital description, instead of the full electron wave function, where the carbon nanotube was decoupled as chains with repeatable atom rings. The positions of atoms on the tube were obtained from the previous work.

![Diagram](image.png)

**Figure 3.5 Iterative process for NEGF based electric transport simulation.**

The calculation was performed as following. First, a block tridiagonal Hamiltonian matrix was built to describe the binding interaction of the CNT. In the *ab initio* region, the nearest neighbor tight binding approximation was utilized and the size of this sub matrix equals to the total number of carbon atoms in this region. In our case, the sub-Hamiltonians for CNT/metal contact regions are $120 \times 120$ and $95 \times 95$ matrix, respectively. The sub-Hamiltonian for the outer/inner shell interface is a $352 \times 352$ matrix. In the semi-empirical region, its Hamiltonian was generated by mode space method. Instead of considering the atom to atom binding, the interaction of two neighbor carbon rings was taken into account. As a result, the size of the Hamiltonian was reduced to $1/90$ corresponding to a full tight binding method. Then, a non-
equilibrium Green’s function was utilized under a given potential with constant scattering factor or potential dependent scattering function [142] and a self-consistent iteration between the NEGF transport and the electrostatic Poisson equation was executed. These two equations were iteratively solved until self-consistency was achieved. Finally, the current was computed using the self-consistent potential. The simulation process is shown in Figure 3.5. In Figure 3.6, a comparison of the simulation result and the experimental measurement of I-V dependence of MWNTs are shown. Although the geometry of simulated CNT was not exactly as same as the experimentally measured one, the two results are qualitatively matched. It is also note that when the constant scattering factor is applied in the NEGF the resistance of the tube is linearly depended on the bias; when the potential dependent scattering function is applied the resistance presents a nonlinear dependence on the bias. Only the latter case matches our experimental results, which indicates that the nonlinear current to voltage dependence in MWNTs is due to stronger phonon oscillation caused by higher bias.

Figure 3.6 Comparison between simulation results and experimental results. Right plot shows an I-V curve measured from a telescoping MWNT. The left plot shows I-V curve extracted from simulation. Blue curve resulted from constant scattering factor and purple one resulted from potential dependent scattering function.

Based on these two simulations, we could assume a strong electromechanical coupling behavior in a telescoping MWNT. For a given bias, the resistance of the tube would be reduced due to the decreasing of intershell distance. However, we have not managed to verify this assumption using simulation because the mechanical deformation breaks the symmetric properties of the original tube and makes the NEGF method invalid. Experimental confirmation is required to verify it.
3.1.4 Experimental Investigation of Electromechanical Coupling of Various MWNTs for Force Sensing

Although the above theoretical analysis indicated the shell engineered telescoping MWNT may be the best candidate for building NEMS-on-a-tip force sensor, we have to investigate different sensor designs to find the best one. Three types of prototyping have been investigated in this work. Type I (Figure 3.1(b)): An entire MWNT is assembled onto a probe with two electrodes. Forces exerted on its free end. Type II (Figure 3.1(c)): A telescoping MWNT is connected to two electrodes by the outermost and the exposed inner layer respectively. Forces are applied on outermost shell of the free end. Type III (Figure 3.1(d)): A telescoping MWNT is fixed on its outermost shell by two electrodes. Forces are exerted on the free end of the inner shell. In this work, all these three types of force sensors are fabricated in a vacuum environment. Series lateral forces are measured by them to examine their performances.

![Fabrication process of a NEMS-on-a-tip force sensor by nanorobotic manipulation and EBID.](image)

Using the nanorobotic manipulation techniques described in chapter 2, we were able to build a flexible experimental environment to test all of our designs in the same conditions. The experimental setup was built inside a Zeiss Ultra55 FESEM at room temperature. In this setup, the material consisting of MWNTs was attached to the SEM sample stage using a conductive silver tape. Two 3-DOF manipulators (Kleindiek MM3A) were mounted onto the stage as well. Two picoprobes (T-4-10-1mm) served as electrodes and picking tools. One of them was fixed but insulated from the SEM sample stage. Another was held in one of the manipulators for picking purposes. Figure 3.7 shows the manipulation sequence to achieve
desired sensor structures. First of all, electron-beam-induced deposition (EBID) was utilized to assemble a selected MWNT onto the free electrode. As discussed in section 2.2.2, we focused the electron beam at 5kV with a magnification of 100,000X on the contact point between the MWNT and the electrode. After 2 minutes, enough amorphous carbon could be deposited on the point and made a strong connection. The same procedure had been used to connect the MWNT to the fixed electrode as well. The telescoping MWNT can be fabricated by mechanical pulling. Parts (a) and (b) of Figure 3.7 clearly show the outermost shell of a MWNT was removed after pulling it from the sample substrate. Figure 3.7 (c) shows the device geometry.

A cantilever deflection method was utilized to characterize the sensors. An AFM cantilever was amounted on another manipulator applied lateral forces on the free end of the MWNT. The forces can be easily derived from the deflection of the cantilever. However, small deflections of a cantilever caused by a few nanoNewton force is difficult to be measured directly inside the SEM, an indirect measurement approach was utilized to estimate it. Figure 3.8 schematically shows the concept of this method. The deflection of the cantilever can be obtained by subtracting the deflection of the MWNT from the driving distance of the manipulator. Since each piezoactuator inside the manipulator responds differently to the driving signals, a careful calibration is pursued to map the exact moving distance for each step in the fine mode for the particular manipulator in the operation direction. Therefore, the driving distance of the manipulator is able to be calculated by counting the number of moving steps. In our experiments, the average moving distance for each fine mode step is 3.5 nm in horizontal direction within the voltage range 30V-46V. The conductivity is measured with a Keithley 6517A Picoammeter with an accuracy of ~1 fA. The voltage is swept from -1 to 1 V, and 101 data points were sampled per sweep. The sweep delay was 0.01 seconds. The resistance was computed from the measured current.

In our experiments, MWNTs were bent by moving the AFM cantilever perpendicular to the tubes. For each sensor design, a series of force versus resistance measurements were performed at different bending states. We used the same MWNT to test the type I and type II force sensors to minimize the influence of diversity of different tubes.
Figure 3.8 Measurement of the AFM cantilever deflection. “a” is the moving distance of the manipulator. “b” is the deflection of a strained MWNT and “c” is the cantilever deflection.

Figure 3.9 Characterization of the Type I force sensor. (a)-(d) SEM images for continues bending process of a MWNT. (e) Sketch of the characterization of a force sensor in the SEM. (f) I-V curves of four bending states of the same MWNT. (g) Resistance vs. force curve.
Type I

An unbroken MWNT was continually bent for the characterization of the type I sensor (Figure 3.9). Figure 3.9 (a) – (d) show a series of SEM images of the bending process from the beginning. Electrical conductivity variations according to the deflection of the MWNT are shown in Figure 3.9 (f) by a series of current-voltage (I-V) curves. Each I-V curve was measured at the corresponding state in parts a-d of Figure 3.9. From Figure 3.9 (g), it can be easily found that the resistance of the tube decreased from 0.98 MΩ to 0.88 MΩ at a 1V bias along with the increasing of bending. This observation agrees well with the electromechanical property reported by Semet et. Al [134] where they attributed the observed drop in resistance during bending to be the result of the increasing number of conduction channels in the nanotube and parallel transport through them. The sensitivity of the sensor can also be measured from the resistance vs. mechanical load curve. When the lateral force was increased up to 9.174 nN, the resistance was reduced by 11.1 %.

Figure 3.10 Characterization of the Type II force sensor. (a)-(e) SEM images for continues bending process of a MWNT. (f)-(g) SEM images for continues releasing process of the MWNT. (h) Sketch of the characterization of a force sensor in the SEM. (i) I-V curves of six bending states of the same MWNT. (j) Resistance vs. Force curves.
A similar process was utilized to test the type II sensor. To clearly compare the performance difference, we used the same MWNT in the Type I experiment. Pulling the tube using the free probe induced mechanical stress which broke the outer shells. Further pulling caused parts of the innershells removed from their outer housing with the front part of the outer shells by van der Waals forces. In Figure 3.10, we can still find the rear part of outer shells on the fixed probe. After the inner shells were connected to the fixed electrode using EBID, the MWNT started to bend. Parts a-e of Figure 3.10 show SEM images of this process. Following the bending process, the MWNT was released from the stress as shown in parts f-g of Figure 3.10. The corresponding changes of electrical conductivity are represented by I-V curves as plotted in Figure 3.10 (i). The resistance vs. mechanical loading force curve is plotted in Figure 3.10 (j).

It can be clearly seen that, similar to type I, the resistance of the MWNT decreased as the mechanical load increased. The sensitivity of this type sensor, however, is much higher than the type I. When the lateral force increased up to 10.209 nN; the resistance of the tube decreased by 44.9 %, which is four times larger than that of type I. Even for a small load with lateral force down to 0.215 nN, the resistance change is still detectable.

A qualitative analysis can also be used to explain the difference of the sensitivity between these two types. Two different electronic transport mechanisms of broken and unbroken MWNTs can be attributes to it. A perfect MWNT can be modeled as a conductor with a number of conductive channels separated by energy barriers. Each channel belongs to one shell which contributes to the overall conductivity. Actually, there are four conductive channels on each shell whose resistance is proportional to the quantum resistance $h/e^2$. Here, we combine the four channels into one. Resistances of each shell are affected by the bond structure, the length and the thermal state of each shell. The energy barriers include the contact barrier and interlayer barriers between the channels prevent electron transition from one channel to another. The contact barrier is determined by the difference between working functions of metal electrodes and carbon nanotubes, while the interlayer barriers are determined by interlayer distances and band structures of neighboring shells. When a bias is applied on a MWNT through metal electrodes, most of low energy electrons likely pass through the channel 0 (outermost shell) to form the drift current. Only the electrons with relatively higher energy are able to overcome the interlayer barriers by radial tunneling or
charge injection [128] to reach inner shells. Because the outermost shell of a MWNT is usually a metallic shell due to its large diameter, it can be treated as a good shield against the applied electrical field. Therefore, the electrons in the inner shells can only form a very weak diffusion current which has little contribution to the conductivity of the tube.

During our experiments the mechanical deformation of a MWNT happened in the front part of the tube. Instead of changing the band structure of the shells bridging between two electrodes, this deformation mainly enhanced the interlayer coupling by narrowing the interlayer distances. In the type I design, the outermost shell of the MWNT kept shorting two electrodes, which means the drift current did not change under the mechanical load. The enhancement of the interlayer coupling only increased the diffusion current. However, in the type II, the fact that electrodes were connected to different shells of a telescoping MWNT means that the interlayer coupling dominated the transport property. Therefore, the conductivity of the MWNT is much more sensitive to the mechanical deformation in our case. We also noticed that when we released the tube, the resistance of the MWNT cannot be restored to the initial value. This is probably attributed to the deposition of amorphous hydrocarbon film on the MWNT during the observation or new defects induced by bending process.

**Type III**

Finally, we preformed the above-mentioned measurement sequence for force sensor type III. Electrical conductivity measurements were executed at four bending states in two directions, as shown in parts a-d of Figure 3.11. The resulting I-V curve can be found in Figure 3.11 (f) and the resistance vs. mechanical load curve is plotted in Figure 3.11 (g). Contrary to the types I and II, this sensor revealed a reverse resistance vs. load dependence. When the deflection of a MWNT increased, the resistance also increased.

This behavior can be easily understood by considering the interlayer sliding in a MWNT. According to the ultra-low sliding friction [35] between the outer and inner shells, the applied transverse force causes a bending coupled with a telescoping behavior of the inner shells during the measurement. Noticed that the intershell interaction between exposed inner shells and their outer housing is weak, which matches the results published in [143, 144]. However, this result cannot be applied to all intershell interactions in MWNTs. In a MWNT, intershell
defects dominated the interaction between two neighbor shells. Only the defect free shells can possess low friction.

Figure 3.11 Characterization of the Type III force sensor. (a)-(c) SEM images for continues bending process of a MWNT. (d) SEM images for bending the MWNT in the opposite direction. (e) Sketch of the characterization of a force sensor in the SEM. (f) I-V curves of four bending states of a MWNT. (g) Resistance vs. Force curves.

As the inner shells slide out from the outer shells, the resistance increases dramatically. From the resistance vs. load curve, we found the sensitivity of this design is higher than type I, but lower than type II. A 6.763 nN load can increase the resistance by 20.1%. However, the measurement range of the sensor in this type is limited because a large force will completely extract the inner shell out from the outer housing.

In conclusion, we found the second prototype is the best candidate to make the functional element in our NEMS-on-a-Tip force sensor. We discovered a solution for the first challenge in the development of such a NEMS-on-a-Tip device.
3.2 Fabrication of Nanoscale Protruding Structures

The second challenge we have to resolve is the development of a nanoscale protruding carrier for the functional element in a NEMS-on-a-tip device. This small part is used not only as a carrier but also as the interface which is employed for exchange of energy and information between NEMS and external systems, such as a control system or a power supply. In addition, this protruding structure can be utilized to facilitate nanomanipulation processes by providing a larger working space and minimizing the influence of support substrates during the manipulation. In this section, we propose a reproducible method to fabricate ultra small protruding electrode pairs (PNEPs) that have nanometric gaps and widths. The overall dimension of a single PNEP is in the range of 300 to 700 nm.

Different methods have been developed to fabricate PNEPs. Nanoelectrodes have been produced by using carbon nanotubes [82] and focused ion beam etching [83]. As we will show in the next section, the yield of these methods is low and the mechanical properties of the resulting electrodes are difficult to be controlled. Recently, Eichhorn et al. [145] developed a new fabrication process which is able to produce PNEPs for four-point-probe measurement of MWNTs with standard microfabrication methods. However, their electrodes can only characterize MWNTs greater than four microns in length.

Compared to existing fabrication methods, our new method utilizes silicon based microfabrication techniques to provide an arbitrary geometric configuration, a high degree of feature size controllability and, importantly, a high production yield. The fabrication process includes several steps of electron beam lithography and dry/wet etching processes. The resulting electrode consists of one metallic bilayer (e.g. 85nm gold/15nm chrome) and one layer of silicon dioxide ($\text{SiO}_2$) underneath. By tuning the etching parameters and the thickness of $\text{SiO}_2$ layer, electrodes with different mechanical properties can be achieved. Using PNEPs, we make a progress towards the commercialization of NEMS on tip devices. Meanwhile, we also demonstrate the use of PNEPs in characterizing the electromechanical properties of a single nanostructure by nanomanipulation.

3.2.1 Fabrication process
To fabricate PNEPs, we tried different methods. The first method utilized a simple focused ion beam (FIB)-based nanofabrication technique for defining electrode pairs with sub 100 nm interelectrode spacing. The fabrication process starts with a 200-nm-thick SiO2 layer created on a Si chip. The chip was horizontally placed into an NV40 FIB workstation. This tool uses a 30 keV Ga+ ion beam for imaging and patterning. First, 10 μm long and 200nm wide platinum nanoelectrodes are deposited on the edge of the chip by a methylcyclopentadienyltrimethyl-platinum precursor. A 40 pA beam current was used for deposition. Then, the chip was turned vertically and a two-step milling (2 nA/60 pA beam current) was used to remove the silicon underneath the electrodes. Finally, the chip was again placed horizontally so that the small interelectrode spacing could be opened by milling. The resulting nanoelectrode pair is shown in Figure 3.12. This is a straightforward method to fabricate nanoelectrode pairs. However, FIB deposition and milling are slow processes which cannot achieve the high yield of electrodes. Moreover, metal deposited by FIB has rather poor electrical properties. Compared to the other metal deposition methods, FIB induces more impurities and defects into the deposited material due to the high energy possessed by ion beam.
In order to overcome these problems, we developed a three-mask fabrication process. The process starts on a 550um thick standard silicon wafer (100) with a relatively high sheet resistance of 1-20 Ω cm\(^{-1}\). The process flow is shown in Figure 3.13. The detailed fabrication steps are listed in Table 3.1:

**Table 3.1. Process steps of three-mask nanoelectrodes fabrication**

<table>
<thead>
<tr>
<th>Process Step</th>
<th>Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grown SiO(_2) by thermal oxidation</td>
<td>136nm SiO(_2) is grown on the silicon wafer using a thermal oven (ATV PEO 603). The process is executed at 950°C using gas mixture (15% N(_2) 85% O(_2)) for one hour.</td>
<td>The thickness of SiO(_2) cannot be access 140nm. Otherwise the layer cannot be patterned using PMMA soft mask by RIE.</td>
</tr>
<tr>
<td>Chip dicing</td>
<td>Wafer is diced into 2.5×2cm chips.</td>
<td></td>
</tr>
<tr>
<td>Spin coating of AZ 5214E</td>
<td>1.5 micro thick AZ 5214E</td>
<td></td>
</tr>
<tr>
<td>Process Description</td>
<td>Details</td>
<td></td>
</tr>
<tr>
<td>----------------------------------------------------------</td>
<td>-------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Image reversal photoresist</td>
<td>Coated on the chip @ 3000 rpm for 40 seconds.</td>
<td></td>
</tr>
<tr>
<td>UV exposure with Karl Suess MA6 mask aligner</td>
<td>Flood exposure / vacuum contact / 402nm / 60s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A large mask is used to protect the device area.</td>
<td></td>
</tr>
<tr>
<td>Resist development</td>
<td>60s in AZ826 MIF</td>
<td></td>
</tr>
<tr>
<td>UV exposure with Karl Suess MA6 mask aligner</td>
<td>Vacuum contact / 402nm / 48 mJ per CM2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Patterning the contact pads and EBL marks</td>
<td></td>
</tr>
<tr>
<td>Reverse backing of AZ 5214E on hotplate</td>
<td>120°C / 45s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reverse backing turns the AZ 5214E to negative resist</td>
<td></td>
</tr>
<tr>
<td>UV exposure with Karl Suess MA6 mask aligner</td>
<td>Flood exposure / vacuum contact / 402nm / 20 sec</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reverse exposure</td>
<td></td>
</tr>
<tr>
<td>Resist development</td>
<td>28 sec in AZ826 MIF</td>
<td></td>
</tr>
<tr>
<td>O2 plasma treatment</td>
<td>150W / 60 sec</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Removing the residual of photoresist</td>
<td></td>
</tr>
<tr>
<td>Metal deposition with the Univex500 system</td>
<td>15nm Cr (@ 1 A/sec) and 185nm Au (@ 2 A/sec)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>E-beam evaporation of metals</td>
<td></td>
</tr>
<tr>
<td>Lift-off</td>
<td>1. 60 min dip in NMP at 50°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2. 2 min rinse in cold acetone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3. 2 min rinse in cold IPA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4. DI water rinsing</td>
<td></td>
</tr>
<tr>
<td>Spin coating of PMMA EBL resist</td>
<td>220nm thick PMMA is coated on the chip</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PMMA 4:1 in CL @ 700 rpm 2 sec / 3500 rpm for 42 sec.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Since the chip size is small and in the rectangle shape, a pre-spinning is necessary to form the uniform coating.</td>
<td></td>
</tr>
<tr>
<td>Step Description</td>
<td>Details</td>
<td>Notes</td>
</tr>
<tr>
<td>------------------</td>
<td>---------</td>
<td>-------</td>
</tr>
<tr>
<td>Raith150 EBL exposure with alignment to contact pads</td>
<td>10 µm Aperture / 30kV / 400µC per cm² / Threshold algorithm based detection of L-shaped alignment markers.</td>
<td>Exposure of the nanoelectrode (50-200nm width with a 200nm separation) pattern, fine L-shape etching marks (50nm width) and I-shape cutting marks (4um×20um) from a mask file.</td>
</tr>
<tr>
<td>Resist development</td>
<td>1:3 MIBK:IPA for 58 secs</td>
<td>Formation of the nanoelectrode pattern in the resist stack. The PMMA layer has an undercut due to over-development.</td>
</tr>
<tr>
<td>Metal deposition with the Univex500 system</td>
<td>15nm Cr (@ 1 A/sec) and 85nm Au (@ 2 A/sec)</td>
<td></td>
</tr>
</tbody>
</table>
| Lift-off | 1. 60 min dip in NMP at 50°C  
2. 2min dip in NMP with ultrasound burst  
3. 2min rinse in cold acetone  
4. 2 min rinse in cold IPA  
5. DI water rinsing | The power of ultrasound must be very low; otherwise, there is a possibility to destroy the metal layer. |
<p>| Spin coating of PMMA EBL resist | 240nm thick PMMA is coated on the chip PMMA 4:1 in CL @ 700 rpm 2sec / 3800 rpm for 40 sec. | The PMMA layer serves as a soft mask in the following RIE etching. Therefore, a thicker layer is performed. However, the thicker resist layer will reduce the resolution of EBL. 240nm is the optimal value from my observations. |</p>
<table>
<thead>
<tr>
<th>Process Description</th>
<th>Conditions</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raith150 EBL exposure with alignment to contact pads</td>
<td>10 µm Aperture / 30kV / 400µC per cm² / Threshold algorithm based detection of L-shaped alignment markers.</td>
<td>Patterning the etching mask for removing SiO2 layer using the pre-defined marks.</td>
</tr>
<tr>
<td>Resist development</td>
<td>1:3 MIBK:IPA for 55 secs</td>
<td>Formations of the etching mask using the resist stack. The PMMA layer has an undercut.</td>
</tr>
<tr>
<td>Reactive ion etching with Oxford Plasmalab 100</td>
<td>150mins CHF3 etching. Details see below.</td>
<td>Removing the SiO2 layer between and near the electrodes</td>
</tr>
<tr>
<td>Ozone treatment</td>
<td>20mins Ozone in room temperature</td>
<td>Removing the byproduct produced in RIE etching</td>
</tr>
<tr>
<td>Dicing chip</td>
<td>30000 rpm</td>
<td>Dicing each device from the chip according to the cutting marks so that the electrodes are located at the edge of a silicon chip</td>
</tr>
<tr>
<td>KOH etching</td>
<td>15min / 30% KOH / 70°C</td>
<td>Removing silicon underneath the electrodes from top/side</td>
</tr>
</tbody>
</table>
**Critical fabrication steps**

1) **Precise alignment for etching mask pattern in EBL**

Since it is not allowed to use metal based hard masks for RIE etching in our cleanroom, we have to choose PMMA as etch mask to remove the SiO₂ around the electrodes. In order to protect the metal layers of electrodes, the PMMA mask have to be precisely aligned on the top of each electrode. Otherwise, the ion beam for RIE will attack the uncovered gold, which produces rough electrode edges and some polymeric byproducts. This is a big challenge due to the small size of electrodes (100 to 150nm). Due to the asymmetric intensity distribution of electron beam and magnification based current drifting, standard automatic EBL alignment procedures can only provide 30nm alignment accuracy. We used a manual alignment procedure which is based on a three-level alignment in single writefield to achieve the precise alignment. The alignment error was less than 15 nm in our case.

2) **RIE based SiO₂ removing using PMMA mask**

As mentioned, we use PMMA as etch mask for RIE etching. In general, as a negative photoresist, PMMA isn’t a good material for making RIE mask for SiO₂ etching. It has relatively low etching selectivity between PMMA and SiO₂ when standard O₂/CF₄ or O₂/CHF₃ mixture is used as etching precursor. Therefore, a special process is developed in order to increase the selectivity. We use CHF₃ as etching precursor and the process is executed in a high pressure (300 mbar) with large flow rate (60 sccm). This process maintains a high concentration of F⁺ which is the etchant of SiO₂. In the meantime, it avoids the formation of volatile etch products of CO, CO₂ and H₂O. The large flow rate is to remove the unstable compounds formed by F residuals in the process. Using this new process, the etching selectivity of PMMA : SiO₂ is 2 : 5.

As results, in

Figure 3.14, SEM images show different PNEP configurations. Final chips are glued on a PCB board using hot pure PMMA/MAA copolymer to make NEMS-on-a-tip devices.
Interconnections between the chips and PCBs are made by wire bonding. The complete devices are shown in Fig 3.15.

Figure 3.14 SEM images of PNEPs with different geometries. (a) Two-finger PNEP. (b) Four-finger PNEP (90°). (c) Four finger PNEP (105°).
3.2.2 Mechanical properties of PNEPs

Multilayer Au/Cr/SiO₂ beams are the basic structures in PNEPs. In order to use them in NEMS-on-a-tip devices or characterizing physical properties of a target nanostructure, the mechanical properties of these beams have to be investigated. FEM simulation was performed to extract the Young’s modulus of this structure. The simulated structure is an Au/Cr/SiO₂ beam with dimensions 2 μm in length, 150 nm in width and 236 nm in thickness (85nm/15nm/136nm for each layer) as shown in Figure 3.16. The result shows the Young’s modulus of the beam is 80GPa. We also experimentally investigated the intrinsic stress caused curvatures for different PNEP configurations. This experiment has been done inside SEM. Figure 3.17 shows the front of view of two PNEPs. Curvatures can be clearly seen in Figure 3.17 (a). The length of each beam in this configuration is in the range of 1.2 to 3.4 μm. The largest displacement of the free end of a beam is measured to be 183nm. However, there is no observed curvature presented in the Figure 3.17 (b). The top view of this PNEP has been shown in
Figure 3.14(b) where the longest beam is 1 µm. When a 1D nanostructure is to be integrated on a PNEP, the curvature has to be taken into account in order to minimize the pre-deformation of the structure and the contact resistances.

Figure 3.16 FEM simulation of bending formability for a protruding Au/Cr/SiO2 tri-layer electrode.
3.3 Characterization of MWNTs Using PNEP

3.3.1 Multishell Electron Transport in MWNTs

A PNEP can facilitate the electromechanical characterization process of individual nanostructures. To demonstrate this ability, we use four-finger PNEPs combining with SEM based nanomanipulation to investigate multishell conduction problem in an individual MWNT. In this section, we present an experiment in which we directly measure the electron transport property of an individual MWNT before and after removing its inner-shells while keeping the electrical contact states constant. Using PNEP, we can minimize CNT damages.
caused by other electrical measurement methods, such as structural defects introduced by EBL and mechanical deformation caused by strong van der Waals force between the large substrate and tube. Therefore, we can perform a nondestructive test on target MWNTs.

Figure 3.18 Experimental setup for multishell conduction measurement using four-finger PNEP and SEM based manipulation.

In order to avoid the effect of electrical contact resistance, we adapted a four point probe I-V electrical measurement. The setup was similar to the system mentioned in section 2.2.1. Figure 3.18 shows the setup. A PNEP was integrated on a PCB and fixed on the sample stage of the SEM. The PCB was connected to an external electric measurement unit through a custom made feedthrough. To minimize charging effects, the PCB was coated by silver paint. Figure 3.19 shows the manipulation sequence to perform the experiment. First, a selected MWNT was picked up by the tungsten probe using EBID, as shown in Figure 3.19 (a). A similar procedure was used to connect the MWNT to the PNEP, as shown in Figure 3.19 (b). The MWNT was successively connected to the electrodes from the lowest one to the highest one. To make sure the tube had been successfully connected to each electrode, we slightly moved the CNT to check if there was deformation on the tube after each connection. Then,
we were able to remove the innershells by mechanical pulling. Figure 3.19 (c) and (d) clearly show the process in which the outermost shell was broken and the innershells were extracted from the housing.

Figure 3.19 Manipulation sequence of removing inner shell of a MWNT. The resistance of tube was measured by four-point-probe method before and after the inner shells was removed.

The resistance of the tube was measured on different currents in two states: 1) the unbroken tube (Figure 3.19 (b). 2) tube with less innershells (Figure 3.19 (d). The applied current is increased from 1 µA to 40 µA with 5 µA stepwise for each state. The corresponding resistance is recorded by a Keithley 2700 multimeter. During the electrical measurement, the electron beam of SEM was shut down. Resulting R-1 curves are found in Fig 3.20. First, it shows a resistance increasing after the inner shells was removed. The resistance of the tube
was increased from 41.23 KΩ to 47.9 KΩ. It can also be found that the resistance of the tube was decreased when the applied current increased. This relationship was observed in both unbroken tubes and tubes without innershells. However, it was more obvious for the unbroken tube. Moreover, the difference of resistances increased with the increasing of applied currents. Similar results were obtained for two other tubes. However, there was also one tube on which no obvious resistance difference was detected. It could be explained by examining the number of remaining shells on electrodes. When the number is larger, the current difference is smaller. According to the electron hopping theory, outer shells always have more contribution to the overall conductivity than the inner ones, especially on the low bias range [48, 146].

![Figure 3.20 Resistance vs current plot for a MWNT with and without some inner shells](image)

The main result of this section shows that the transport characteristics of MWNTs change between the low- and high-current regimes. It is indicated that for low current, the conductivity of a MWNT is mainly determined by the current carried on the outermost shell while for high current, the conductivity of the tube is determined by the current carried on both outer and inner shells. This result perfectly matches the theoretical calculation in ref. [136]. When the current or applied bias is high enough, electrons not only move along the outermost shell but also move in the radial direction of the tube by electron hopping effect in the intershell spacing. It results in the contribution of some inner shells to the overall conductivity. Based on the Landauer-Buttiker model, each involved shell has only four
conductive channels. When a few of such shells are removed from the electrodes, electrons can only transport along the conductive channels in the remaining outer shells. Therefore, the overall conductivity of the tube is reduced. This is the first experiment that measures the conductivity change of an individual MWNT before and after removing the inner shells with an unchanged electrical contact state. The result provides direct evidence to confirm the multishell conduction of MWNTs as proposed in reference [135, 137].

3.3.2 Electromechanical Coupling of Telescoping MWNTs

Figure 3.21 Manipulation sequence of electromechanical coupling measurement of a telescoping MWNT.

Using the same experimental setup, we also investigated the electromechanical coupling property of a telescoping CNT. Figure 3.21 shows the operation sequence of this work. In this experiment, a single MWNT was connected on a four probe PNEP for resistance measurement, as shown in Figure 3.21 (a). Electrode 1, 2 and the probe were ground. After the first measurement, the outer shells were removed to create a telescoping tube and the
exposed innershells were connected to electrodes 1 and 2 so that the broken site was located at the gap between electrodes 2 and 3, as shown Figure 3.21 (b). Then, a tungsten probe was used to push electrode 1 up and down in order to repeatedly bend and release the tube, while the conductivity of the tube was measured again. Figure 3.21 (c) shows the SEM image when the tube was bent; (d) shows image when the tube was released from bending. A 20 µA current was applied to measure the resistance under different deformation conditions. The results show that the resistance of the tube was decreased up to 24% when the tube was bent. After the tube was released, the resistance went back to the original value (see Fig 3.22).

![Resistance of the tube](image)

**Figure 3.22** Reversible resistance change of a telescoping MWNT under different mechanical deformation state.

This result shows a strong piezoresistive behavior of a telescoping MWNT. Furthermore, compared to our previous results in section 3.2, this one is more reliable. First, the four point probe measurement minimized the effect of contact resistance. Second, the repeatability of the piezoresistive behavior was much better than previous results. This result shows the possibility to design and fabricate new force sensors based on telescoping MWNTs. The new sensor should include at least one tube as functional element that is connected to a small, freestanding microfabricated beam on which the external force can exert.
3.4 Summary

The concept of NEMS-on-a-Tip has been presented as a complement to NEMS-on-a-chip for applications requiring a protruded probe. Compared to other architectures, NEMS-on-a-Tip has several advantages: 1) NEMS-on-a-Tip allows bringing the tool to the sample, rather than bringing the sample to the tool. This is convenient for a combination with an AFM or a nanomanipulator for in situ probing multiple objects or areas with a same tool. 2) With a protruding architecture, NEM-on-a-tip can be used for the investigation in a narrow feature such as a trench on a surface, which is not attainable by NEMS on a chip. With a built-in sensor, it is more advantageous than a sharp AFM tip. 3) NEMS-on-a-Tip is more compact in dimensions. It is possible to integrate them into micro- to nano-sized independent/automate systems to enhance their performance.

As examples, force sensors based on the electromechanical coupling property of an individual telescoping MWNT have been designed, fabricated and characterized. Two major challenges in this work have been solved. First, the electromechanical coupling property of shell engineered MWNTs have been intensively studied. Quantitative results show that this kind of tube has strong piezoresistive properties. Therefore, it is a good candidate not only for force sensors but also for many other NEMS-on-a-tip devices. Second, ultra-small protruding electrode pairs have been fabricated as carriers and interfaces for NEMS-on-a-tip device integration. These small electrodes have also been used to enhance the ability of nanomanipulation based nanostructure characterization.

The multishell electron transport property has been experimentally studied and the contribution of inner shells to the overall conductivity of a MWNT has been concluded. Results show that the contribution of the inner shell conductivity is determined by geometry, mechanical deformation and the external field applied on the tube. Meanwhile, the electromechanical coupling property of telescoping MWNTs has been also investigated. The result clearly shows a strong piezoresistive behavior in telescoping MWNTs. In order to utilize the property to its full potential, a CNT/nanobeam structure has been proposed for future sensing applications.
4 Synthesis and Characterization of Ferromagnetic Filled Carbon Nanotubes

In the previous chapters, we described methods for construction of various shell structures in MWNTs in order to extend their applications in sensing and actuation. In this chapter, we present a simple but efficient method to fill CNTs with different ferromagnetic materials. Recent development of various magnetic filled carbon nanotubes (MFCNTs) has stimulated the research on their applications in diverse fields. Especially, MFCNTs may be the most important building blocks for nanomedicine applications [78, 147]. For instance, they have the potential to carry drugs in the organism as they are much smaller than blood cells and can be easily functionalized by a broad range of chemical methods [63, 64, 68]. In order to turn these ideas into reality, three challenges have to be solved. First, a batch synthesis method must be found to efficiently produce MFCNTs with predefined geometry and magnetic filling ratio. Second, a reliable method should be developed to attach DNA or protein molecules on the surface of nanotubes so that the tubes can be functionalized as drug carriers. So far, many methods have shown their efficiency to achieve this aim [81, 148-150]. Finally, a wireless control system is required to control the location and movement of MFCNTs inside human body in order to guide the tubes to a target organism. Among these challenges, batch synthesis is the most important and fundamental one.

In this work, electrochemical deposition and chemical vapor deposition (CVD) techniques have been combined to produce ferromagnetic filled CNTs (FFCNTs) with controlled physical properties. The structural, mechanical and electrical properties of resulting tubes have been investigated by various characterization methods.

4.1 Synthesis Carbon Nanotube Filled with Ferromagnetic Materials

Many methods have been developed to obtain magnetic carbon nanotubes. Open-end magnetic CNTs can be synthesized by filling magnetic particles into a open-end CNT with large diameter [151]. However, the open-end feature impedes the tube to be further functionalized by chemical methods. FFCNTs can be obtained during the CNT growth process. In-situ filling of nickel, iron and cobalt has been achieved using solid or liquid source
chemical vapor deposition [152-155]. The resulting CNTs show long and continue metal filling inside the tube. However, these methods cannot control the tube’s geometry and achieve uniform filling rates for every tube. The uniformity of tube geometry and filling rate is crucial to their biomedical applications, especially target drug delivery. In order to remotely move a group of FFCNTs to approach target organisms, magnetic force is exerted on the tubes by external magnetic fields. For every FFCNT in the group, its geometry and filling rate decide how much driving and resistance force it can have. Controlled group movement only can be achieved when all the group members share the same geometry, size and filling. In order to produce such FFCNTs, we have developed a template based method to grow nickel/iron filled CNTs. The similar method can also be easily extended to grow CNTs filled other transition metals or their alloys.

4.1.1 System Selection for Carbon Nanotube Growth

We use the chemical vapor deposition technology to grow FFCNTs. CVD is a convenient method for the synthesis of different types of CNTs ranging from single-walled to the multi-walled CNTs with or without metal filling[156-158]. The method is suitable to produce large quantities with satisfactory quality and allows a scaling-up with moderate cost for industrial mass production. In the CVD process, chemical reactions take place which transforms hydrocarbon precursors into solid CNT walls on the surface of a substrate. It is a catalytic process where a catalyst (in this case a transition metal) is involved to control the kinetics of reactions such as the decomposition of the precursor.

Various configurations have been employed for chemical vapor deposition: thermal reactors, linear injector reactors or reactors with plasma enhancement. Thermal furnaces which consist of a horizontally or vertically aligned heated-tube with a gas in- and outlet are the most often used equipment for CNT growth. The tube is heated by electric heater and the gas pressure in the tube can vary between some fractions of an mbar (LPCVD) to some bar. In general, catalyst size, reaction temperature, time and pressure are the major factors which affect the result of CNT growth. In our case, the size of catalyst cannot be changed too much. The reaction temperature, time and pressure are the parameters we can adjust to optimize the growth process.

Linear injector reactors are used in an open system at atmospheric pressure (APCVD), which employs high gas velocities to achieve short residence time. By using multiport injection to
prevent mixing of the reactant gases until they are dispensed into the deposition region, this type of reactor is able to use highly reactive mixtures at atmospheric pressure while achieving good CNT quality.

Plasma enhanced CVD (PECVD) is another important tool for CNT growth [144]. In PECVD, a radio-frequency (RF) source excites electrons in an electromagnetic field set up between the top electrode and the grounded substrate. The excited electrons collide with precursors to form ions, reactive neutrals or plasma. The frequencies usually lie between some kHz and some MHz. An advantage of PECVD is the ability to deposit at much lower temperatures and pressures than would be required for thermal CVD for CNT growth. It also provides a possibility to control the orientation of the tube. A disadvantage is usually a higher concentration of defects on the created CNTs and a lack of uniformity over larger surface areas. Moreover, in our case, our catalyst is embedded into the AAO template which can be easily etched by PECVD unless a very low power is used to excite the plasma. The etching process runs parallel with the decomposition process of carbon precursor, which prevents the decomposed carbon atoms to form CNT walls. Therefore, PECVD is not a practical tool for us.

4.1.2 Synthesis of Open-end Carbon Nanotubes Filled with Iron Nitrate Nanoparticles

Our first idea of synthesis FFCNTs with predefined geometry was to grow them inside an anodic aluminum oxide (AAO) template whose pores were pre-filled with iron nitrate particles. Fe/Al₂O₃ nanocomposite can be used as catalyst for CNT growth [159, 160]. Based on this fact, we assumed that iron would appear inside resulting CNTs if there were enough iron nitrate particles inside the template. These particles were reduced to iron by a high temperature hydrogen treatment and then served as catalyst to together with Al₂O₃ for CNT growth. The shape of resulting CNTs should be determined by the pore size of AAO template. The filling rate of iron should be determined by parameters for hydrogen pretreatment and CNT growth.

The synthesis process started with a commercial available AAO template (60 um thick Whatman Anapore Filter with 200 nm diameter pores) which was placed on a clean glass plate. A drop of Iron nitrate solution (10% in weight) was dripped and covered the template. The template was left in room temperature until the solvent was fully evaporated. This coated
sample was turned face down and placed inside a LPCVD (Centrothermo ATV PEO 603) for CNT growth.

![SEM images of CNTs grown from AAO template filled by iron nitrite nanoparticles. (a) as-grown CNTs on AAP template. (b) A broken CNT on Si substrate after removing the template.](image)

The CNTs were grown with a methane (CH₄) precursor in a horizontal quartz boat which was located in a large furnace with a volume of 15.37 dm³. The following growth condition was utilized in our process. The furnace was firstly ramped up to 850 °C in air in 10 minutes. After reaching the temperature, it was stabilized for 5 minutes while the furnace was pumped down until the chamber pressure reached 2.1 mbar. Then, H₂ was supplied with the flow rate 3 slm. The gas was switched off after 31 seconds to maintain the pressure to 300 mbar. The H₂ environment was kept for 12 minutes in order to remove the oxidation layer and active the surface of Ni nanowires. H₂ was then removed from the furnace and 0.2 slm H₂ and 1slm CH₄ were introduced into the chamber for 41s and 37s, respectively, to get the mixture gas for CNT growth. After 80 minutes CNT growth, the chamber was pumped again to remove the residual gas. Finally the chamber was purged with N₂ and cooled down to room temperature. The final sample was firstly checked by SEM, and then immersed into a 20% by weight aqueous NaOH solution in order to dissolve the alumina. However, the phase of alumina appeared to be transformed from γ to α which made the alumina was difficult to be dissolved. In order to enhance the dissolving ability, we treated the solution with ultrasound bath at 50°C for 1 hour. Then, the sample was treated by buffered HF (BHF) for 5 minutes at room temperature. After removal of the alumina template, resulting CNTs were rinsed in DI water to ensure complete removal of etchants. The final CNT suspension was placed on a silicon
chip and dried for SEM investigation. The Figure 4.1 shows the results. Some long CNTs come out from the template vertically (as shown in Figure 4.1 (a)). However, after the template was removed, only a few broken CNTs were found on the silicon chip (as shown in Figure 4.1 (b)). No obvious filling had been found. It was also noticed that most resulting CNTs were broken. Small pieces of CNT shell could be found in Figure 4.1 (b) as well. The tubes might be broken by HF etching or ultrasound treatment. For CNTs with good crystalline structure, neither HF nor short ultrasound would destroy them. This fact indicated that our tubes were constructed by amorphous carbon instead of graphene layers. From these results, we can conclude that this method cannot produce good FFCNTs as we expected. Another method must be pursued to produce high quality FFCNTs.

4.1.3 Synthesis of Carbon Nanotubes Filled with Nickel Nanowires

![Figure 4.2 Schematic drawing of the synthesis process of Ni filled CNTs.](image)

A second approach was to cover carbon lays on ferromagnetic nanowires grown inside an AAO template in order to produce CNTs filled with a ferromagnetic nanowire. The schematic diagram of this method is shown in Figure 4.2. The diameter of CNTs was confined by the pore size of AAO template while the geometry of nickel filling was determined by the shape of original nanowires and the CNT growth conditions. In addition, the resulting CNTs should be vertically aligned on a silicon chip with small gaps, as shown in Figure 4.2 (d). This feature prevents the formation of CNT bundles which were commonly found in CNTs grown by CVD.
4.1.3.1 Fabrication of AAO Templates and Nickel Nanowires

Figure 4.3 Top view SEM image of an AAO template. The diameter of pores is in the range of 80 to 90nm.

In this process, we started with a clean silicon chip. 6nm titanium and 12nm gold were deposited on the chip using electron beam evaporation for adhesion and conduction purposes, respectively. Then, an 800nm to 1.2um thick aluminum layer was evaporated on top of the chip for electrochemical anodization. This step was important and a high vacuum condition was expected during the deposition in order to reduce the intrinsic stress of the thick aluminum layer. Anodic aluminum oxide templates were prepared using a one-step anodization process. The chip was anodized in a 0.3M oxalic acid solution at 5°C with a constant supplied voltage of 40V while the electrolytic was monitored by a lab-view program through a GPIB interface. Initially, electrolytic current decreased rapidly from the original peak value to a minimum, and then rose to reach the highest value where the progress should be stopped. Anodization process can be divided into several steps. In the first step, the electrochemical reaction makes a uniform oxide form. The conductivity of the aluminum changes from the high conductive state to the low conductive state. Therefore, the current decreases rapidly. In the second step, the pores nucleate randomly on the oxidation membrane and in the later step pores grow gradually. The process is halted when the current ranges from 0.1-0.25 Amps to decrease the barrier layer thickness, otherwise the growth of nanowires is
not possible. After the anodization, the pores of the AAO template were widened by dipping the chip into a 0.1M phosphoric acid solution for 15 min. Resulting AAO template can be seen in Figure 4.3.

Figure 4.3 SEM images of electrodeposited Ni nanowires inside AAO template. (a) top view image (b) cross section image.

The electrodeposition of Ni had been carried out galvanostatically with a pulse mode. The pulsed electrodeposition had been applied due to its reliability for filling metals into high aspect ratio structures, such as the AAO layer [147]. Before the process got started, the

Figure 4.5 Top view SEM image of vertical aligned Ni nanowire array
sample was immersed into a Watts nickel bath and served as cathode. During the process, a sequence of current controlled galvanostatic pulse with a relatively high current density was employed. An anodic pulse (potentiostatic, voltage control) with a set-point voltage of 3-5 volts had been applied to prevent damage to AAO pore structure since formation of hydrogen became dominant for PED. With the anodic pulse, the electrodeposition stopped and discharged the capacitance of barrier layer in order to deplete the impurities. Finally, a rest phase of 600ms was utilized to reload the metal ion concentration at the electrodeposition sites. Finally, the AAO template was removed by 10% NaOH and vertically aligned nanowires had been obtained.

SEM images of grown Ni nanowire arrays are shown in Figure 4.4 and Figure 4.5. It can be observed from the Figure 4.5 that the Ni nanowire arrays have been grown uniformly in a relatively large area even though there are a few regions where the nanowires are absent. The density of Ni nanowires is found to be about 10\(^{10}\) cm\(^{-2}\) and all the nanowires are self-standing. The inset shows a close view image of the nanowires. The density of nanowires should be close to the pore density of the original AAO template, meaning most of the pores are filled by nanowires, as shown Figure 4.4 (a). Figure 4.4 (b) shows a cross section view of nanowires inside AAO template. It can be seen the diameter of the nanowires is about 90 nm and the length is about 360 nm. All the nanowires share the same shape and volume.

4.1.3.2 Synthesis of Ni Filled Carbon Nanotubes using LPCVD

The Ni filled CNTs were grown with a CH\(_4\) or C\(_2\)H\(_2\) precursor in LPCVD system (Centrothermo ATV PEO 603). It is noted that the sample should be prepared with pre-deposited Ni nanowires embedded inside the template. Before putting the sample into the CVD system, it was cleaned in IPA in order to remove the residuals from the electrolytic bath. When the CH\(_4\) was utilized as a precursor, the same CNT growth process as described in section 4.1.2 was used to produce FFCNTs.

When C\(_2\)H\(_2\) was used, a different growth condition was applied. The temperature ramping-up and catalyst reduction processes are similar to the previous one. The only difference is the final temperature is 700\(^{\circ}\)C instead of 850 \(^{\circ}\)C. After H\(_2\) was removed from the furnace, and 1 slm H\(_2\) and 0.5 slm C\(_2\)H\(_2\) (10% in Helium) were introduced into the chamber for 37 s and 42s, respectively, to get the mixture gas for CNT growth. The final C\(_2\)H\(_2\): H\(_2\) ratio in the mixture was 1: 20 in volume and the chamber pressure were be maintained at 200mbar during the
whole deposition. After 60 minutes, the chamber was pumped again to remove the residual gas. Since \( \text{C}_2\text{H}_2 \) is a highly concentrated carbon source and can be decomposed in rather low temperature, byproducts, such as amorphous carbon, can be generated during the growth process. Therefore, \( \text{H}_2 \) was again introduced into the chamber with 3 slm for 20 seconds and reacted with the sample for 60 mins at 300 mbar and 700 °C. This additional step aimed to remove the byproducts by transforming amorphous carbon into \( \text{C}_n\text{H}_n \) gases. Then, gases were removed. The chamber was cooled and purged by N2 flow.

### 4.1.4 Results and Carbon Nanotube Growth Mechanism

#### 4.1.4.1 Carbon Nanotubes Grown by CH\(_4\) Precursor

![SEM image of Ni filled CNTs grown by CH\(_4\) standing on the substrate with the AAO template.](image)

One major problem associated with CH\(_4\) based CNT growth was the use of a high temperature. Due to very strong C-H bonds in methane molecule (440 kJ/mole) its non-catalytic thermal decomposition occurs at very high temperatures (>1200°C). Although transition metal catalysts, Ni in our case, can be used to reduce this temperature, 850 °C is still needed to efficiently decompose CH\(_4\) in our work. As previously mentioned, after such a high temperature treatment the AAO template could not be easily removed, especially when the template was attached onto a silicon chip. Figure 4.6 shows an overall SEM image of produced nanotubes obtained for 30 mins deposition. The length of the tubes is in the range of
1 to 15µm. The following features can be noted from this image. First, the CNTs are straighter than commercial CNTs grown by CVD. This fact might indicate the lower concentration of defects in our CNTs. These tubes are vertically aligned according to the substrate, which is advantageous over the random orientation of the carbon nanotubes prepared by standard CVD method. Second, as we expected, the CNTs have the same outer diameter as that of the pores of the template.

Figure 4.7 High resolution SEM image of Ni filled CNs. Bright parts show the location of Ni filling.

Moreover, the Ni filling was also observed by increasing the acceleration voltage of the SEM to 30KV. Fig 4.6 shows a high magnification SEM image of nickel filled inside a CNT, where the contrast clearly distinguished these two materials. We found the nickel filling was distributed into several parts with the total length 200 to 400 nm. The diameter of the filling varied from 40 to 60 nm. The carbon layer was about 30 nm thick. It was also interesting to find the thickness of carbon layer was quite uniform while the diameter of nickel changed a lot. It indicates that the morphology of the tube was determined by the shape of Ni, as shown in Fig 4.7. The separation of nickel parts might be caused by high partial pressure during the
growth and could also mean the tip growth mechanics which will be discussed in Section 4.1.5.

Figure 4.8 Close view images of a Ni filled CNT. The morphology of the tube is determined by Ni part.

Figure 4.9 SEM image of Ni filled CNTs released from AAO template by BHF etching
Various methods have been tried in order to release the Ni filled CNT from AAO template. The only method which can dissolve α phase alumina is using hydrofluoric acid (HF). The AAO template can be removed by 15 minutes buffered HF (1:50 HF: NH₄F) treatment. However, only a few CNTs can be found after this treatment, and Figure 4.9 shows one of them. It is because HF may etch not only alumina but also CNTs when they have high concentrated defects.

In order to investigate the materials composition of our FFCNTs, we used energy dispersive microanalysis of X-ray spectroscopy (EDX). It is a technique used for identifying the elemental composition of the sample, or an area of interest. The EDX system works as an integrated feature of a SEM and cannot operate on its own without the latter. During EDX Analysis, the specimen is bombarded with an electron beam inside the SEM. The interaction between the bombarding electrons and the specimen released certain amount of energy by emitting an X-ray. The amount of energy depends on the electron configuration of the elements in the sample. Thus, by measuring the amounts of energy present in the X-rays, the identity of the atom from which the X-ray was emitted can be established. The output of an EDX analysis is an EDX spectrum which is a plot of how frequently an X-ray is received for each energy level. An EDX spectrum normally displays peaks corresponding to the energy levels for which the most X-rays had been received. Each of these peaks is unique to a single element. The higher a peak in a spectrum, the more concentrated the element is in the specimen (quantitative EDX analysis).

Figure 4.10 shows the EDX spectrum of Ni filled CNT grown by CH₄. To minimize background noise, we used spot scanning mode of SEM while the energy of X-ray was collected. As shown in the inset of Figure 4.10, the electron beam only illuminates the selected region where the filling can be clearly seen. Nickel is able to be identified from the result. The other materials, such as aluminum, gold and silicon were from the substrate where the CNT was located.

Although CH₄ based CNT growth provides good results, we cannot remove the CNTs efficiently from the substrate. In order to solve this problem, the growth temperature must be low. Therefore, C2H2 is a more suitable precursor for us.
Figure 4.10 EDX spectrum of Ni filled CNT. The peak of Ni can be seen. The inset is showing the tube onto which the spectrum was obtained.

4.1.4.2 Carbon Nanotubes Grown by C₂H₂ Precursor

Figure 4.11 SEM images of template free Ni filled CNTs grown by C₂H₂.

Using C₂H₂ as precursor, we could grow Ni filled CNT at lower temperature (650°C to 700°C). This allowed us to remove the AAO template after the CNT growth. The template can be completely removed by immersing the final sample into 10% NaOH at 50°C for at least 1 hour. Figure 4.11 (a) and (b) show SEM images of CNT obtained for 1 hour deposition. Compared to the CNTs obtained by CH₄, we found there were several major differences presented in the new tubes. First, the density of CNTs was much higher. Figure 4.11(b) shows a 45° view of vertical aligned Ni filled CNTs on substrate. The density could be calculated by accounting the number of CNTs in a unit area, which results in the density of 100 CNTs / µm².
Second, the lengths of resulting CNTs were much shorter than the CH4 ones. The typical length of the new CNTs was in the range of 800nm to 3 μm. For all the CNTs we obtained, the lengths do not vary too much. Statistically, we found the length of 80% tubes is shorter or equal to 1 μm. No extreme long tube was found. Third, the diameter of each nanotube was quite uniform along the tube axis. The surface of individual tubes was very smooth. However, we also found a lot of wrinkles on the top end of CNTs, as shown in Figure 4.11 (a). With higher magnification, we found there were some carbon films which were attached on the surface of our Ni filled CNTs. I believe the reason of the presence of these carbon films is the existing of unexpected nickel layer which was attached on the surface of AAO template. This layer might be the residual of the nickel bath.

![Figure 4.12 SEM images of longer Ni filled CNTs. grown by C2H2. The Ni filling can be seen by contrast differences and the filling are not continue](image)

Two modes were found with regard to Ni filling. 1) In most nanotubes, Ni filling continued and the diameter of the filled nanowire did not change, as shown in Figure 4.12 (a). The Ni wire completely filled the inner space of the tube. The diameter of the nanowire was quite uniform expect the tip where the diameter shrunk. 2) There were a few nanotubes that did not have continuous filling. The Ni parts were mainly located at the tip and base region of the tube, Figure 4.12 (a) shows such a tube. In this image, only the tip filling can be seen. However, this kind of tip and base filling can be confirmed by TEM investigation.

Bright field TEM images were taken to confirm our SEM observations. These images were taken from a Philippe CM12 TEM using 100kv acceleration voltage. CNTs with different
filling mode could be seen in Figure 4.13(a) and (b). Figure 4.13 (a) shows a continuous filling. It can be clearly seen that the lower part of the tube was filled with a nickel nanowire.

Figure 4.13 Bright field TEM images of Ni filled CNTs with different modes. (a) continues filling (b) tip/base filling.

Figure 4.14 HRTEM images of Ni filled CNTs. (a) the thickness of carbon layer increased when the diameter of Ni filling decreased (b) hollow space located at the tip of the tube.

The nickel nanowire almost completely filled the inner space of the tube but the diameter of the nanowire shrunk when it came to the tip. The thickness of the carbon layer was very thin at the bottom part and became thicker at the tip region. In Figure 4.13 (b), tip/base filling mode was found and a hollow inner space appeared inside the tube. A close view image of the
hollow space inside a tube can be observed by high resolution TEM imaging, as shown in Figure 4.14 (b). The thickness change of carbon coating could be closely examined in Figure 4.14 (b). However, the carbon shell of the tubes did not exhibit prefect graphite sheet lattice fringes. Figure 4.14 (a) may show some shell structures, but not very clearly. There are two reasons for this problem. First, our TEM can only work under lower acceleration voltage and the diameter of the tube is over 100nm. Multiple electron scattering would reduce the resolution of the image. The 0.34nm shell spaces cannot be distinguished. Second, the sample could only be composed of poorly ordered graphene layers. At lower decomposition temperatures, the degree of ordering in the graphite lattice can be less. Although transition metal helps the formation of highly oriented graphite, 700°C might not be sufficiently high to achieve this.

Figure 4.15 Raman spectra of four Ni filled CNT samples

In order to further investigate the crystalline structure of our CNTs, micro Raman spectroscopy was utilized. Raman scattering is an optical process involving the simultaneous emission or absorption of a phonon associated with the scattering of a photon. This shifts the frequency of the scattered photon. It offers a unique tool to characterize carbon materials such as graphite, diamond and carbon nanotubes, since the amount of ordering and degree of $sp^2$ and $sp^3$ bonding leaves a unique Raman “fingerprint”.
Figure 4.15 shows Raman spectra of four Ni filled CNT samples. The data were taken when CNTs were vertically aligned on the substrate after the AAO template was removed. The Raman spectra consist of two broad peaks located at 1355 cm\(^{-1}\) (the D peak) and 1590 cm\(^{-1}\) (the G peak). The D and G peaks are attributed to the small crystallite graphite materials or the so-called disordered graphite and the in plain symmetric C–C stretching (E\(_{2g}\)), respectively. In this cases, a large D peak in the Ni filled CNTs means there is amorphous carbon inside the tube. The Raman intensity ratio between the D and G bands (I\(_d\)/I\(_g\)) of the Ni filled CNTs was 1.17 which is much larger than that of commercial MWNTs and also indicates the highly disordered carbon structure.

4.1.5 Growth Mechanism of CNT and Process Optimization

4.1.5.1 Growth Mechanism of CNT

![Diagram of growth process of in-situ filled CNT with metal](Adapted from Ref. 80)

Understanding the growth mechanism of FFCNTs is a key requirement to optimize the synthesis process in order to produce ideal tubes for our application. However, even for hollow CNTs, there is no generally accepted growth mechanism to be found. For FFCNTs, the situation is much more complex. During the growth, the filling state continually changes the contact status of the ferromagnetic materials and carbon precursors. Since ferromagnetic
materials themselves are the catalyst for CNT growth, the dynamically changing contact makes the decomposition of the precursor a dynamic process as well. In this section, we propose a new theory for the growth mechanism by which FFCNTs were grown from nickel nanowires inside AAO template.

Figure 4.17 Basic growth modes for CNTs (a) base growth mode. (b) tip growth mode. (Adapted from Ref. 80)

Most existing methods for FFCNT growth use an in-situ filling growth process, as shown in Figure 4.16 [72, 80]. In the process, both carbon and targeted filling material are supplied as precursors. These two precursors react inside the CVD system and form the FFCNT. However, we use a traditional catalytic method to form our Ni filled CNTs. The only difference between the standard catalytic CNT growth and our method is that we use a large, high aspect ratio catalyst which is embedded inside an AAO template. It is deduced from our experimental observations that our CNT follows a vapor-liquid-solid (VLS) growth mechanism with a hybrid tip/base growth mode. Tip and base growth are two basic modes in VLS mechanism. The basic idea is shown in Figure 4.17 [80]. When the catalyst is exposed to a precursor which is catalyzed on the surface of the catalyst particle, an exothermic decomposition occurs. The carbon concentration and temperature are higher on the surface of the catalyst than the inner part of it. It cause the carbon to diffuse from the surface into the catalyst. When the catalyst can wet the substrate (small contact angle), the diffusion flow is mainly parallel to the surface. Carbon atoms appear on the side wall of the catalyst and leave the base on the surface. When the
catalyst cannot wet the substrate (large contact angel) the diffusion flow is mainly perpendicular to the surface. Carbon atoms appear at the bottom of the catalyst and push the catalyst to the tip.

Figure 4.18  High resolution SEM image of the cross section of Ni nanowire embedded into AAO template

Figure 4.19 Schematic drawing of hybrid tip/base growth mode for template based Ni filled CNT growth.
In standard catalytic CNT growth process, the size of the catalyst is small. The interface between catalyst and substrate is the only interface which presents a contact angle. So, the tube growth must follow one of the two modes. In our case, the catalyst, e.g. Ni nanowire, is a one-dimensional nanostructure which is embedded in an AAO template. Therefore, our catalyst system can have two interfaces: one Ni/AAO interface and one Ni/Ni interface. From the SEM image of a cross section of the sample, shown in Figure 4.18, we found the contact angle between Ni and alumina is above 90°, while the contact angle between the tip of the nanowire and the rest is 0°. This catalyst system can be modeled as Figure 4.19. In the horizontal direction the tip growth mode can be applied while the base growth model is applied in the vertical direction. This mechanism explains why we have a tip type filling in our Ni filled CNTs. Also, the CNTs are rather short and their lengths do not change much for longer deposition times. This fact is due to the large stress in the carbon walls during the growth, which is mainly caused by the special horizontal tip growth mode and large tube diameter.

4.1.5.2 Process Optimization

In order to find the best growth conditions for Ni filled CNTs in our system, a set of experiments has been performed to establish the relationship between the growth time/temperature/pressure and the resulting nanotubes.

*Time Dependency*
We first investigated the time dependency for our growth process. Ni filled CNTs were grown at constant pressure (200mbar) and temperature (700°C) for 15 mins, 30mins and 60mins, respectively. The results are shown in Figure 4.20. It was found that the growth of nanotubes start in the first 15 mins, as shown in Figure 4.20 (a). It was a little longer than other’s reports which shows that the deposition can be achieved in 5 mins. It might be because of the longer diffusion time needed for large catalysts. After 30 mins deposition, a uniform carbon coating could be found on the tubes, as shown in Figure 4.20 (b). For 60 mins deposition, resulting tubes were as same as what we got for 15mins except a few longer ones, as shown in Figure 4.20 (c). However, the longer parts of tubes were almost empty. As a conclusion, we found 30 mins was the best deposition time for this experiment. Longer deposition would not improve the result.

Temperature Dependency
Figure 4.21 SEM images of Ni filled CNTs with different growth temperatures. (a) 600°C (b) 650°C (c) 700°C

Temperature may be the most important process parameter in CVD based CNT growth. It determines the decomposition rate of precursors and the crystalline structure of the resulting CNTs. In this experiment, we grew CNTs at 200 bmar for 30mins using different temperatures, ranging from 600 °C to 700 °C. Growth temperatures cannot be higher than 700°C, otherwise the AAO template is difficult to be removed after the processes. Theoretical analysis suggested the higher temperature helps the growth. Our results, shown in Figure 4.21, confirmed it. The catalytic growth of nanotubes started at a temperature of 600°C, but only a few nanotubes were observed at this temperature, as shown in Fig 4.21 (a). A high density of tubes was obtained at temperature of 650 °C or higher, as shown in Fig 4.21 (b) and (c). Although the densities of CNTs did not appear to be different in the samples of 650 °C and 700 °C, the higher temperature was preferred because it can help the formation of crystalline structures in CNTs.

Pressure Dependency
The role of deposition pressure in our process has not been clarified. Previous publication shows the yield of CNT grown by PECVD was reduced when the deposition pressure was lower than 3 torr [161, 162]. However, the lowest pressure that our CVD system can achieve is 20 mbar. We kept the deposition time (30mins), temperature (700°C) in constant and run the deposition under different pressures (200mbar to 500mbar). There was no difference observed from the results, as shown in Figure 4.22. However, pressure might play a role when it goes really low.

As a conclusion, our best Ni filled CNT growth conditions are: 700°C/200mbar/30min with C₂H₂:H₂ (1:20).

4.2 Physical Properties of Ni Filled Carbon Nanotubes

In order to use the resulting Ni filled CNTs for different applications, their physical properties, especially the mechanical and electrical properties, have to be known. To date, most research efforts have been focused on the synthesis methods of FFCNTs and their magnetic properties. Only a few theoretical efforts have been reported with regard to the fundamental electric and mechanical properties of these new materials. In this section, the electrical resistance and Young’s modulus of individual Ni filled CNTs are measured using SEM based nanomanipulation.
4.2.1 Electrical Resistance of Ni Filled CNTs

The electrical resistance of a single Ni filled CNT has been directly measured using a two-electrode nanomanipulation system. The target nanotube was produced by the method described in section 4.1.4.2. The experimental setup was as same as it described in section 2.2.1. One electrode was hold by a nanomanipulator and another electrode was mounted on the SEM sample holder. As shown in Figure 4. 23 (a), a selected Ni filled CNT was fixed between the two electrodes using EBID. A good contact could be confirmed by stretching the tube between electrodes. A DC sweep analysis was performed to measure the electrical resistance of the tube. The applied voltage increased from 0V to 5V with 50mv per 0.1 second steps and current was recorded by a picoammeter (Keithley 6517A). Resulting I-V curve can be seen in Figure 4. 24. We found there was no significant current at the beginning. When the voltage was increased to 2.3V, a 12.109 nA current was recorded. After this, current rapidly increased until the voltage increased to 2.55V. Then, the current increased linearly with the voltage until the tube was broken at 4.9V. The measurement resistance was 2.87 MΩ. Figure 4. 23 (b) shows the broken tube in which a nickel core could be observed.

Figure 4.23 Characterization of electrical property of Ni filled CNTs using nanomanipulation inside SEM (a) A tube bridges between two electrodes (b) electric broken tube part, a nickel core can be seen.

This phenomenon might indicate the Ni filled CNT was a highly disordered conductive system [163]. At low bias range, the conductive regions in the tube cannot couple. Electrons could not transport in the tube. At a certain bias, the conductive region coupled due to joule heating or strong local electric field. Electrons could move through the tube. Finally, the
current was high enough to burn the tube. It is important to note that the tube was suddenly broken by electrical breakdown. This is different than the electrical breakdown process in MWNTs where step-down current behavior can be observed. It also indicated there was less continuous shell structure inside the carbon wall of the tube than unfilled MWNTs.

![I-V Curve of a Ni Filled CNT](image)

**Figure 4.24** I-V for a Ni filled CNT

### 4.2.2 Mechanical Properties of Ni Filled Carbon Nanotubes

The mechanical properties of carbon nanotubes can be experimentally investigated by atomic force microscopy (AFM) or electron microscopy (EM) based nanomanipulation. In the last ten years, many tensile and axial compressive nanomanipulation experiments have been performed on hollow CNTs in order to study their mechanical properties, such as the Young’s modules (E), and their mechanical failure modes [31, 118, 164]. However, no work has been done on FFCNTs. The most closely related work, by Costa et al[165], measured the Young’s modules of Zn(Ga)S filled CNTs through buckling deformation tests using TEM based nanomanipulation. They applied classical Euler beam theory to the deformed tube. Their findings show the modulus was more than two orders of magnitude lower than that of Zn and three orders of magnitude lower than CNT modulus. This result indicates that filling CNTs with other materials can dramatically reduce the bending/buckling strength of the tubes. The authors proposed that the initial curvature of tubes and high-defect density in the heterostructures could be the reason which caused the reduction of the Young’s modulus. However, the exact explanation of the behavior remains an open question.
We quantitatively measured the effective Young’s modulus of Ni-filled CNTs using the buckling test. We present experimental results on a Ni-filled CNT with a length and diameter of 104 nm and 1.98 µm, respectively. The CNT was synthesized using AAO template-based CVD. The buckling experiment was performed inside an SEM and used a nanomanipulator as actuator and an AFM cantilever as the load sensor. The experimental setup is shown in Figure 4. 25. A selected FFCNT was attached between a tungsten probe and a 130 µm long gold coated AFM cantilever with a spring constant of 5.647 N/M. Both ends of the tube were fixed using EBID. The buckling force was applied by the probe which was driven by a SEM based nanomanipulator. The AFM cantilever was utilized to measure the applied force through its deformation.

Figure 4. 25 SEM images of buckling test setup. (a) a low magnification SEM images shows the experimental setup used. (b) a high magnification SEM image shows a Ni-filled CNT connected between a tungsten probe and a AFM cantilever.

Figure 4. 26 a-e shows a series of SEM images taken during the buckling process for a Ni-filled CNT with 104nm diameter and 1.98um length. Figure 4. 26 (a) shows the CNT in its neutral shape without any compressive load. The tube was straight. Figure 4. 26 (b) and (c) show two buckling states of the tube under different compressive loads. These images recorded the tube under strains of 11.5% and 28.4%, respectively. The corresponding compressive loads were calculated from the cantilever deflections, which were directly obtained from the images with reference to the force baseline. When the tube was deformed into a buckled configuration it started to bow at the tip region instead of the middle point. Figure 4 (d) and (e) show the buckling states of the tube when the load was partly and
completely removed. The length of tube was decreased by 4.4% due to residual plastic deformation. Therefore, the Ni-filled CNT does not have a large elastic range. Table 4.1 shows the stress-strain response of the tube.

Figure 4.26 SEM images of the buckling process of the Ni-filled CNT. (a) CNT without any compressive load. (b) and (c) CNT being compressed with increasing load. As strain of 11.5% and 28.4% were found in these two images. (d) CNT was partly released from compressive load (with 5.8% strain). (e) CNT was fully released from compressive load. A residual strain of 4.4% was found, indicating the plastic deformation of the tube.

<table>
<thead>
<tr>
<th>Strain (%)</th>
<th>0</th>
<th>11.5</th>
<th>28.4</th>
<th>5.8</th>
<th>4.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive Load (nN)</td>
<td>0</td>
<td>609.4</td>
<td>451.52</td>
<td>325.28</td>
<td>20.08</td>
</tr>
</tbody>
</table>

Table 4.1 Compressive load - strain response of the Ni-filled CNT

In order to quantitatively analyze the elasticity of Ni-filled CNT, the tube can be modeled as a continuous elastic column. Euler beam theory can be used to describe the buckling procedure. When a compressive force F is applied to the perfectly straight column with length L, Young’s modulus E and area moment of inertia I, the corresponding deflection y(x) can be calculated by Euler’s equation[166]:

$$EI \frac{d^4y}{dx^4} + F \frac{d^2y}{dx^2} = 0$$

(4.1)

In our experiments, both ends of the tube were fixed on their supports by EBID. Therefore, Eq. (4.1) can be solved with the boundary conditions y(0) = 0; y(L) = 0; y'(0) = 0; y'(L) = 0 to get the relationship between the critical buckling load Fcr and E. It can be expressed as:

$$F_{cr} = \frac{4EI\pi^2}{L^2}$$

(4.2)

If we can extract the exact critical buckling load from our experiments, the Young’s modulus of the tube can be obtained by Eq. (4.2). However, it is difficult to directly measure the critical buckling load from our experimental observations because the nanotube was not
perfectly straight. Even if the tube was straight, it is impossible to determine from SEM images the exact instance when the tube started to buckled. In order to address these problems, we use a more realistic model [166, 167] that assumes that the initial curvature of the tube can be described as a sinusoidal function $A \sin(\pi x/L)$, where $A$ is a constant. Then, the deflection of the tube can be expressed as

$$y(x) = \frac{A}{1 - F/F_{cr}} \sin(\pi x/L) \quad (4.3)$$

For a given point on the tube, its displacement is a function of $F$, $F_{cr}$ and $A$. As discussed above, $F$ can be directly measured from the images. The values of $A$ and $F_{cr}$ can be obtained by solving Eq. (4.3) for two different deflection states, as shown in Figure 4. 26 (b) and (c). When the $F_{cr}$ is known, the effective value of $E$ can be calculated by Eq. (4.2).

Using this method, we calculated the critical force $F$ and the Young’s modulus of the tube to be 897.35 nN and 25.1 GPa, respectively. Surprisingly, it was found that the value was much lower than the elastic modulus of pure nickel or CNTs. The $E$ of bulk nickel is 200 Gpa while the $E$ of multiwalled carbon nanotubes is in the range of 270 Gpa to 1 Tpa [26, 109]. The results show that encapsulating Ni NW into CNTs using AAO template based CVD method would significantly reduce the buckling strength of these CNTs, in contrast to the conventional knowledge that filling could increase the mechanical strength of hollow structures. By carefully investigating the microstructure of our samples, the two following features were found to attribute to the reduction of its buckling strength.

First, in the Figure 4.27 (a), we found that the asymmetric nickel filling inside the hosting CNT breaks the cylindrical symmetry possessed by most MWNTs. This means that the cross-section of the Ni-filled CNT is not constant along the tube. This feature could significantly affect the elasticity of the tubes. In Ref. [168], MD simulations have been conducted to investigate the effects of asymmetrical filling of C60 inside CNTs on their buckling strength. Their results suggested that the induced asymmetries cause asymmetric force distribution along the circumferential direction of the tube. Extremely high stress can concentrate in certain local areas and can then generate additional bending moments, leading to a reduction in buckling strength. The reduction is more severe for tubes with larger diameters. The same phenomenon happens in our case. Moreover, we found the degree of asymmetry changes along the tube axis. The highest asymmetry region in the Ni-filled CNT is its upper region.
where the Ni NW shrinks. This also explains why the tube starts to bow at this region instead of the middle point of the tube.

Second, kinks are found inside the carbon shells of the tube, as shown in Figure 4. 27(b), which indicates that the carbon shells plastically deformed during the growing process [169]. Then, the atomic carbon structure of Ni-filled CNTs is different from hollow CNTs. When carbon atoms in the tube are not arranged periodically, the tube will be easily bent. Liu et al.[170] used a combination of finite element analysis and nonlinear vibration analysis to show that kink deformation can cause a large reduction in the effective bending modulus for CNTs.

Figure 4. 27 TEM images of Ni-filled CNTs. (a) asymmetrical nickel filling inside carbon shells. (b) kinks on carbon shells.

In summary, the effective elastic modulus and critical compressive load of Ni-filled CNTs with 104nm diameter and 1.98 um length were measured. Nanotubes grown by the AAO template and CVD method were subjected to in-situ buckling tests inside a SEM. The effective modulus of Ni-filled CNTs was found to be 25.1 GPa with a critical load of 897 nN, which is much lower than that of bulk nickel and hollow CNTs. Based on the TEM analysis of microstructures of these Ni-filled CNTs, we found that the effect of nickel filling on the reduction of the buckling strength of CNTs is dominated by the asymmetric filling pattern of nickel and the initial plastic deformation located in the carbon shells. These two features change the uniformity of the axial compressive load distribution on the cross section of the
tube and reduce the buckling strength of the tube. The smaller value of Young’s modulus also indicates that the plastic deformation can more easily happen during the buckling process.

4.3 Summary

A high yield synthesis method of ferromagnetic filled carbon nanotubes has been presented. Precise control of tube geometry and filling rate is achieved by using anodic aluminum oxide template method. The resulting nickel or iron filled CNTs provide a full capability for realizing magnetic controlled target drug delivery. A CVD based CNT growth process has been optimized for this purpose. The electrical and mechanical properties of Ni filled CNTs have been experimentally investigated. These results provide a comprehensive understanding of this new material towards different applications and indicates that Ni filled CNTs are highly disordered one-dimensional systems.
5 Conclusion and Future Directions

Nanotechnology has been recognized as a promising new growth innovator. Nanomaterial, nanofabrication and nanorobotics are three important branches in the field. They are closely related to each other in this doctoral research. Nanorobotic manipulation with the help of nanofabrication techniques accelerates the progress in addressing several remaining issues with regards to new nanomaterials, especially carbon nanotubes. Recent development in nanofabrication brings nanomaterials to their full potential as functional elements in nanorobotic applications. Nanomaterials with extraordinary properties are integrated into nanorobots that provide new tools and strategies in nanofabrication processes. The primary contributions of this effort include:

- The SEM/TEM based nanorobotic manipulation procedures have been optimized for characterization and fabrication nanoscale structures. This method has been demonstrated by modification and integration multi-walled carbon nanotubes for new NEMS applications.

- A new NEMS-on-a-tip architecture has been proposed. This architecture is based on the integration of one-dimensional functional nanostructures on nanofabricated protruding carrier. Devices based on this architecture are suitable for tasks, such as 3D scanning probe microscopy or NEMS/microrobot integration. The architecture has been demonstrated by telescoping multi-walled carbon nanotube based force sensors.

- The multishell conductance in multi-walled carbon nanotubes has been investigated. Directly experimental evidence has been provided to confirm the multishell electron transport property. The nonlinear current to voltage relationship of MWNTs has also been explained by electron hopping based multishell conductance.

- The electromechanical coupling property in telescoping MWNT has been experimentally studied using SEM based nanorobotic manipulation and four-finger protruding nanoelectrode pairs. Strong piezoresistive behavior has been found in telescoping carbon nanotubes.

- High yield synthesis method of ferromagnetic filled carbon nanotubes has been developed and optimized. Uniform geometry and filling rate have been achieved for resulting tubes. Structural and material properties of these tubes have been studied using
electron microscopy and Raman spectroscopy. A new growth mechanism has been proposed for understanding the synthesis process.

- As a highly disordered system, electrical and mechanical properties of Ni filled carbon nanotubes have been investigated. Results are different from original carbon nanotubes. Electrical resistance of the tubes is very high and Young’s modulus of the tubes is 40 times smaller than hollow carbon nanotubes.

Though significant progress has been made, challenges still exist in many fields. In the field of nanorobotics, a new actuation system is required to provide stable and smooth movement with nanometer resolution. Although stick-slip piezoactuators are able to provide high moving resolution within a rather large working space, mechanical shocks always appear when the driving mode changes from piezoactuation to stick-slip. This uncontrolled shock makes nanomanipulation more difficult. Furthermore, new end effectors and sensing systems which can be integrated onto a manipulator are required. Currently, all nanomanipulation systems rely on electron microscopes or scanning probe microscopes. The development of useful sensing system is the key to use the manipulators independently from the microscopes. New end effectors should be designed with a balance between size and function. NEMS-on-a-tip devices can be good candidates to achieve this purpose.

Another interesting topic is to design new NEMS mechanical sensors based on electromechanical coupling of telescoping carbon nanotubes. The new device can share the same structure as used for electromechanical coupling measurement. Based on this configuration, the new sensor can be used for position or force sensing.

As described in the Chapter 4, Ni filled CNTs presents many interesting physical properties. In contrast to carbon nanotubes which are high ordered systems with many symmetric and periodic properties, Ni filled CNTs can be used as new research objects to experimentally investigate the electrical and mechanical properties of low dimensional disordered system. New phenomena may be found, such as strong electromechanical coupling or magnetic induced shifting in transport properties.
Reference

46. Arunkumar, S., Batch fabricated, supramolecular transducers based on multiwalled carbon nanotubes, 2008, Zürich : ETH.
57. Christoph, S., Electromechanical transducers based on single-walled carbon nanotubes, 2007, Zürich : ETH.


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