DETERMINATION OF SHEAR STRESS BETWEEN SINGLE-WALLED CARBON NANOTUBES AND SUBSTRATES USING NEMS DEVICES

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Abstract

With numerous applications of carbon nanotubes (CNTs) in various nanoelectromechanical devices, the mechanical interactions between these quasi-one-dimensional nanoelements and contacting materials can have a large effect on the device performance. Few results have been published on this topic in literature because of the experimental challenges involved. Due to the nanometer scale dimensions of CNTs and nanoNewton level of the interfacial forces, all of the reported experiments that look into the interfacial forces or shear stress are based on atomic force microscopy (AFM). However, those measurements have many disadvantages and limitations such as difficult force calibration, complicated data analysis, and requirement of low substrate roughness.

In this work, a novel and easily controllable technique based on a NEMS device, a ZYVEX nanomanipulator, and a scanning electron microscope (SEM) along with a theoretical model is developed to study the shear stress between SWNTs and substrates. A small SWNT bundle is assembled across two cantilevers by dielectrophoresis, with one cantilever much more flexible than the other. The flexible cantilever is then pushed away from the stiffer cantilever in order to produce slip between the SWNTs and the cantilever surface. When the cantilever returns to its initial position, axial slack is observed in the SWNTs. A theoretical model has been developed to calculate the shear stress between the SWNT bundle and the cantilever surface, based on the measured axial slack. This new technique overcomes some disadvantages of the AFM-based methods and gives the first determination of the shear stress between dielectrophoretically assembled SWNTs and substrates.
In this work, an average shear stress of 87 MPa between SWNTs and gold surfaces is obtained. For the tests on the self-assembled 2-aminoethanethiol surface, an average shear stress of 142 MPa is obtained. For the self-assembled 2-phenylethanethiol surface, the shear stress is determined to be around 7.2 MPa with an estimated work of adhesion of 0.5 J/m². The gold cantilever surfaces have been modified through physical treatments including N₂ annealing, e-beam irradiation and e-beam induced carbon deposition. Preliminary testing results indicate increased shear stresses between SWNTs and gold surfaces with each of these surface treatments.
Preparation of the NEMS cantilever based device for testing

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Introduction

1.1. Motivation

The study of the interfacial interactions between CNTs and surfaces has found interesting due to the increasing use of CNTs in nanoscale devices. Such interactions play an important role in a variety of applications of CNTs in nanotechnology.

To integrate CNTs with micro/nano scale devices, there are several different assembly methods reported in the literature such as template guided fluidic self-assembly [1-3], substrate transferring [4], dispersion of CNT solution onto substrate [5-8] and dielectrophoretic assembly [9, 10]. For all these assembly methods, it involves CNTs contacting with different substrate surfaces during the assembly process and it also requires high enough interaction forces between the tubes and the substrates for it to survive the following processes. It has been found that a SWNT film peeled off from a silicon dioxide substrate by strong blow-drying with nitrogen gas due to relatively weak interactions at the tube-substrate interface [1]. With more knowledge of the interfacial forces between CNTs and substrates, we will understand these assembly processes better.

For most nanoscale devices with CNTs in contact with surfaces, the device performance can be directly influenced by the mechanical interactions at the CNT-surface interface [11-14]. In the CNT-based nanotweezer [11], CNTs are attached to gold electrodes as the tweezer probes. The interaction forces at the tube-electrode interface have to be high enough to build the device. The working principle of this nanotweezer is to apply a DC voltage between two CNT probes to pull them together to manipulate nanoparticles. When the nanoparticle is released from the probes by
turning off the voltage, the interactions between the CNTs and the nanosubject has to be weak enough to break the adhesion. Other CNT-based devices also suggest the importance of the interaction forces between the tubes and substrates. In the work of both the CNT-based nanorelays [15] and nanoswitches [14], an electrostatic force between cantilevered tubes and an electrode bring the tubes into contact with the electrode to turn on the device. The restoring force in the tube breaks the contact to turn it off after removing the voltage. Therefore, the interaction forces here can not be too high to prevent turning the device off. In the previous work on SWNTs-based nanoswitches in our group [13], with a small SWNT bundle suspended over an actuation electrode, a large decrease in the threshold voltage was observed after the first actuation. This actuation voltage decrease was caused by the nanotubes slipping inward on their supports as they were pulled down toward the actuation electrode, increasing the axial slack in the SWNT bundle. Thus it is clear that the frictional force or shear stress at the CNT-substrate interface affects the performance of these nanoelectromechanical nanotube-based devices.

However, few results are published on this subject due to the experimental challenges involved. Aside from the work on SWNT-based switches [13] axial slip between SWNTs and surfaces has only been previously reported by Davis et al. [16, 17]. They applied an AFM tip onto a SWNT grown across a trench to study the threshold axial tension in the tube to cause it to slip on the trench surface. Furthermore most of the existing publications on interactions between CNTs and surfaces focus on multi-walled carbon nanotubes (MWNTs) rather than SWNTs. The reported experiments are all based on atomic force microscopy (AFM) due to the nanoscale dimensions and force levels involved. This circumstance motivates our work to develop an efficient method to study the interactions between CNTs and different substrates.
1.2. Carbon nanotubes

1.2.1. History of carbon nanotubes

Carbon nanotubes (CNTs) were first discovered by Sumio Iijima’s group in 1991. They observed multi-walled nanotubes (MWNTs) formed in a carbon arc discharge by using Transmission Electron Microscopy (TEM) [18]. Then two years later, in 1993, single-walled nanotubes (SWNTs) were reported independently by both Sumio Iijima’s group [19] and Donald Bethune’s group [20]. Since then, CNTs have been of great interest, and broadly investigated by researchers all over the world for fundamental properties and for potential applications.

1.2.2. Structural properties of carbon nanotubes

MWNTs are comprised of 2 to 30 concentric graphene layers, with diameters usually in the range of ~10 to 50 nm and length generally in micrometer range. On the other hand, SWNTs are much thinner with diameters of about 1 nm. Therefore, with large lengths and relatively small diameters, both SWNTs and MWNTs hold large aspect ratio. This large aspect ratio makes CNTs quasi-one-dimensional elements, which along with their unique electrical and mechanical properties leads to essential applications of CNTs in various fields.

Unlike a graphene sheet, which has a zero band gap, SWNTs may be either metallic or semiconducting depending on the chirality, which is defined as the orientation around which the graphene sheet is rolled to form a cylinder. The chirality and the tube diameter are uniquely specified by a vector \( \overrightarrow{c_h} = n\overrightarrow{\alpha_1} + m\overrightarrow{\alpha_2} = (n, m) \), where \( n, m \) are integers, \( \overrightarrow{\alpha_1}, \overrightarrow{\alpha_2} \) are the unit vectors of the graphene lattice, and \( \overrightarrow{c_h} \) connects two crystallographically equivalent sites, \( A \) and \( A' \), as shown in Figure 1.2. A SWNT is formed by connecting together the points \( A \) and \( A' \) and
the joint is made along the lightly dotted lines perpendicular to \( \overline{c_h} \). The diameter of the cylinder tube is defined by \( d = \frac{|c_h|}{\pi} = \alpha \sqrt{n^2 + nm + m^2}/\pi \), where \( \alpha = 1.42 \times \sqrt{3}\AA \) is the lattice constant [21]. Based on the roll-up/ chiral vector \((n, m)\), SWNTs can be classified into three groups: armchair \((n = m)\), zigzag \((n = 0 \text{ or } m = 0)\) and chiral \((\text{any other } n \text{ and } m)\).

**Figure 1.1 (a),(b): The roll-up/chiral vector \((n, m)\) of the nanotube is defined by the base vectors \( \overline{a_1} \) and \( \overline{a_2} \) [21, 22]; (c): (1) armchair, (2) zigzag, and (3) chiral SWNTs[23]**

SWNTs with \( n - m = 3k \), where \( k \) is an integer, are metals, and all the others are semiconductors with a band gap that varies inversely with the nanotube diameter. Therefore, two thirds of all possible configurations are semiconducting and one third metallic.

As for MWNTs, a MWNT consists of more than one concentric carbon shell, and each of which can be metallic or semiconducting. In other words, the chirality of individual tube layers in a MWNT structure may be different. However, the chirality of a MWNT referred to in the
literature usually refers to the one of the outer tube layer. The spacing distance between individual tubes in a MWNT can be considered equal to the spacing of adjacent graphite layers (approximately 0.34 nm) [24].

Due to their special quasi-one-dimensional structure, CNTs exhibit unique electrical, mechanical, optical and chemical properties. Based on these novel properties, CNTs are potentially useful in many areas such as electronics, optics, and other fields like composite material science. We will focus on their mechanical properties in the following sections.

1.2.3. Mechanical properties of carbon nanotubes

Many studies have been done exploring mechanical properties of CNTs for their potential applications in composite material due to their high tensile stiffness and high yield strength. Also in order to study the mechanical interaction between CNTs and substrates in this work, it is necessary to understand the elastic property of the tubes first. Thus in the following, I will focus on how people measured the tensile stiffness and yield strength in the literature and conclude with a reasonable value for the calculation in our experiments.

The tensile stiffness as measured by the Young’s modulus $E$ is defined as the stress $\sigma$ -strain $\varepsilon$ ratio when a material is axially loaded. The elastic potential energy per unit volume is given by:

$$\frac{U_e}{A_0 z_0} = \frac{E \Delta z^2}{2 z_0^2} = \frac{E \varepsilon^2}{2}$$  \hspace{1cm} (1-1)

Where $U_e$ is the elastic potential energy, $A_0$ is the cross section area, $z_0$ is the initial length and $\Delta z$ is the stretched length. From equation (1-1), the Young’s modulus $E$ can be calculated as the second derivative of the potential energy density (energy/volume) with respect to the corresponding axial strain as:
where $V_0$ is the equilibrium volume $A_0z_0$, $E$ the strain energy and $\varepsilon$ the axial strain here that is defined as $(z - z_0)/z_0$. Also $z$ stands for the length of the nanotube and $z_0$ corresponds to its equilibrium value [25]. Also from equation (1-1), it can be obtained that $U_e = \frac{EA_0\Delta z^2}{z_0}$. The stress is equal to the derivative of potential energy $U_e$ relative to volume, $\sigma = \frac{d U_e}{dV} = \frac{d U_e}{dz} \frac{1}{A_0} = \frac{E\Delta z}{z_0} = E\varepsilon$. Therefore, the definition of young’s modulus as stress/strain for uniaxial loading is equivalent to equation (1-2).

According to equation (1-2), the way to calculate the volume $V_0$ of a nanotube has a direct effect of the Young’s modulus value. In the literature, the equilibrium volume of a SWNT is sometimes defined as the volume of a hollow cylinder [26-29] and sometimes as the volume of a solid cylinder [30-32], which results in a wide range of Young’s modulus values reported by different groups. The Young’s moduli for references [26-32] are all calculated based on tube extension instead of bending. Yu et al. [25] compared theoretical calculated results of Young’s modulus by different groups (in Figure 1.2) and explained the reasons for the difference.
For all the hollow cylinder models, the equilibrium volume is $V_0 = 2\pi z_0 R \delta l$, where $R$ is the radius of the nanotube and $\delta l$ is its wall thickness. It is clear that Young’s modulus strongly depends on the definition of SWNT wall thickness here. For the solid cylinder model (light blue triangular in the figure), the equilibrium volume is written as $V_0 = \pi z_0 R^2$, and it only depends on the length $z_0$ and the radius $R$. Since the strain energy $E$ (proportional to the length $z_0$) is calculated along the whole length of the tube, Young’s modulus doesn’t change with the length of the tube for both models. As for the effect from diameter, Young’s modulus is proportional to $1/R$ in a hollow cylinder model and $1/R^2$ in a solid cylinder model. Also the larger the radius $R$ of a SWNT, the larger its second derivative of strain energy versus strain $\frac{\partial^2 E}{\partial^2 \varepsilon}$, and the amount of augmentation of $\frac{\partial^2 E}{\partial^2 \varepsilon}$ is larger than the amount of reduction of $1/R$ whereas it is smaller than the amount of reduction of $1/R^2$ when the radius increases. Therefore, in Figure 1.3, the variation of Young’s modulus with the radius in a solid cylinder model (light blue triangular in the figure) has
the opposite trend to the variation in a hollow cylinder model.

As for the effect of wall thickness, it is now very clear that Young’s modulus of a nanotube is inversely proportional to its wall thickness in the hollow cylinder model, while a solid cylinder model does not involve wall thickness directly. There are different ways to define the wall thickness of a SWNT. In Figure 1.2, the wall thickness is defined as the thickness of the electron cloud of a SWNT (0.32 nm) in the ‘present’ model; Lu [33] takes the interwall distance (0.34 nm) as the wall thickness; Cai [28] considers the wall thickness to be twice as large as a C-C bond length \((2 \times 0.1412\,\text{nm} = 0.2824\,\text{nm})\); Yakobson [29] uses 0.065 nm for the wall thickness. Therefore, the five times larger Young’s modulus in Yakobson’s model than those in the others’ models is directly due to the five times lower value of the wall thickness Yakobson used in his model. It is clear now the wide-range scatter in the Young’s modulus of CNTs mainly come from different values of the wall thickness of the tubes in the commonly used hollow cylinder model.

Beyond the above theoretical calculations, few experimental results of the Young’s modulus of CNTs have been reported in literature due to the difficulty of testing such small-size elements. Also the problems on whether to assume the tube as a solid or a hollow cylinder, and for a hollow cylinder what value to use for the wall thickness still exist for the experimental results. The earliest experimental measurement of Young’s modulus of MWNTs gave an average value of 1.8 TPa. In that work, the amplitude of thermally excited vibrations was measured in a transmission electron microscopy (TEM) and analysis of the temperature dependence of the vibration amplitude gives an estimate of the Young’s modulus. They considered a MWNT as a clamped hollow cylindrical cantilever with a certain inner diameter (from 1.0 to 6.6 nm) and
outer diameter (from 5.6 to 24.8 nm) [34]. Later a slightly smaller value of 1.28 TPa of Young’s modulus was reported by bending a individual MWNT cantilever beam by an atomic force microscope (AFM) tip and fitting the measured static response (lateral F-d curves) to the analytical solution for a solid cantilever beam [31]. Yu et al. presented results of 15 SWNT bundles (with the diameter of each SWNT as 1.36 nm ) under tensile load and found Young’s modulus values in range from 0.32 to 1.47 TPa (average of 1.002 TPa) [35] and also performed tensile loading experiment of MWNTs which yielded a Young’s modulus from 0.27 to 0.95 TPa [36]. Both experiments assumed the thickness of the nanotube to be the interlayer distance in graphite, 0.34 nm. A Young’s modulus of 1.2 TPa for SWNTs was obtained by Tombler et al. [37] using an AFM pushing-retracting cycle method. For this method, based on the curve of the force applied on a suspended SWNT versus the nanotube deflection, the Young’s modulus was calculated assuming the cross-section area of the tube as $A=\pi dt$, where $d$ is the diameter of the tube (3.1 nm) and $t$ is the nanotube wall thickness (0.34 nm).

Salvetat et al. [38] used the same AFM-based method to obtain Young’s moduli for different size SWNTs with diameters in the range of 3 to 20 nm by treating the tube as a ‘filled’ solid cylinder. According to their result, Young’s modulus decreases by more than one order from 1 TPa for small SWNTs with diameter of 3 nm to 0.067 TPa for SWNTs with diameter of 20 nm. The scatter in the reported experimental data of Young’s modulus does not only result from whether the tube is treated as hollow cylinder or solid cylinder, but also result from the different size of the tubes and experimental errors.

The diameter of the SWNT from Brewer Science we use in our experiments is 1.3 nm according
to the supplier. In our model, the tube is assumed to be a hollow cylinder and the cross-section area is calculated based on a radius of 0.65 nm and a wall thickness of 0.34 nm. As discussed above, the modulus depends on the geometrical details of the cross section. Therefore, it is reasonable to use the experimentally tensile-tested average modulus of 1 TPa by Yu for SWNTs with a diameter of 1.36 nm (which is very close to the size of SWNTs in our work) and wall thickness of 0.34 nm [35]. For theoretical calculation, from figure 1.3, for a zigzag tube (16,0) with a diameter of ~1.3 nm, the Young’s modulus is ~1 TPa according to Lu’s calculation with a wall thickness of 0.34 nm. Molecular dynamic simulation also suggests that the Young's modulus is insensitive to the tube chirality [39, 40]. Therefore, the theoretical results in figure 3 does support the 1 TPa Young’s modulus for the particular size SNWTs used in our work with their chirality not fixed.

As for the work done to measure the tensile yield strength of CNTs in the literature, Yu [35] used the tensile loading testing method to obtain 15 values of the breaking strength of SWNTs (each tube diameter of 1.36 nm, bundle length of 1-2 µm) ranging from 13 to 52 GPa (mean 30 GPa) with the maximum breaking strain of 5.3%. In the same experiments, the Young’s modulus was found to be 1 TPa on average. By using an AFM in a lateral force mode, Walters et al. [41] observed that SWNTs (bundle length of 3.7 µm) can survive at a maximum strain of 5.8±0.9%, with tensile strength exceeding 45±7 GPa (should be much higher for a 5.8% strain) based on a 1.25 TPa Young’s modulus. A breaking strain of 13.7% was reported for a 195 µm long SWNT bundle also by tensile loading tests [42]. In this work, a breaking strain of 5.3% is used to estimate the shear stress for the cases where tubes break based on Yu’s work [35], in which the SWNTs have similar diameter and bundle length compared to the SWNTs used in our
1.3. **Background of interactions of carbon nanotubes with substrates**

1.3.1. **The effect of carbon nanotube-substrate interactions on the applications of carbon nanotubes in nanotechnology**

The study of the interfacial interactions between CNTs and surfaces has drawn attention due to the increasing use of CNTs in nanoscale devices. Such interactions play an important role in a variety of applications of CNTs in nanotechnology. To integrate CNTs with micro/nano scale devices, there are several different assembly methods developed in the literature such as template guided fluidic self-assembly [1-3], substrate transferring [4], and dielectrophoretic assembly [9, 10]. For all these assembly methods, the CNTs contact different substrate surfaces during the assembly process. After assembly, sufficiently high interaction forces between the tubes and the substrates are necessary for the assembled nanotubes to survive the following processes. Also, for most nano devices with CNTs in contact with surfaces, the device performance can be directly influenced by the mechanical interactions at the CNTs-surface interface [12-14, 43].

Take our previous work on SWNTs-based nanoswitches [13] for an example, with a small SWNT bundle suspended over an actuation electrode, a large decrease in the threshold voltage was observed after the first actuation. This actuation voltage decrease was caused by the nanotubes slipping inward on their supports as they were pulled down toward the actuation electrode, increasing the axial slack in the SWNT bundle. Thus it is clear that the frictional force or shear stress at the CNT-substrate interface affects the performance of these nanoelectromechanical nanotube-based devices.
However, few results are published on this subject due to the experimental challenges involved. Aside from the work on SWNT-based switches [13] axial slip between SWNTs and surfaces has only been previously reported by Davis et al. [16, 17]. They applied an AFM tip onto a SWNT grown across a trench to study the threshold axial tension in the tube to cause it to slip on the trench surface. Furthermore most of the existing publications on interactions between CNTs and surfaces focus on multi-walled carbon nanotubes (MWNTs) rather than SWNTs. The reported experiments are all based on atomic force microscopy (AFM) due to the nanoscale dimensions and force levels involved. This circumstance motivates our work to develop an efficient method to study the interactions between CNTs and different substrates.

1.3.2. Historical study on interactions of carbon nanotubes with substrates

1.3.2.1. Interaction mechanism

CNTs can interact with substrates of different surface properties through various mechanisms including chemical covalent bonds and all different sorts of non-covalent bonds like Van der Waals bonds, pi-pi bonds, and hydrogen bonds et al. as discussed in the following.

As for the covalent bonds, there can be different forms depending on the substrate material itself. One common covalent bond is the Si-C bond between a CNT and a Si substrate achieved by growing CNTs on Si substrate in thermal chemical vapor deposition system at 1000 °C [44]. It has been predicted that the Si-CNT interaction results in a large variety of changes in the electronic structure of a CNT. However, direct observation of this bonding has not been reported due to the lack of suitable characterization techniques. Therefore, under a certain special conditions like high temperature in the above case, chemical bonds can be formed between
carbon atoms in tubes and atoms in the substrates and these bonds would contribute to the interfacial adhesion between CNTs and the substrate surface and modify the electrical contact between them as well.

In physical chemistry, the van der Waals force (vdW) is the sum of the attractive or repulsive forces between molecules (or between parts of the same molecule) other than those due to covalent bonds or to the electrostatic interaction of ions with one another or with neutral molecules. In general, vdW force includes the force between two permanent dipoles (Keesom force), the force between a permanent dipole and a corresponding induced dipole (Debye force) and the force between two instantaneously induced dipoles (London dispersion force). Rance et al. [45] studied the application of vdW interactions between MWNTs and gold nanoparticles (AuNPs) for controlled assembly of composite nanostructures. In their experiments, a certain number of AuNPs are adsorbed onto MWNT surface by attractive vdW forces, which overcome an energy barrier provided by electrostatic repulsion between negatively charged nanotube and AuNP surfaces. It is understandable that vdW forces have a pronounced effect on the surface interactions at the nanoscale.

In supramolecular chemistry, an aromatic interaction (or pi-pi bonding) is a noncovalent interaction between organic compounds containing aromatic moieties. Aromatic group chemicals are known to interact strongly with the basal plane of graphite via pi-pi bonds and are also found to strongly interact with the sidewalls of CNTs in a similar manner [46]. For interaction between CNTs and substrates of aromatic group chemicals, this pi-pi bond effect would dominate over other effects for interactions.
It is now clear that there are many origins to the interacting forces between CNTs and different substrates. The interaction energy may consist of short-range, attractive interaction energy due to all kinds of chemical bonding, short-range repulsive energy and long-range attractive vdW energy. For chemical bonds between CNTs and substrate atoms, the bond distance is within the covalent distance range. For instance, C-Si bond length (or bond distance) is 0.186 nm and C-C bond length is 0.143 nm, with the bond length defined as the average distance between nuclei of two bonded atoms in a molecule. However, like the C-Si covalent bonds formed at high temperature, these chemisorptions of CNTs on substrates require some special process and thus are relatively stronger than long-range attractive vdW bonds. Therefore, it is common for researchers in literature to just consider vdW interactions as the main contribution to the interaction of CNTs physisorbed on regular substrates after regular assembly process. For these cases, the minimum distance between the atoms on the CNTs and the atoms on the substrate is longer than the covalent distance of chemical bonds but in the range of vdW interaction (≥ 0.3 nm) [47-49].

1.3.2.2. Theoretical and experimental studies

With the difficulties in experimentally measuring the interacting force between the CNTs and substrates, theoretical models were developed to predict the interfacial adhesive force dating back to the 1990s. In 1999, Buldum and Lu [48] used molecular statics and dynamics methods to study the motion of nanotubes on a graphite surface. In their work, the interaction between the tube and the graphite surface atoms was modeled based on an empirical potential of the Lennard-Jones type, and the tubes were assumed to be rigid. According to their calculations, the effective
contact area and the interaction energy scale varied with the square root of the radius of the nanotube. The sliding force depended on the chirality of the tube. As they claimed, for a SWNT with a radius of 13 nm (a value picked by them for calculation) and length of 600 nm, the sliding force was estimated as \(~87\) nN (shear stress of 10 MPa, assuming the contact width as the radius) for an armchair tube and \(~43\) nN (shear stress of 5.5 MPa, assuming the contact width as the radius) for a zigzag tube.

Other groups have investigated the interfaces in CNT-polymer composites by using molecular dynamics (MD) simulations. For example, Gou et al. [50] studied the interfacial bonding of SWNTs reinforced epoxy composites using a combination of computational and experimental methods. According to their results, the interfacial shear strength between the nanotube and the cured epoxy resin was up to 75 MPa. In order to get a quantitative understanding of the friction between two carbon structures, Cheng and Lu [49] performed the same MD simulation to study the interactions between nanotubes and a graphite surface. First, they calculated the variations of the potential energy with spinning and rotating of a CNT and then simulated the motions of sliding and rolling of a CNT on a graphite substrate to study the dynamic frictional behavior. They concluded that the dynamic friction depends on the rotation angle of nanotube axis significantly because of the matching of lattice between the tube and the graphite surface. Coffin et al. [51] estimated the energy of peeling separation of two carbon nanotubes (or binding energy) as \(0.3\) nJ/m by using a continuum model with accounting the vdW interaction between carbon structures. The vdW interaction in their model was represented by a Lennard-Jones potential between carbon atoms.
In all of the above theoretical calculations only vdW forces are considered for the interactions of CNTs with substrates, and in most cases, the substrate is limited to graphite by modeling the vdW interactions utilizing a known potential energy between carbon atoms. It is quite clear that the unknown vdW interacting potential energy between carbon atoms and other material atoms places major limitations on the models for other substrates rather than graphite.

Experimental measurements to study the interactions between CNTs and substrates have been conducted by using many different methods in the literature but only few measurements on the shear stress. Most of these measurements are based on AFM due to the nanoscale dimensions of CNTs and the low force level of the interactions. Hertel et al. [47] studied the deformation of carbon nanotubes due to their surface vdW forces with substrates. In their experiments, AFM images show elastic bending and deformation of a MWNT over an obstacle like another MWNT, with the strain energy built up in the tubes compensated by a gain in binding/adhesion energy as the tubes maximize their contact area with the substrate. Profiles along the tube principal axis (height vs distance) were calculated by minimizing the total energy as an integral of the strain energy and the binding energy over the entire tube profile. From a fit of calculated profiles to the experimental profile of a 95 Å-diameter MWNT, an average value of the binding energy for a MWNT on a passivated silicon surface as 0.80±0.3 eV/Å (1.28±0.48 × 10⁻⁹ J/m) was obtained, which was believed to be attributed entirely to vdW interactions. The molecular dynamic mechanics calculations by Hertal et al. [47] also indicate that the width of the contact region can lie between 5% and 50% of the nanotube diameter, depending on the tube radius and number of shells. The addition of more shells inside a tube increases its rigidity, thereby reducing the area of the tube wall in contact with the substrate for MWNTs with more tube layers. To study how to
control the shape and position of individual MWNTs dispersed on a surface, Hertel et al. [7] manipulated MWNTs on a silicon surface by using AFM and showed how a MWNT can be bent, straightened, translated, rotated and cut under certain conditions. A lateral frictional force of 5 nN along a bent nanotube was estimated to keep the tube in place pinned on the substrate with certain strain energy. A shear stress of 10 MPa was obtained between the MWNT and the silicon substrate by dividing the frictional force 5 nN by the estimated contact area $A$ of $\sim 5 \times 10^{-16} \text{ m}^2$ as length $0.9 \mu \text{m} \times \text{ contact width (5% of tube diameter 100 Å)}$.

In 1999, Falvo et al. [8] used an AFM setup to study frictional and mechanical properties of CNTs. They demonstrated that a large MWNT (diameter of 39 nm) rolls and slides on a graphite substrate when pushed by an AFM tip in contact mode. A $\sim 90 \text{ nN}$ lateral force peak for a rolling tube and a lower than 20 nN sliding force in the lateral force data were obtained. Their understanding of the above results is that the tube goes through a series of pull-off events in rolling motion as the contacting regions at different points along the tube’s circumference release from the surface. Thus the pull-off force during rolling can be much higher than the force required to slide the tube. While performing a similar experiment on a SWNT bundle (800 nm long and 15 nm in diameter) on a mica substrate, the bundle structure showed ‘cable-like’ behavior (very low bending rigidity), which is due in part to the very weak inter-tube vdW interaction, as they explained. They also looked into how a relatively small MWNT (13 nm in diameter, 800 nm in length) bent and relaxed on a mica substrate in an AFM manipulation process and found that the MWNT can survive at a local strain of $\sim 16\%$ on the outside tube surface.
To further study the frictional interaction of CNTs with substrates, Falvo’s group [5] conducted more experiments on nanometer-scale rolling and sliding of CNTs on graphite substrate. For the sliding case, an in-plane rotation of a MWNT about a pivot point was observed, accompanied by a relatively smooth lateral force trace from the applied AFM cantilever. With a JKR modeled contact width of 3 nm for a MWNT with radius of 13.5 nm, a shear stress of 2 MPa was obtained for the sliding case, with their measurements of 0.006 N/m for the friction force per unit length. Besides the sliding case, a pronounced, periodic, stick-slip modulation without in-plane rotation referred to as rolling in the manipulation of MWNTs (500 nm long, radius of 13.5 nm) was observed. The stick-slip signatures in the lateral force data show a periodicity corresponding to the nanotube circumference. To compare rolling and sliding cases in a single tube, energy loss was calculated for both cases as the area under the lateral force trace (integration of the lateral force in terms of the pushing displacement). An energy loss of $(8 \pm 3) \times 10^{-16}$ J per revolution for the rolling case and an energy loss of $3 \times 10^{-16}$ J for a distance as the tube circumference (85 nm) for the sliding case were calculated, based on a manipulated MWNT with radius of 13.5 nm and length of 590 nm. They speculated that rolling may occur only when both the nanotube and the underlying graphite have long-range order (lattice registry) since the characteristic rolling was only observed on graphite.

The above speculation that rolling only occurs when the CNT is in lattice registry with a graphite surface was confirmed in [52, 53] by finding that in certain discrete orientations the lateral force of manipulation dramatically increases as they rotate the MWNT in the plane of HOPG surface with the AFM tip. The threefold symmetry (60 degree intervals) of these discrete orientations indicated commensurate contact of the hexagonal graphene surfaces of the HOPG and the
MWNT. As the CNT moves into commensurate contact, they observe the motion change from sliding/rotating in-plane to stick-roll motion. For manipulation experiments of MWNTs on mica, MoS\(_2\), SiO\(_2\), Si\(_3\)N\(_4\), there was no example of commensurate contact or rolling like on graphite surface as they claimed in [52].

In 2000, Akita et al.[54] investigated mechanical properties of a MWNT fixed onto a commercially available Si probe by using a Si\(_3\)N\(_4\) cantilever to apply force on the axial direction of the tube to cause it to buckle to obtain the Young’s modulus of the MWNT based on the applied force causing tube buckling. They also applied force on the side face of the tube to study the force constant of the nanotube cantilever inside SEM. To study the adhesion effect between the MWNT and a digital versatile disk (DVD) surface, tapping-mode AFM images of pits of 4.7 GB DVD were taken under a weak tapping amplitude of ~ 40 nm. It is found that a strain force on the nanotube corresponds to the adhesion force between the side face of the nanotube and the wall of the pit as ~ 10 nN with the force constant of the nanotube cantilever already known.

Miura et al. [55] observed that a MWNT (600 nm in length, 13nm in diameter) in commensurate contact with a graphite surface rolls naturally without a driving force after being pushed by a frictional force microscopy (FFM) tip, and the tube loses kinetic energy and stops after rolling about two revolutions. Also they found that this natural rolling only occurs under an argon atmosphere, which can be influenced by relative humidity. In another paper [56], they claimed sliding (in-plane rotation around a pivot) occurs very often on KCl (001) surface but not on graphite for stacked SWNT bundles, which is an opposite case for MWNTs reported by Falvo [52]. The frictional force was estimated to be about 11 nN from a FFM data for a point in the
SWNT bundle slides by 6.8 nm, which is 111 nm away from a pivot point, with the number of SWNTs from 10 to 200 and the lengths on the order of 100 µm. There is no stress value given in the paper since only a very small portion in the huge bundle slides during the pushing.

In 2003, Decossas et al. [57] showed germanium (Ge) (spherical cap shape, about 500 nm wide and 50 nm high) nanodots on an oxidized silicon substrate act as strong pinning centers for MWNTs. An AFM tip is applied with a normal load force (to the substrate surface) of 54 nN to push a MWNT (diameter of 20 nm and length of a few micrometers) originally contacting with a Ge nanodot away from the dot, while the nanotube does not move at a low load force like 34 nN. It actually requires a lateral force to push a MWNT, however this paper only reported the corresponding normal force of an AFM during the manipulation and claimed that the lateral pushing force varies linearly with the normal load force. In their experiments, the MWNTs tend to lie at the border of Ge dots rather than over the dots with interacting both with the dot and the substrate, which increase the total Vdw interactions forces as they explained.

In 2006, Whittaker et al. [16] studied the adhesion force between SWNTs and silicon dioxide substrate surface by using an AFM tip to push tubes vertically into a trench structure while the tubes axially slip on the trench top surfaces. In their experiments, the tubes slipped at an axial tension of 8 nN across 250-nm-wide silicon dioxide trench tops and 10 nN after selectively coating the tubes on the trench top surfaces with another silicon dioxide layer. They found that critical tension for causing slip did not depend on the contact length of the tube and surface over the narrow range of contact lengths they investigated (140-246 nm), which is not consistent with the simple macroscopic frictional force per unit length model. One year later, Davis [17] from
the same group did the same experiments with varying the contact lengths between the nanotubes and silicon dioxide from 230 to 850 nm. Their study showed the tension at which nanotubes slip begins to increase with contact length in that range. Therefore, they claimed that the contact length independent adhesion is a uniquely nanoscale behavior.

In 2008, Bhushan et al. [58] used a MWNT AFM probe to scan across a SWNT suspended over a 2μm-wide trench to study the adhesion and friction between the two tubes. The adhesive force between nanotubes was measured from the vertical cantilever deflection when the MWNT tip end detached from the shell of the SWNT. The frictional force between tubes was obtained by analyzing the dissipated vibrational power of AFM cantilever since the interaction between the tubes caused the attenuation of vibrational amplitude of the AFM cantilever. A coefficient of friction of 0.006±0.003 was obtained by dividing the friction with the adhesion measured (4±1 pN/0.7±0.3 nN). The shear strength between the MWNT AFM probe and the suspended SWNT was derived to be 4±1 MPa by using a continuum model with the estimated contact area of 0.9 nm² by using the JKR model based on a reported value of 0.22 N/m as the work of adhesion between nanotubes.

Also Ono et al. [59] investigated the interaction between a vibrating tip of an AFM and CNTs suspended over a trench on a Si wafer in water and in air and suggested that the adhesion force between the AFM tip and CNTs is weaker in water than in air. Strus et al. [60] developed a theoretical model and applied a MWNT AFM probe to conduct a MWNT peeling from a HOPG surface process to look into the adhesive nanomechanics between nanotubes and substrate surface. Their results showed multiple sudden transitions of the peeling force as the geometric
configuration of the MWNT changes during the peeling process. They obtained the force to peel a MWNT from a HOPG surface is \( \sim 15 \) nN.

In 2009, Hsu and Chang [6] also performed lateral manipulation in an AFM to move a MWNT on a silica (silicon dioxide) surface. MWNTs rotate around a pivot point during the pushing by an AFM tip. In their calculations, the frictional force between the tube and the substrate was equated to the lateral pushing force and 5% of the MWNT diameter was used for the contact width. For two different individual MWNTs on the substrate, each was pushed several times and each push for the same MWNT ended up with quite different shear stress values. For example, for MWNT1 (100 nm in diameter, 4.2 \( \mu \)m in length), a shear stress of \( \sim 60 \) MPa, \( \sim 80 \) MPa, and \( \sim 110 \) MPa were obtained for 3 pushes with different push point on the tube. The problem should come from simply using the pushing force at a point of the tube as the assumed uniform frictional force for the MWNT rotating around a pivot. By considering the equilibrium of the rotating moments around the pivot caused by the pushing force and by the frictional force along the whole length of the tube, the frictional force per unit length can be obtained for each push as 0.49 N/m, 0.55 N/m, and 0.55 N/m, respectively. Based on the assumed 5% of the MWNT diameter as the contact width, an average shear stress for 3 pushes of MWNT1 and MWNT2 (60 nm in diameter, 1.8 \( \mu \)m in length) can be calculated as 106 MPa and 138 MPa. These values are much higher compared to the previous reported shear stress of MWNTs on other substrates such as 2 MPa on graphite [5], 4 MPa on SWNT [58], and 10 MPa on silicon [7]. In comparison, all these reported shear stress values by different groups are shown in table 1.1. Therefore, it is clear that the interaction between CNTs and substrates depends greatly on the intrinsic surface property of the substrate materials.
Table 1.1. Results on shear stress between MWNTs and different substrates in literature

<table>
<thead>
<tr>
<th>Author</th>
<th>Technique</th>
<th>Substrate</th>
<th>MWNT Diameter (nm)</th>
<th>MWNT Length (nm)</th>
<th>Contact Length (μm)</th>
<th>Shear Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hertel [7]</td>
<td>AFM</td>
<td>Silicon</td>
<td>10</td>
<td>10×5%</td>
<td>0.9</td>
<td>10</td>
</tr>
<tr>
<td>Falvo [5]</td>
<td>AFM</td>
<td>Graphite</td>
<td>13.5</td>
<td>3 (JKR model)</td>
<td>0.59</td>
<td>2</td>
</tr>
<tr>
<td>Bhushan [58]</td>
<td>AFM</td>
<td>SWNT</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>Hsu [6]</td>
<td>AFM</td>
<td>Silica</td>
<td>100</td>
<td>100×5%</td>
<td>4.2</td>
<td>106</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>60</td>
<td>60×5%</td>
<td>1.8</td>
<td>138</td>
</tr>
</tbody>
</table>

After that, there is not much work been done to directly look at the adhesion or frictional force between CNTs and substrates. Only a few relevant papers were published. In 2010, Ke et al. transferred SWNT bundles to a copper grid and used a piezo-driven nanomanipulator to peel a branch of SWNT from its originally bound SWNT bundle under SEM. Based on a nonlinear elastic model, they estimated the adhesion energy between bundles (0.126-0.162 nJ/m) according to the deformation curvature of the delaminated SWNT bundle during the peeling process [61].

In 2013, this same group pulled an embedded SWNT out from PMMA using a pre-calibrated AFM cantilever in a SEM to look into the interaction force at tube-polymer interface. A interfacial stress of 85–372 MPa was obtained between the SWNT and PMMA surface by dividing the maximum pulling force during the process by the tube surface area [61].

As we can see, most of the experiments to measure the adhesion or frictional force between CNTs and substrates developed so far use an AFM, which brings operational difficulties and analysis complications. For those tests with manipulation of the nanotubes on a substrate surface,
the CNTs move perpendicular to the axis of the tube and the substrate has to be very smooth, with the roughness lower than the diameter of the nanotube, for an AFM to acquire good images of the tube on the surface. Therefore, shear stress of CNTs has only been measured on a few substrates like graphite, silicon and silicon dioxide. For those nanoelectromechanical devices with CNTs contacting metallic electrodes [13], the shear stress between CNTs and these metallic substrates could have a great effect on the device performance. However, there are no reported results on the interaction of CNTs with metals like gold in the literature yet.

It is very useful to develop an easily controllable method to study the interactions of the nanotubes with different surfaces. In our research, a novel technique based on a NEMS cantilever is developed and used along with modeling to determine the interfacial shear stress between a SWNT bundle and cantilever surfaces using a ZYVEX nanomanipulator combined with a SEM system. As discussed in the later chapters, this method does not use an AFM and can be used on a range of different substrates.
Preparation of the NEMS cantilever based device for testing

The new technique used in this work to determine the shear stress between dielectrophoretically assembled SWNTs and surfaces is based on simple NEMS cantilever beams, a nanomanipulator, an scanning electron microscope (SEM) along with a mechanic model. In this chapter, I will focus on the fabrication process of the NEMS devices.

2.1. Structure design

The initial design consisted of a flexible cantilever and a stationary electrode with a SWNT bundle assembled between them on the top surfaces, as shown in figure 2.1. The idea was to use a piezo-driven nanomanipulator to push the flexible cantilever away from the stationary electrode by a certain distance to cause SWNTs to slip on the surfaces as the gap between the electrodes increases. After releasing the cantilever, the gap recovers and there will be a certain amount of axial slack (increased length relative to the initially taut length) in the initially taut SWNT bundle produced due to the axial residual displacements from both sides. When the gap is increasing, the frictional force resists the tubes slipping on the surfaces, and the displacement of the tube due to slipping depends on the frictional force. Therefore, the axial slack depends on the frictional force (or shear stress). The basic principle of this technique is to measure the axial slack to determine the shear stress between SWNTs and substrates.
The corresponding fabricated testing device is shown in figure 2.2. To calculate the shear stress, the contact length of the SWNT bundle with the substrate surface should be known. However, with the whole electrode made of gold here, the nanotubes can touch the side wall or even the bottom surfaces of the electrodes during the dielectrophoretic assembly. Even with the nanotubes touching the top surfaces of the electrodes, the length of the nanotube on the surface can not be measured based on SEM images because of poor contrast, as shown in figure 2.3.
Figure 2.2 SEM of the fabricated cantilever based testing device at a side view (dried by critical point drying process after the structure is released by wet etch)

Figure 2.3 SEM of the fabricated cantilever based testing device with a SWNT bundle on the electrode surfaces
To solve this problem, I redesigned the structure and the improved structure is shown in figure 2.4. This improved structure has two cantilevers in between two triangular electrodes on the sides. The gap between the two side electrodes is \(~1.6 \, \mu\text{m}\) and the gap between the two cantilevers is \(~300 \, \text{nm}\). The electrode gap is limited by the SWNT length (the average length is 1 \, \mu\text{m} according to the supplier) in order to assemble SWNT bundles between the electrodes. To minimize the chance of introducing contaminants onto the cantilever surfaces, regular N\(_2\) blow drying is conducted after the cantilevers are released. Therefore, the gap between the cantilevers has to be big enough to avoid the two cantilevers being pulled together by the meniscus force during normal N\(_2\) blow drying. Another consideration of the gap size is that the suspended SWNT bundle over the gap has to be seen clearly to check its status after tests. The dimensions of the cantilever beam are chosen so that the restoring force in the cantilever beam will overcome the meniscus force pulling the cantilever toward the substrate during N\(_2\) drying. With the thickness and width set to be 300 nm, cantilevers with different lengths were fabricated to check the right length range for successful release by N\(_2\) drying. As shown in figure 2.5, the cantilevers with lengths below 6 \, \mu\text{m} are all successfully released while the ones longer than 6 \, \mu\text{m} fall down on the substrate after N\(_2\) drying. Therefore, the length of the cantilever is set to be \(~5.5 \, \mu\text{m}\) for the test device.
Figure 2.4 SEM of the fabricated redesigned cantilever structure (side view)

Figure 2.5 SEM of an array of cantilevers beam with different length after $N_2$ blowing drying
After dielectrophoretic assembly, a SWNT bundle is aligned between the side electrodes, across the top surfaces of the two cantilevers, as shown in figure 2.6. The contact length between the SWNT bundle and the cantilever surfaces is just the width of the cantilevers, which can be measured easily.

![Figure 2.6 SEM of the device with a SWNT bundle assembled between the electrodes](image_url)

From a high-rate nanomanufacturing point of view, arrays of devices rather than individual device are fabricated. For each array, there are 8 devices connecting to two big pads on the sides, as shown in figure 2.7. An AC voltage is applied across these two pads in dielectrophoretic assembly so that each individual device in the array has the same chance to get CNTs assembled.
2.2. Fabrication process

In this section, I will cover the details of the NEMS device fabrication process. The micro/nano-fabrication is conducted in the George J. Kostas Nanoscale Technology and Manufacturing Research Center at Northeastern University.

The process starts with a regular 3 inch, P type, <100> silicon wafer. A 1 um layer of oxide is grown on the wafer by thermal wet oxidation, which is done in the Bruce Furnace 7355B at 1100°C for 2 hours and 15 minutes. Then a 60 nm Tungsten layer is deposited in the MRC 8667 Sputtering system at a DC power of 365 W and pressure of 13mTorr, as shown in figure 2.8 a).

The electron-beam lithography is conducted to pattern the structure on a 150 nm thick layer of PMMA, which is spin-coated at 5000 RPM for 1 minute and prebaked at 180 °C for 1 minute 30
seconds. This PMMA has a molecular weight of 970 and is diluted 1:3 with anisol before the spin-coating process. The electron-beam writing was done with two NPGS writing entities per pattern. The 10 µm aperture is used for writing the smaller cantilever device patterns for better resolution as shown in blue color in figure 2.8. The 120 µm aperture is used for the array pattern including the connection area and the big probing pads as shown in red color in figure 2.8 for higher writing speed. The 120 µm aperture with an associated beam current of ~5.6 nA allows for writing the array area in 15 seconds while it takes ~ 50 seconds for writing the device pattern using the 10 µm aperture with an associated beam current of ~ 41 pA . Each array structure has 8 cantilever patterns over a field of ~300 µm. For the cantilever device pattern writing, a line dose of 0.8 nC/cm was used for polyfill CAD entities with a center to center spacing of 5 nm and line spacing of 20 nm. For the array area, a line dose of 1 nC/cm was used for polyfill CAD entities with both center to center and line spacings of 20 nm. Following the writing, the sample is developed in a solution of 1:3 MIBK: IPA for 70 seconds followed by 20 seconds of IPA alone for de-scumming.
After the e-beam lithography process described above opened windows in the PMMA, the remaining PMMA is used as a mask to etch the exposed tungsten layer. The exposed tungsten layer is etched through by a 10 mTorr SF6 and Ar inductively coupled plasma (ICP) (Unaxis
PlasmaTherm 790) etch with 60 W RF1 and 200 W RF2 with flow rates of 15 sccm of SF6 and 5 sccm of Ar for 3 minutes. This yields the structure in figure 2.9 b with the tungsten layer selectively etched. Then the silicon dioxide layer in the open window is isotropically etched down 500nm in 1:10 buffered oxide etch (BOE) solution for 11 minutes. The isotropic etch forms an undercut beneath the tungsten layer, which prevents the deposition of metals on the side wall during the subsequent metal evaporation. E-beam evaporation of 2 nm thick chromium and 300 nm thick gold layers is performed after the BOE etch. The chromium layer here works as an adhesion layer between the gold and the silicon dioxide. After the metal evaporation, the sample is immersed in 1:3 of 29% NH₄OH to 30% H₂O₂ solution for a lift-off process overnight. The solution etches the tungsten away and so takes the excess chromium and gold on top of it, leaving only the chromium and gold in the etched silicon dioxide area, as shown in figure 2.9 d. An extra sonication of the samples has to be performed to achieve fully lift-off when excess Cr/Au, which is supposed to be on top of tungsten, do not come off completely during tungsten etch. One possible reason to cause that is, contaminants may be caught on the SiO₂ surface prior to tungsten sputtering from the air or during tungsten sputtering from the sputtering chamber. The contaminants may come off from the SiO₂ surface in post processes before Cr/Au deposition and leave pinholes in the tungsten layer. In the pinhole area, the deposited Cr/Au does not come off by tungsten wet etch. The extra sonication is used to physically remove the excess Cr/Au.

After the lift-off, silicon dioxide is etched through in BOE for 23 minutes to release the cantilever structure and the final released structure is shown in figure 2.9 e). This BOE wet etch is an isotropic etching process. With the silicon dioxide etched down by 1 μm in the vertical direction, the device layer is undercut by approximately the same amount laterally. Therefore the
cantilever structures with widths (300-400nm) much less than 2 μm are completely released while the other larger areas end up with undercuts. A N₂ gun is used to blow the sample to dry the structure.

![Fabrication process of the NEMS cantilever structure](image)

*Figure 2.9 Fabrication process of the NEMS cantilever structure*

With the cantilevers finally released, a dielectrophoretic assembly is conducted to aim at getting one small single SWNT bundle between the two triangular side electrodes. To achieve that, the assembly parameters are optimized based on try-out experiments. The SWNT solution used here, dispersed in deionized (DI) water with a CNT weight percentage of 0.046 % (CNTRENE® C100), is from the Brewer Science company. For the assembly, microliter scale diluted CNT solution with a concentration of 310 ng/ml is placed over the array structure and a 3.4 Vpp, 500 KHz AC
voltage is applied between the two triangular side electrodes for 30 seconds. The samples are transferred to IPA directly after DEP to prevent them from drying in air. A liquid carbon dioxide critical point drying process (Tousimis Critical Point Dryer with model #Samdri®-PVT-3D) is performed to prevent the meniscus force from pulling the nanotubes toward the lower silicon surface.

A common step in micro/nano-fabrication is wet etch to release structures from the substrate. After the etch, a traditional post drying process will cause the released structures to adhere to the substrate due to capillary/ meniscus force coming from the trapped liquids. The cantilever structure designed in this work encounters the same problem. This meniscus effect has been studied and some methods have been developed to prevent it, like adding small areas with convex corners to the microstructures et al. [62]. A most common solution to that now is critical point drying (CPD) process. In normal drying process, it is the surface tension at the solid-liquid interface pulls the structures that the liquid is attached to during the liquid-gas transition. The CPD process idea is to precisely control the temperature and pressure to let the liquid medium to pass a supercritical region, where the densities of the liquid phase and vapor phase becomes equal so the direct liquid-gas transition will be avoided. An air annealing process is conducted to remove organic contaminants on sample substrates at 80 °C for 20 seconds by using a hotplate right after critical point drying.
Figure 2.10 NEMS structure with a CNT bundle before and after cutting
For the final structure, a CNT bundle goes across the tops of the cantilevers with their end portions contacting the triangular electrodes after DEP assembly. Before the nanomanipulation experiment, the CNT bundle is cut off from the side electrodes, so that it only contacts the top surfaces of the cantilevers. This cutting process is done by exposing an ultra-small area like a point of a CNT bundle under electron beam by using the spot mode at 500 KX magnifications in the Supra 25 SEM system. The SEM pictures of the structure before and after cutting are shown in figure 2.10.

A few typical things in the fabrication or experiment procedure I want to mention here. First, the Cr/Au deposition is done right after the half thickness of SiO₂ etch and to minimize the contaminants from air onto the samples. Second, on average, the time between the final SiO₂ etch in BOE and DEP assembly is ~ 30 minutes. Third, on average, the time between DEP assembly and the final Zyvex nanomanipulation is ~ 2 days. During that time, the samples are kept in 3 inch wafer holder in side cleanroom except when they are taken out for SEM imaging and SWNT bundle cutting.

2.3. Gold cantilever surface treatments with alkanethiols

To extend the variety of substrates for studying their interactions with CNTs, substrate surface treatments of the originally fabricated gold cantilevers are conducted in this work. By chemical functionalization, alkanethiol monolayers can be formed on the gold cantilever surfaces through strong covalent bonds to further study the interactions between SWNTs and functionalized gold surfaces.

Self-assembly of a monolayer of alkanethiols on gold is a quite common functionalization
process to modify gold surface. As illustrated in figures 2.11 a and b, both 2-phenylethanethiol and 2-aminoethanethiol have thiol (SH) functions connected to different end-groups via a two-carbon linker. The alkanethiols self-assemble onto the cantilever surface through relatively strong gold–sulfur bonding.

(a) Chemical structure of 2-phenylethanethiol

(b) chemical structure of 2-aminoethanethiol

(c) Assembled alkanethiol layer on a gold surface with the end-groups as the topmost surface layer

Figure 2.11 Alkanethiols and self-assembly of an alkanethiol layer on a gold surface
The pure alkanethiol in either liquid or powder form is dissolved in ethanol to produce a 1 mM solution. The samples with the final released gold cantilevers are pre-cleaned in a piranha solution at ~110 °C for 10 minutes, rinsed in DI water, and then immersed into the alkanethiol solution for 24 hours. The samples are then taken out of the solution, rinsed with 5 batches of ethanol solution in a beaker with each batch for 5 minutes, dried with a N2 gun. This assembly process produces a closely packed alkanethiol self-assembled layer on the gold cantilever surface with the corresponding end-groups exposed as the topmost surface layer, as shown in figure 2.9 d [63].

Alkanethiols with different endgroups are stable in a variety of solvents [64]. These self-assembled monolayers with a properly chosen functional end-group are essential ingredients to perform controlled modifications of surface properties like wettability, adhesion, lubrication, and corrosion. That is simply because these end-groups will be exposed as the topmost layer of the assembled film for a standing-up configuration with the SH head-group bonded with gold. Therefore, this monolayer self-assembly process offers us such a great surface treatment for gold substrate to investigate the interaction of CNTs with a variety of different chemicals. Some preliminary work for the untreated gold substrates is presented in [65] and all the results for gold substrates with or without an alkanethiol layer is published in [66].

2.4. Three post-assembly treatments of the devices
Besides alkanethiol self-assembly on the gold surface prior to assembly, the gold cantilever/SWNT interaction may also be modified by post-assembly treatments. The three examples studied here are annealing in N2, e-beam irradiation, and carbon deposition. One big difference between these three surface treatment approaches and the alkanethiol self-assembly is
these three treatments are done after SWNTs are assembled on the electrodes while the alkanethiol self-assembly ends up with the end-groups exposed as the topmost surface on the cantilever prior to assembly of the SWNTs.

It has been demonstrated that the electrical contact resistance between a CNT and metal electrodes decreases by several orders of magnitude after annealing in nitrogen [67]. In the work of SWNT-based nanoswitch [13], a small SWNT bundle was suspended over an actuation gold electrode between two side gold electrodes, an anneal of the devices at 350 °C in N₂ for 5 minutes results in a three orders of magnitude reduction in the contact resistance between the SWNTs and the side gold electrodes. It is clear that the annealing process does improve the electrical contact between the tubes and electrodes a lot. It is also very interesting to look into the effect of the annealing on the mechanical interactions. Therefore, in this work, one surface treatment is annealing the devices (with SWNTs assembled) in N₂ in a Bruce Furnace 7355B at 350 °C for 5 minutes before further nanomanipulation tests to investigate how the annealing affects the mechanical interactions between the tubes and gold surfaces.

Another post-assembly treatment is to irradiate the contact area with an electron beam with a certain exposure dose and electron energy. Similar to the N₂ annealing, e-beam irradiation has been found to be an effective way to improve the electrical contact between CNTs and metal electrodes in literature [13, 68]. It is reported that a total e-beam exposure dose of 0.7 C/cm² at 20 keV for the contact area results in a decrease in contact resistance by four orders of magnitude [68]. In this work, a contact area of 0.3μm × 1μm is exposed to the e-beam with a beam current of 130 pA (30 μm aperture and 3 KV accelerating voltage) for 16 seconds to achieve an exposure
dose of 0.7 C/cm² to study how the e-beam irradiation affects the mechanical shear stress. In addition it is noted that besides this intentional e-beam irradiation of contact area to modify the interactions, all tested devices are exposed to a certain amount of e-beam irradiation during SEM imaging before the manipulation tests. To minimize this e-beam irradiation effect, the exposure time during imaging is minimized. For an imaging area of ~ 3.7 µm × 5.7 µm at a magnification of 20 KX, if the total exposure time is approximately 10 seconds, with a beam current of 130 pA, the overall exposure dose for the device area is 130 pA×10 s/(3.7 µm × 5.7 µm) = 6×10⁻³ C/cm², which is over 100 times lower than the intentional e-beam exposure dose for surface treatments described above.

The post-assembly treatment approach conducted in this work was to expose an area adjacent to the cantilever surface to an electron beam to intentionally deposit an amorphous carbon layer on the devices. It is quite well known that during imaging an electron beam can interact with residual organic contamination in an SEM, which results in buildup of carbon contamination layers on nearby surfaces [69]. To minimize the e-beam irradiation during the carbon deposition, the cantilever surfaces are not exposed during this process. To modify the cantilever surface with this amorphous carbon layer, usually the tip of the triangular electrode close to the narrow cantilever is exposed to the e-beam for 30 minutes or 1 hour. However, the amount of carbon deposition is dependent on how clean the SEM chamber is at the time. O₂ plasma cleaning can be done to clean the chamber to minimize the carbon deposition. For the nanomanipulation process, a 30 minute O₂ plasma cleaning of the SEM chamber (Evactron 25) is performed beforehand to minimize the carbon deposition during the nanomanipulation. While for the intentional carbon deposition process, it is hard to control the resultant deposited carbon amount on the device
surfaces. But the tubes apparently grow bigger after a carbon deposition process or even for those devices without intentional carbon deposition, which indicate the presence of the carbon layer from the SEM. Therefore, it is very interesting to look into how this e-beam induced carbon deposition affects the mechanical interaction between CNTs and substrates.
Experimental methods

This chapter covers the experimental testing method used to determine the shear stress between a dielectrophoretically assembled SWNT bundle and different cantilever surfaces using the fabricated NEMS structures introduced in chapter 2.

3.1. Testing procedure overview

Nanomanipulation is conducted on the NEMS cantilever structures with the SWNT bundle cut off from the side electrodes that were described in Chapter 2. A Zyvex nanomanipulator is used to push the flexible cantilever away from the stationary cantilever which induces an axial tension in the suspended portion of the nanotube bundle. The axial tension increases as the gap between the two cantilevers increases. At some point, this induced axial tension makes the SWNT bundle start to slip on both cantilever surfaces. When the axial tension increases to the value of the interfacial shear force corresponding to the width of the narrow cantilever, the SWNT bundle slips across the whole cantilever and the axial tension stops increasing. After releasing the flexible cantilever, the originally taut nanotube bundle ends up with a certain amount of axial slack (the increased length of the originally taut SWNT bundle in between the two cantilevers), which is a function of the shear stress between the nanotube and the substrate surface. After the nanomanipulation, the SWNT bundle is checked in SEM and images of the bundle at two different angles (90° apart) are taken. These two 90°-apart SEM images give a 3 dimensional view of the bundle and allow further image analysis using Matlab to determine the axial slack amount after Zyvex Nanomanipulation

3.2. Zyvex nanomanipulator

The Zyvex S100 nanomanipulator system is a positioning and testing tool for micro- and nanoscale research and development applications. It can be used to position micro and nanoscale
samples in SEM and Focused Ion Beam (FIB) Systems. As shown in figure 3.1, the S100 head stage, which can be put in an SEM chamber, can be assembled with two, three, or four positioners (P1, P2, P3, P4), based on the needs. End effector probes are attached to the positioners to locally manipulate samples. The positioners have 3 degrees-of-freedom (DOF) moving in positive and negative X, Y, and Z axes with maximum range of motion of 12 mm. The positioned resolution is 100 nm in the coarse axes mode and 5 nm in the fine axes mode. The position is controlled using a keypad and joystick control unit. For our nanomanipulation experiment, we use a tungsten probe with a tip radius of 50 nm as the end effector probe.

Figure 3.1 S100 head assembly [70]

3.2.1 Zywex nanomanipulation

The completed NEMS devices consist of the gold cantilevers and the nanotube bundles as shown in figure 2.7, with one SWNT bundle lying across the two cantilever surfaces. An in-situ
nanomanipulation experiment is conducted on the NEMS device using the Zyvex nanomanipulator in SEM system. First, a tungsten probe is moved to the end of the long flexible cantilever. The way to determine if the probe tip is at the same height as the cantilever surface is to bring the probe tip into the same focus as the top surface of the cantilever. This part is done with great care since the sharp probe tip can be damaged very easily if it is moved too fast toward the substrate. Figure 3.2 a shows the cantilever before it is contacted and pushed by the probe. Figure 3.2 b shows the cantilever pushed by a certain displacement from its original position. This is followed by moving the tungsten probe back in the direction that the cantilever comes back towards its original position. When the cantilever hits its original position, the tungsten probe is controlled to move along the cantilever on the side and release the cantilever in the lateral direction. The release procedure is done this way to prevent the vibration of the cantilever in the pushing direction due to the adhesion at the tungsten probe-cantilever interface. The SWNT bundle slips on the cantilevers during pushing tests, and an axial slack in the bundle is produced after this nanomanipulation test.
(a) Before pushing

(b) After pushing by a certain displacement

Figure 3.2 Nanomanipulation experiment of the NEMS cantilever device
The NEMS device is imaged in SEM at two different angles (90° apart) so that the condition of the suspended portion of the SWNT bundle can be seen very clearly. Importing these SEM images into Matlab and further image analyzing allows to determine the axial slack caused during the nanomanipulation test.

3.3. Image analysis

3.3.1. SEM imaging before and after nanomanipulation

SEM images of a testing device at a top view and a side view are taken to confirm the SWNTs are originally taut before the nanomanipulation test, as shown in figure 3.3.

(a) Top view
After the nanomunipulation, SEM images of the device with a buckled SWNT bundle are taken at -20 degree and at 70 degree, shown in figure 3.4. These two images provide a 3-dimension coordinates of the tube bundle in the gap.
Figure 3.4 SEM images of the testing NEMS device after nanomanipulation
3.3.2. Axial slack of SWNT bundles induced in pushing tests

To obtain the amount of axial slack, SEM images at the -20 degree angle and 70 degree angle are imported into Matlab for analysis. A Matlab program is developed to analyze the SEM image in order to get a 3-dimensional coordinates of the SWNT bundle curve. The Matlab program codes are attached in Apendix 1. For the image at each angle, the SWNTs curve is fitted by a dotted line in Photoshop first, as shown in figure 3.5a and b.

(a) Fitted SWNT bundle at a -20 degree view
Then a developed Matlab program is run to plot the SWNT bundle curve for each angle view. The principle of the program is to obtain the coordinate information of the SWNT bundle by recognizing the pixel intensity of each fitted dot on the image. The results are shown in figure 3.6 by plotting the obtained coordinates for each image at different angle with figure 3.6a corresponding to the buckled SWNT bundle at -20 degree view and figure 3.6b corresponding to the buckled SWNT bundle at 70 degree view. Combining these two 2-dimensional coordinates together gives us a 3-dimensional SWNT bundle curve as in figure 3.6c. As shown in figure 3.6, function \( y(x) \) is for the -20 degree view image while function \( z(x) \) is for the 70 degree view image. The curve length of the buckled tube bundle is calculated in equation (3.1). The axial slack is simply equal to the length of the buckled tube bundle minus the original bundle length.
\[ L_{\text{curve}} = \int_0^L \sqrt{1 + \left(\frac{dy}{dx}\right)^2 + \left(\frac{dz}{dx}\right)^2} \, dx \] (3.1)

(a) Plotted tube bundle curve corresponding to figure 3.5a

(b) Plotted tube bundle curve corresponding to figure 3.5b
Figure 3.6 Plotted 3-dimensional tube bundle curve corresponding to the SWNTs in figure 3.5 by Matlab image analysis
Shear Stress between SWNTs and cantilever surfaces

4.1. Theoretical modeling

The modeling was done by PhD student Yu-chiao Wu in the Mechanical Engineering department [71]. For completeness, a summary of this analysis is presented below.

Here a theoretical model to determine the shear stress from the experimental measurements of nanotube slack is presented. In order to calculate the shear stress at the nanotube-cantilever interface we need to know the tension stiffness of the SWNTs. Reported values of the Young’s modulus of SWNTs depend on whether the test uses extension or bending and also on whether a solid or a hollow circular cross-section is used in the calculation [25, 27-29]. In each type of test it is either the extensional or flexural rigidity which is measured. The calculation of the modulus depends on the geometrical details of the cross-section which is not always well-defined. In our model in which tension stiffness, but not bending stiffness is included, a Young’s Modulus of 1 TPa is assumed for a hollow tube with a radius of 0.65 nm (from the supplier) and a wall thickness of 0.34 nm, according to reference [25] for this particular tube size.

In order to calculate the shear stress, we also need to know the contact width between the SWNTs and the cantilever. The contact width between a SWNT and surface depends on the rigidity of the tube cross-section [47]. A smaller SWNT diameter is more rigid than a larger one, which results in less elastic deformation in a smaller tube when contacting a surface. Less elastic deformation corresponds to a lower binding energy as the contact width decreases. However, there are many difficulties in obtaining the contact width. First, the contact width between tubes and substrates is not well defined or studies. There is one paper [7] claimed that Molecular mechanics simulations indicate that the contact width can lie between 5% and 50% of the
nanotube diameter, depending on the tube radius and number of shells, by referring to another paper [47] published in the same group. However, this referred paper [47] does not really give any number on the contact width. Also, for different substrates, the contact width can be different due to different interaction forces. It is further noted that it is actually the product of the shear stress and contact width (i.e. the shear force per unit length which is known as the shear flow in the mechanics literature) which is determined. However the use of shear stress allows ready comparison of values obtained for different cross-sectional dimensions. We assume the contact width \( b \) to be equal to the tube radius 0.65 nm in this work with SWNTs to convert the shear force per unit length to the shear stress for all tested substrates. Furthermore, in the present analysis, the effective contact width of the nanotube bundle is taken to be equal to the sum of the contact widths of the individual nanotubes, i.e. the nanotubes are assumed to spread out on the contact surface. With this assumption, the shear stress becomes independent of the number of SWNTs in a bundle.

Initially the longer, narrower cantilever is pushed away from the shorter, wider, stationary cantilever which causes the gap to elongate. In order to accommodate this increase in the gap, the SWNT bundle slips over part of the contact length on each cantilever and the bundle elongates. This region of slip is accompanied by a constant shear stress \( \tau \) between the nanotube and the cantilever surface. This first state is called the double partial-slip state. The slip displacement (the difference between the final position and the original position of the tube) \( u_{PS} \) at the end of the suspended section is given by:

\[
 u_{PS} = \frac{T_0^2}{2EA \pi b} \quad (4-1)
\]

where \( E \) and \( A \) are the elastic modulus and the cross-sectional area of the SWNT bundle.
respectively. The tension \( T_0 \) in the suspended portion can be obtained by equating the gap elongation \( u_G \) to the sum of the nanotube stretch in the suspended section \( (T_0L/EA) \) and the slip displacements \( u_{PS} \) on each cantilever leading to:

\[
T_0 = \frac{\tau b}{2} \left( \sqrt{\frac{4}{\tau b} EAu_G + L^2} - L \right)
\]  

(4-2)

where \( L \) is the as-fabricated length of the suspended section.

When the gap elongation \( u_G \) is sufficiently large, the entire length of the SWNT bundle on the narrow cantilever \( (L_C) \) will slip. With increasing gap elongation the friction force on the narrow cantilever side remains constant at \( \tau b L_C \) because the slip length can no longer increase. Due to the force balance, the tension \( T_0 \) of the suspended portion equals the friction force and the SWNT bundle maintains the partial slip state on the wider cantilever. This state is called the complete-partial-slip state. On the complete slip side (the narrower cantilever), the slip displacement \( u_{CS} \) at the end of the suspended section is given by:

\[
u_{CS} = u_1 + \frac{\tau b L_C^2}{2EA}
\]  

(4-3)

where \( u_1 \) is the free end displacement of the SWNT at the narrow cantilever side. This quantity can be found by equating the gap elongation and the sum of the nanotube stretch in the suspended section and the slip displacements \( u_{CS} \) and \( u_{PS} \) by Eqns. (4-1) and (4-3) respectively:

\[
u_G = \frac{\tau b L}{EA} + u_{CS} + u_{PS}
\]  

(4-4)

From Eqns. (4-4), it is easy to get:

\[
u_1 = \nu_G - \frac{\tau b}{EA} L_C (L + L_C)
\]  

(4-5)

After the probe allows the longer cantilever to bend back to its straight equilibrium position (i.e.
gap recovery) the SWNT bundle undergoes reverse slip over half the length of each slip zone. This result is necessary in order for the SWNT bundle on the cantilevers to remain in equilibrium with the suspended nanotube bundle which has zero tension after gap recovery. Thus on the partial slip side, the slip displacement \( u_{PSR} \) at the end of the suspended portion after gap recovery is given by:

\[
u_{PSR} = \frac{T_{0\text{max}}}{4EA} \frac{\tau b}{2}\]

(4-6)

where \( T_{0\text{max}} \) is the maximum value of the tension \( T_0 \) during the gap elongation process. On the complete slip side, the slip displacement \( u_{CSR} \) is given by:

\[
u_{CSR} = u_G - \frac{\tau b}{EA} L_c \left( L + \frac{3}{4} L_c \right)
\]

(4-7)

Nanotube buckling occurs after gap recovery due to the slip displacements at both ends of the suspended portion. The sum of these two slip displacements is equal to the axial slack \( u_S \).

Accordingly in the double partial-slip state, the slack \( u_S \) is obtained by:

\[
(u_S)_{D-P} = \frac{\tau b}{8EA} \left( \frac{4}{\tau b} \frac{EAu_G + L^2 - L}{L} \right)^2
\]

(4-8)

whereas in the complete-partial-slip state, the slack \( u_S \) is found as:

\[
(u_S)_{C-P} = u_G - \frac{\tau b}{EA} L_c \left( L + \frac{1}{2} L_c \right)
\]

(4-9)

Summarizing, the frictional shear stress \( \tau \) can be determined by equation (4-8) for the double partial-slip state or by equation (4-9) for the complete-partial-slip state with the original gap width \( L \), the gap elongation \( u_G \), the width of the narrow cantilever \( L_c \), and the measured slack \( u_S \).

The analysis above is applicable to the higher shear stresses found for the gold and the gold/2-
aminoethanethiol surfaces. However, for the cantilevers with a self-assembled layer of 2-phenylethanethiol the axial slack was measured to be greater than the gap elongation (This will be explained by the tendency of the nanotube bundle to adhere to the sides of the cantilevers in the section below). This counter-intuitive result of greater axial slack than the gap elongation can be explained by a sufficiently low shear stress $\tau$ which causes a very low induced tension as well as a low corresponding strain energy. Hence the following analysis neglects elastic strain energy but includes the work of adhesion between the SWNT bundle and the surface, i.e. the SWNT bundle is considered to be an inextensible string.

![Diagram](image)

*Figure 4.1 Processes of a SWNT bundle slipping on the cantilever surface with a sufficiently low value of the shear stress $\tau$ and the adhesion effect. (a) state before testing, (b) during gap elongation, and (c) after gap recovery.*

The cross-section of the device before testing is shown in figure 4.1a. Before testing, the SWNT bundle on the cantilever surfaces is held in place by pinning forces at both ends of the suspended portion. During gap elongation, the pinning forces are broken which causes the bundle to...
become mobile. Then the SWNT bundle slips only on the narrow cantilever surface as shown in figure 4.1b because the total shear force at the wide cantilever side exceeds that at the narrow cantilever side. This induced mobility of the SWNTs can allow the tubes to adhere to the curved sides of the cantilevers if the resulting reduction in adhesion energy is greater than the work done by the shear stress \( \tau \). This work done by the shear stress is given by:

\[
W_S = -\tau b L_N \left[u_G + R_N \left( \theta_N - \sin \theta_N \right) + R_W \left( \theta_W - \sin \theta_W \right) \right] \tag{4-10}
\]

where \( \theta_N \) and \( \theta_W \) are the attached angles which form during gap elongation on the curbs at the narrow and wide cantilevers respectively. The adhesion energy is given by:

\[
W_A = -\Delta \gamma b \left( L_N + R_N \theta_N + R_W \theta_W \right) \tag{4-11}
\]

Then a total potential energy can be defined as the difference between the adhesion energy and the energy dissipated by the shear stress: \( \Pi = W_A - W_S \). It is noted that although the friction force is nonconservative, a potential can nevertheless be defined, but only during the phase in which the slip is unidirectional. The equilibrium state exists when

\[
\frac{\partial \Pi}{b R \partial \theta_N} = -\Delta \gamma + \tau L_N \left( 1 - \cos \theta_N \right) = 0 \tag{4-12a}
\]

\[
\frac{\partial \Pi}{b R \partial \theta_W} = -\Delta \gamma + \tau L_N \left( 1 - \cos \theta_W \right) = 0 \tag{4-12b}
\]

From equation (4-12) the values of \( \theta_N \) and \( \theta_W \) can be easily proved to be equal: \( \theta_N = \theta_W = \theta \). It is noted that the vertical difference between two attached lengths \( R_N \theta \) and \( R_W \theta \) results in a tilt angle of the suspended portion. That tilt angle is sufficiently small to be neglected in this model. In order to keep the total potential energy at a minimum, the adhesion increases the contact lengths \( R_N \theta \) and \( R_W \theta \) on both curbs at the narrow and wide cantilevers respectively.
A parameter $\mu$ with the dimensions of length is defined as the ratio of the work of adhesion $\Delta \gamma$ to the shear stress $\tau$:

$$
\mu = \frac{\Delta \gamma}{\tau} = L_N \left( 1 - \cos \theta \right) \quad (4-13)
$$

For the limiting case when the parameter $\mu$ approaches zero, the attached angle $\theta$ approaches zero, implying that the work of adhesion $\Delta \gamma$ is too small for this effect to be important.

After gap recovery, as shown in figure 5c, the gap elongation $u_G$ and the attachment of the CNT to the curb produces a slack: $u_s = u_G + R_N (\theta - \sin \theta) + R_w (\theta - \sin \theta)$. The parameter $\mu$ can now be determined from:

$$
u_s = u_G + \left( R_N + R_w \right) \left( \cos^{-1} \frac{L_N - \mu}{L_N} \right) - \left( R_N + R_w \right) \sin \left( \cos^{-1} \frac{L_N - \mu}{L_N} \right) \quad (4-14)
$$

It is noted that gap recovery allows more of CNT bundle to attach to the curbs. Therefore the final observed attached angles (figure 4.1c) are larger than those during the gap elongation (figure 4.1b).

Summarizing, for this case corresponding to a low shear stress $\tau$ between the CNT bundle and the surface, the slack is larger than the gap elongation $u_G$ because of the tendency of the nanotube bundle to adhere to the sides of the cantilevers. This phenomenon was not observed until after the pinning forces of the nanotubes to the cantilever surfaces were broken during gap elongation, causing the tubes to become mobile. The parameter $\mu$ can be determined by equation (4-13) with an observed slack $u_s$, a measured original contact length $L_C$, two measured curvatures $R_L$ and $R_R$ for the left and the right curbs respectively, and a given gap elongation $u_G$. 


4.2. Shear stress between SWNTs and different substrate surfaces, and shear stress with post-assembly modifications

The nanomanipulator-based experiments have been performed on cantilevers with surfaces of untreated gold, gold with self-assembled layers of 2-phenylethanethiol and 2-aminoethanethiol, and with untreated gold cantilevers that were annealed, electron-beam irradiated or carbon deposited after assembly of the SWNTs.

4.2.1. Untreated gold substrate

For the untreated gold substrate, after nanomanipulation, the slack was less than the gap elongation and therefore the model with negligible work of adhesion was used to calculate the shear stress. The experimental parameters and calculated shear stresses, with an average value of 87 MPa and a range of 71-108 MPa for untreated gold surfaces, are shown in table 4.1. These 6 test results illustrate that the measurement is reasonably repeatable from device to device.

**Table 4.1.** Shear stress calculated for 6 tests on untreated gold surfaces

<table>
<thead>
<tr>
<th>Test</th>
<th>Original gap $L$ (nm)</th>
<th>Contact length $L_C$ (nm)</th>
<th>Gap elongation $u_G$ (nm)</th>
<th>Axial slack $u_S$ (nm)</th>
<th>Shear stress $\tau$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>338</td>
<td>380</td>
<td>45</td>
<td>32</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>338</td>
<td>380</td>
<td>89</td>
<td>80</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>270</td>
<td>373</td>
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<td>20</td>
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</tr>
<tr>
<td>4</td>
<td>275</td>
<td>370</td>
<td>22</td>
<td>13</td>
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<tr>
<td>6</td>
<td>361</td>
<td>364</td>
<td>42</td>
<td>28</td>
<td>108</td>
</tr>
</tbody>
</table>
4.2.2. Self-assembled 2-aminoethanethiol surface

Like the untreated gold, for the 2-aminoethanethiol surface, the measured slack after nanomanipulation was also less than the gap elongation. Therefore the model with negligible work of adhesion was used to calculate the shear stress. The experimental parameters and results for 7 tests are shown in table 4.2. The average shear stress is 142 MPa with more scatter in these results than for the untreated gold surface.

Table 4.2. Shear stress calculated for 7 tests on 2-aminoethanethiol surfaces

<table>
<thead>
<tr>
<th>Test</th>
<th>Original gap $L$ (nm)</th>
<th>Contact length $L_C$ (nm)</th>
<th>Gap elongation $u_G$ (nm)</th>
<th>Axial slack $u_S$ (nm)</th>
<th>Shear stress $\tau$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>437</td>
<td>257</td>
<td>54</td>
<td>44</td>
<td>113</td>
</tr>
</tbody>
</table>

4.2.3. Self-assembled 2-phenylethanethiol surface

For the 2-phenylethanethiol surface, the axial slacks $u_S$ are observed to be larger than the gap elongations $u_G$ for all tests conducted. As discussed earlier, this extra slack is caused by the decrease in the adhesion energy overcoming the frictional resistance between the tubes and the cantilever edge curb surface during nanomanipulation. Thus, the model for a low shear stress, which includes the work of adhesion, is applied to these tests. The results for 9 independent tests are shown in table 4.3. In addition to these 9 results, we conducted two tests that gave an axial slack smaller than the gap elongation. However, in these two tests, an obvious electron charging
phenomenon (which didn’t occur with the other 9 tests) was observed when the tungsten probe contacted the cantilever during nanomanipulation. This charging may be due to a grounding problem, and may have affected the SWNT-surface interface.

Theoretical results for the binding energy between a benzene molecule and a carbon nanotube are reported as 0.1-0.2 eV/atom [72, 73]. These values are expected to be relevant for approximating the work of adhesion between a nanotube and a 2-phenylethanethiol moiety in which the phenyl ring is allowed to interact with the nanotube. By considering a phenyl ring to have an interaction similar (in energy and area density) to a benzene molecule attached to a nanotube [72], one 2-phenylethanethiol moiety is assumed to interact with a nanotube with radius of 0.65 nm per 0.6 nm of length. It is noted that the packing density of the 2-phenylethanethiol monolayer on the gold surface (4.65 molecules per square nanometer) [74] does provide adequate moiety density on the surface. Then the work of adhesion obtained is 0.5 J/m² based on the binding energy of 0.2 eV/atom [73]. The shear stress can then be calculated from the parameter $\mu$ to have an average value of 7.2 MPa based on the 9 tests in table 3. It is noted that the strain energy is neglected in the model for this kind of result, as follows: the tension of the suspended portion is equal to the friction $\tau b L_c$ on the narrow cantilever during gap elongation. Then, for example in the case of Test 8, the work done by the shear stress and the strain energy are 718 eV and 6.5 eV respectively, so that the strain energy is only 0.9% of the work done by the shear stress. For the other cases in table 3, the ratio of the strain energy to the work by the shear stress is between 0.17% and 0.90%. Therefore the strain energy can reasonably be neglected compared with the work by the shear stress under these conditions. On average, the sensitivity of the calculated shear stress to the work of adhesion is 14.4 MPa/(J/m²).
Table 4.3. Shear stress calculated for 9 tests on 2-phenylethanethiol surfaces

<table>
<thead>
<tr>
<th>Test</th>
<th>Original gap $L$ (nm)</th>
<th>$L_R$ (nm)</th>
<th>$L_L$ (nm)</th>
<th>$u_G$ (nm)</th>
<th>$R_L$ (nm)</th>
<th>$R_R$ (nm)</th>
<th>$\mu = \Delta \gamma / \tau$ (nm)</th>
<th>Shear stress $\tau$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>37</td>
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</tbody>
</table>

4.2.4. Nitrogen annealed devices

For the N$_2$ annealed gold substrate, 4 tests have been conducted by now and the results are shown in table 4.4. The first test ends up with the SWNT bundle broken obviously after the nanomanipulation, as shown in figure 4.2. For this specific testing device, the gap $L$ is 487 nm, the narrow cantilever width is 294 nm and the maximum gap elongation $\mu_G$ is 42 nm during nanomanipulation. If we assume the contact length $L_c$ on the narrow cantilever when the tube bundle breaks is exactly the cantilever width 294 nm, and the tube bundle breaks when the gap increases at a certain amount. Then the strain in the tubes when the tubes break is $\varepsilon_{break} \leq \frac{\mu_G}{L+L_c} = 5.4\%$ with corresponding shear stress of 283 MPa. For another extreme case, if we assume the tubes do not slip during the gap elongation at all with an infinite shear stress, then the
strain in the tubes when the tubes break is $\varepsilon_{\text{break}} \leq \frac{\mu u_G}{L} = 8.6\%$. The tensile yield strength of a SWNT bundle with the tube diameter of 1.36 nm in the literature is reported to be around 5.3% [35] (a 13.7% yield strain was reported for a 194 µm long SWNT bundle in the literature [42]). Therefore, it is reasonable that the SWNTs in this test break before the gap is elongated to its maximum size. This SWNTs breaking after tests suggests a relatively higher shear stress for the annealed surface compared to untreated surfaces, the estimated shear stress is discussed later.

<table>
<thead>
<tr>
<th>Test</th>
<th>Original gap $L$ (nm)</th>
<th>Narrow cantilever width (nm)</th>
<th>Gap elongation $u_G$ (nm)</th>
<th>Axial slack $u_S$ (nm)</th>
<th>Shear stress $\tau$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>294</td>
<td>42</td>
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<tr>
<td>2</td>
<td>497</td>
<td>271</td>
<td>62</td>
<td>61</td>
<td>301*</td>
</tr>
<tr>
<td>3</td>
<td>526</td>
<td>260</td>
<td>68</td>
<td>68</td>
<td>314*</td>
</tr>
<tr>
<td>4</td>
<td>571</td>
<td>240</td>
<td>90</td>
<td>76</td>
<td>340*</td>
</tr>
</tbody>
</table>

* Estimated based on breaking strain of 5.3% [35].
(a) SEM of the device before nanomanipulation with the SWNT bundle (the upper one) not cut off from the side electrodes yet

(b) SEM of the same device with the tube bundle broken (the upper one) after nanomanipulation

Figure 4.2 SEM of a device annealed in N₂ before and after nanomanipulation in test 1
In another two tests (test 2 and 3), the axial slack in the tubes after the tests is almost equal to the gap elongation and one test resulted in a very non-uniform bundle in the gap after nanomanipulation, as shown in figure 4.3. On the other hand, the nanotube in figure 4.4 appears to be nearly uniform. For test 2, during gap elongation the shear stress at the interface may be high enough to resist complete slipping at the narrow cantilever surface and the increasing strain in the tubes causes the bundle to start to break. The interactions between the tubes are not strong enough to hold the tubes together and some tubes may slip relative to each other in the bundle, which causes an apparent plastic deformation of the bundle in the gap after nanomanipulation. For test 3, though there is no apparent plastic deformation of the bundle seen in the SEM image, it may still be possible that a high shear stress at the interface causes the tubes about to break but the tubes haven not started to slide in the bundle yet. During gap elongation, if the shear stress is large enough that the bundle does not reach the complete slip state, the strain would be greater than 8.1 and 8.7%, respectively for test 2 and test 3, assuming that the nanotubes do not break. The corresponding shear stress values would be at least 460MPa, 515MPa respectively for test 2 and test 3 by assuming the slipping length of the tubes is exactly the narrow cantilever width. For another extreme case, if we assume the tubes do not slip at all at the tube-substrate interface during gap elongation, then the strain in the tubes when the tubes break is \( \varepsilon_{\text{break}} \leq \frac{\mu \sigma}{L} = 12.5\% \) for test 2 and 15.8% for test 3, which is much higher than the reported yield strain 5.3% in the literature [35]. Therefore it is reasonable that if the shear stress is high enough and the tubes do not reach complete slip on the surfaces, the strain in the tubes will cause the tubes to break.
Figure 4.3 SEM of a device annealed in N$_2$ with the tube bundle not completely intact (the second upper bundle in the image) after nanomanipulation in test 2

Figure 4.4 SEM of a device annealed in N$_2$ with the axial slack in the bundle equal to the gap elongation after nanomanipulation in test 3
In the last case of the N\textsubscript{2} annealed gold surface, the axial slack (76 nm) is smaller than the gap elongation (90 nm) but the initially uniform SWNT bundle also become nonuniform after the test, as shown in figure 4.5. The shear stress is calculated as 133 MPa for this case without considering the fact that the tubes are not completely intact after the nanominipulation, which makes the calculated shear stress value suspicious. In fact, this nonuniform tube bundle may also indicate partial breaking and sliding of SWNTs under a high strain during the nanomanipulation. A high shear stress at the interface which resists slipping of the SWNTs on the surface can is necessary to break the nanotubes. Therefore, the test results for the annealed gold substrates suggest a high shear stress compared to the untreated gold surfaces. If we assume the tubes start to break at a strain $\varepsilon_{\text{break}}$ of 5.3% for all the tests, with the contact length $L_c$ smaller than the narrow cantilever width, the shear stress is determined to be greater than 280 MPa, 301 MPa, 314 MPa, and 340 MPa for test 1, 2, 3 and 4 respectively according to $\varepsilon_{\text{break}} = \frac{\tau b L_c}{E A}$, where $b$ is the contact width.
(a) SEM of the device before nanomanipulation at a top view

(b) SEM of the device before nanomanipulation at a side view
4.2.5. **Electron-beam irradiated devices**

For the electron beam irradiated device with an exposure dose of 0.7 C/cm², 5 tests were conducted. The results are shown in Table 4.5. The three tests give an average shear stress of 202 MPa, while the other two tests have axial slack very close to the gap elongation. These two tests, numbers 4 and 5 in the table, resulted in nonuniform tube bundles. The top views of the two devices are shown in figure 4.6. As discussed previously for the annealed substrates, the SWNT bundles may be partially broken and tubes may slide in the bundle, resulting in what appears to be plastic deformation after nanomanipulation, and which suggests a high shear stress, greater than the limits shown in the table. Again, if we assume the tubes start to break at a strain $\varepsilon_{\text{break}}$ of 5.3% for these two tests, with the contact length $L_c$ of the slipping tubes as the width of the narrow cantilever, the calculated shear stress is greater than 314 MPa and 307 MPa for tests 4
and 5 respectively according to $\varepsilon_{\text{break}} = \frac{r_{\text{b}} L_c}{E A}$.

### Table 4.5. 5 test results for electron-beam irradiated gold surfaces

<table>
<thead>
<tr>
<th>Test</th>
<th>Original gap $L$ (nm)</th>
<th>Narrow cantilever width (nm)</th>
<th>Gap elongation $u_G$ (nm)</th>
<th>Axial slack $u_S$ (nm)</th>
<th>Shear stress $\tau$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500</td>
<td>273</td>
<td>48</td>
<td>30</td>
<td>163</td>
</tr>
<tr>
<td>2</td>
<td>532</td>
<td>253</td>
<td>54</td>
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<tr>
<td>3</td>
<td>526</td>
<td>260</td>
<td>46</td>
<td>23</td>
<td>214</td>
</tr>
<tr>
<td>4</td>
<td>519</td>
<td>260</td>
<td>40</td>
<td>38</td>
<td>314*</td>
</tr>
<tr>
<td>5</td>
<td>494</td>
<td>266</td>
<td>53</td>
<td>53</td>
<td>307*</td>
</tr>
</tbody>
</table>

* Estimated based on breaking strain of 5.3%.

(a) SEM of the device after nanominipulation for test 4
(b) SEM of the device after nanomanipulation for test 5

Figure 4.6 SEM of two different devices with e-beam irradiated contacts with after nanomanipulation

4.2.6. Carbon deposited devices

For the carbon deposited devices, four tests were conducted, with the results shown in table 4.6. The SEM images of the devices are shown in figure 4.7, 4.8, 4.9, and 4.10 for test 1, test 2, test 3 and test 4 respectively. In fact, the amount of carbon deposited on the substrate is not easily controlled in the experiment. It really depends on the contamination condition of the SEM chamber at the time the experiments are done. For tests 1 2 4, the carbon deposition step was conducted for 30 minutes, while for test 3, the carbon deposition step was conducted for 60 minutes. Theoretically, if the chamber condition was the same, then the relatively higher shear stress for the test 3 may be due to the longer carbon deposition time which probably gives a thicker carbon layer on the device. Some efforts were made trying to look at the thickness of the deposited carbon layer by analyzing the device surface components in the SEM with an energy-
dispersive X-ray spectroscopy (EDS). But no energy peak is found for the carbon material on the surface, which may be due to the small amount of carbon. However, from the SEM images for each test, it is quite obvious that the tube bundle become bigger after the nanomanipulation in figure 4.7, 4.8, 4.9, and 4.10. For test 4, the axial slack is even larger than the gap elongation which is not consistent with the other 3 tests. From the SEM image of the device after nanomanipulation in figure 4.11, the SWNT bundle may be not long enough to cover the whole cantilever width on the right. One possibility is the shear stress is very low as for the 2-phynelethantiol surface which always ends up with a larger axial slack than gap elongation after nanomanipulation. But this may be not true with all the other 3 tests having a quite high shear stress. There may be something unknown occurred for test 4 which really is a mystery for now.

**Table 4.6.** 4 test results for carbon deposited gold surfaces

<table>
<thead>
<tr>
<th>Test</th>
<th>Original gap $L$ (nm)</th>
<th>Contact length $L_C$ (nm)</th>
<th>Gap elongation $u_G$ (nm)</th>
<th>Axial slack $u_S$ (nm)</th>
<th>Shear stress $\tau$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>487</td>
<td>279</td>
<td>46</td>
<td>32</td>
<td>124</td>
</tr>
<tr>
<td>2</td>
<td>474</td>
<td>279</td>
<td>52</td>
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<td>200</td>
</tr>
<tr>
<td>4</td>
<td>503</td>
<td>284</td>
<td>52</td>
<td>65</td>
<td>--</td>
</tr>
</tbody>
</table>
Figure 4.7 SEM of the devices with carbon deposited substrate in test 1
(a) Before nanominipulation

(b) After nanomanipulation

Figure 4.8 SEM of the devices with carbon deposited substrate in test 2
(a) Before nanomanipulation

(b) After nanomanipulation

Figure 4.9 SEM of the devices with carbon deposited substrate in test 3
Figure 4.10 SEM of the devices with carbon deposited substrate in test 4
4.3. Discussion

With all the shear stress values found for SWNTs on gold, with and without alkanethiols and also for devices modified using N₂ annealing, e-beam irradiation and e-beam induced carbon deposition after SWNT assembly, the results are discussed below.

4.3.1. Shear stress for gold surfaces with and without alkanethiols

In comparing our results to the relatively small number of results found in the literature, it is important to note that the SWNT bundles in our work are dielectrophoretically assembled while the CNTs reported in Refs. [5-8] are randomly dispersed on surfaces, as discussed in the section 1.2.2.2. In addition, in the experiments reported here, the nanotubes slip along the tube axis while in all those AFM-based nanomanipulation experiments with reported shear stress [5-8], the nanotubes slide in a direction perpendicular to the tube axis, with only one exception of CVD-grown CNTs slipping along the tube axis on a silicon dioxide surface [16, 17]. But in the work of [16, 17], there is only threshold axial tension in the tube to cause it to slip reported.

The test results illustrate that the shear stress between nanotubes and an untreated gold surface is larger than the shear stress between nanotubes and silicon (10MPa) [7], graphite (2MPa) [5], and silica (60MPa) [6] surfaces, likely due to charge transfer interactions between the metal and the SWNT surfaces. Upon coating the Au surface with a monolayer of either 2-aminoethanethiol or 2-phenylethanethiol, the Au-SWNT charge transfer interactions are significantly reduced and likely shut down completely. Interestingly, the SWNT-2-aminoethanethiol interface has the highest shear stress of the three interfaces tested, 2 times higher than that for untreated gold. This behavior must result from enhanced bonding between the amino end-groups and the SWNTs, as compared to untreated gold. In fact, enhanced charge transfer interactions between several
amines and CNTs have been reported. The amines include ammonia, butylamine and 3-(aminopropyl) triethoxysilane [75] as well as polyethyleneimine [76] and even proteins [77]. Conversely, the shear stress between SWNTs and the 2-phenylethanethiol surface is 10 times lower than that for untreated gold. This reduced shear stress implies weaker interactions between the 2-phenylethanethiol surface and SWNTs, as expected. The exposed phenyl groups of the 2-phenylethanethiol surface are not expected to participate in charge transfer interactions with SWNTs. Instead, they bind to the SWNT surfaces via relatively weak $\pi-\pi$ stacking interactions.

Thus, we have demonstrated that through simple modification of the Au surface, the interaction energies and associated shear stresses between SWNTs and the Au cantilever can be tuned in either direction, and by a factor of 20 overall.

For untreated gold substrates, it is mostly likely that the interaction with SWNTs mainly comes from van der Waals (vdw) bonding, while for the 2-phynelethanthiol surface, it is reported that there would be pi-pi stacking between phynel end-groups and CNTs [46]. For the interaction between CNTs and substrates of aromatic group chemicals (like 2-phynelethanthiol), this pi-pi bond effect would likely dominate over other interactions. The SWNTs used in the experiment is functionalized with unknown quantities of $-\text{COOH}$ groups which could make the originally hydrophobic tube surface hydrophilic if sufficiently numerous. Though many $-\text{COOH}$ groups are at the cap ends of tubes, the nanotube processing will like lead to a certain density of $-\text{COOH}$ groups on the tube side surface s which would affect the interfacial interaction between tubes and substrate surfaces. Untreated gold substrates are reported to be hydrophilic with contact angle of $\sim62^\circ$ [78]. Aromatic group functionalized gold substrate tends to have higher contact angle like 86-88$^\circ$ [79]. Therefore, the vdw force between SWNTs and untreated gold substrates should be
higher compared to that for 2-phynelthaniol surfaces. However, as is stated earlier, the pi-pi bond probably dominates over vdw interactions between SWNTs and 2-phynelthaniol surfaces. In addition, it has been reported that there is no simple correlation between adhesion and friction/shear stress, but that friction/shear stress does correlate with adhesion energy hysteresis [80]. How the shear stress/friction is related to the adhesion due to these different bonding mechanisms is not studied directly in this work. For 2-aminoethanethiol surfaces, there may be covalent coupling between –COOH groups and –NH₂ groups, which can induce stronger adhesion energy compared to that due to noncovalent bonding.

4.3.2. Shear stress for annealed, e-beam irradiated, carbon deposited devices

In the literature, it has been shown that electrical contacts between metallic pads and SWNTs can be reduced by 3 to 4 orders of magnitude through either annealing in nitrogen [67, 81] or by e-beam irradiation [68, 81]. Electrical contact resistance between a MWNT and Ti-Au electrodes decreases by 3 to 4 orders of magnitude to the range of 0.5-50 KΩ after nitrogen annealing at 600-800 °C for a given time of 30 seconds [67]. Electrical contact resistance between a SWNT bundle and Au electrodes decreases also by 3 orders of magnitude to be in the range of 10-100 MΩ by either a nitrogen annealing at 350 °C for 5 minutes or electron-beam irradiation (the irradiation time and condition are not reported in the reference) [81]. It is also reported [68] that with a irradiation dose of 0.7 C/cm², the electrical contact resistance between a MWNT and gold electrodes decreases by 4 orders of magnitude from an initial value greater than 100 MΩ to ~30 KΩ. Intentional e-beam induced carbon deposition has been used for clamping CNTs onto AFM cantilevers [36, 82] and there is no further tests conducted to measure how effective the clamping was. It is interesting for us to study how the above processes affect the shear stress between the
dielectrophoretically assembled SWNTs and gold surfaces. Some preliminary results have been obtained on the mechanical interaction between SWNTs and gold surfaces modified through these three approaches.

For the $N_2$ annealed gold surface, one test result has the SWNT bundle completely broken after nanomanipulation suggesting a relatively high shear stress than untreated gold surfaces, while the other three test results can be explained by a high shear stress at the interface as well. By assuming the critical stain to cause the tubes to break as 5.3%, the shear stress is estimated to be greater than 280 MPa, 301 MPa, 314 MPa, and 340 MPa for 4 tests respectively with an average value of 309 MPa. This is much higher than the average shear stress of 87 MPa for the untreated gold surfaces and even higher than the average shear stress of 142 MPa on the 2-aminoethanethiol surface. One possible explanation is $N_2$ annealing process at 350 °C removes contaminants and enhances the contact between the nanotube and the gold surface. Another possibility is that bonding between the $-COOH$ functional groups and the surface is enhanced by the anneal. Therefore, $N_2$ annealing seems to be a more effective way to increase the shear stress compared to modifying the gold surfaces with amino end-groups. For a device with a narrow cantilever width of ~300 nm, a shear stress larger than 280 MPa would cause stain larger than 5.3% in the tubes when the tubes completely slip on the narrow cantilever surface. Therefore, with the current testing device dimensions, a shear stress over 280 MPa is not detectable, which agrees well with the results of the calculated shear stresses.

For electron-beam irradiated surfaces, an average shear stress of 202 MPa based on 3 independent tests and an estimated average shear stress larger than 311 MPa based on 2
independent tests with partially broken tubes are obtained. This indicates that the shear stress for the electron-beam irradiated gold surfaces is even larger compared to the shear stress for 2-aminoethanethiol surfaces. The electron-beam irradiation may increase the shear stress between the tubes and the gold surface by joule heating the contact area. With 3 of the stress values lower than 280 MPa, the electron-beam irradiation may be not as effective as N₂ annealing in terms of enhancing the mechanical interactions between tubes and gold surfaces.

For the electron-beam induced carbon deposition, shear stresses of 94 MPa and 124 MPa are found for two 30 minute-deposited devices respectively and a shear stress of 200 MPa is obtained for a 1 hour-deposited device. This shows that the shear stresses are increased with carbon deposition compared to untreated gold surfaces. Also carbon deposition for longer period of time appears to increase the shear stress more compared to the shorter time, which may be due to a thicker deposited carbon layer for the longer deposition case, but this is only based on one sample. It is reasonable that with a carbon coating covering the device surface, the SWNTs may anchor to the gold better, giving a higher shear stress for the bundle compared to the untreated gold surface. Also there is no evidence of SWNTs partial breaking for the carbon deposition cases. This is probably because the shear stress at the interface is not high enough to cause the strain in the tubes to reach the yield strain.

4.3.3. The effect of bundle size and contact width on the shear stress

In our modeling, it is assumed that the bundle spreads out such that each SWNT is in contact with the substrate surface. The contact width for each tube is assumed to be equal to the tube radius and the effective contact width of the nanotube bundle is assumed to be the sum of the
contact widths of the individual nanotubes. With this assumption, the shear stress becomes independent of the number of SWNTs in a bundle. In fact, the internal tension in the tube bundle is \( n_1 T \) with \( n_1 \) as the number of tubes in the bundle, while the contact width is \( n_2 b \) with \( n_2 \) as the number of tubes in contact with substrate. If all the nanotubes are in contact with the cantilever, then \( n_1 = n_2 \), the shear stress is \( \tau = \frac{n_1}{n_2} \frac{T}{b L_c} = \frac{T}{b L_c} \). For the dielectrophoretically assembled individual SWNT bundle in our work, an average bundle height of 5.6 nm was measured on a very smooth SiO\(_2\) surface by an AFM by another student Peter Ryan [13]. Based on a 91% nanotube packing density due to the voids between the tubes, the number of tubes (tube diameter of 1.3 nm) in the bundle was estimated to be 34 by assuming the bundle cross section to be semicircular. For a diameter length of the semicircle, there are at maximum 5.6/1.3=4 tubes arranged together. If we assume the number of tubes in contact with the substrate is \( n_2 = 5.6/1.3=4 \), and with \( n_1 = 34 \), the shear stress should be around 8 times higher than the current determined values. However, with high interaction forces between SWNTs and a substrate, it is unlikely correct to consider a SWNT bundle to be a semicircle. High interactions with a substrate would make tubes to spread out to contact with the substrate while the tube-tube interactions try to keep the original bundle shape. Therefore, higher tube-substrate interactions lend to relatively more tube numbers in contact with the substrate, which means a higher \( n_2 \) and lower \( n_1/n_2 \). For different surfaces, the number of the tubes contacting with the substrate can be different. For example, the higher shear force per unit length on 2-aminoethanethiol compared to untreated gold surfaces may partially result from more tubes contacting with the substrate.

Besides the number of the tubes contacting with the substrate, the effective contact width between a tube bundle and a substrate also depends on how each tube contact with the substrate.
This is discussed in the modeling part in section 4.1.

4.3.4. The effect of incidental e-beam exposure on the shear stress

It has been demonstrated in sections 4.2.5 and 4.2.6 that the mechanical interactions between SWNTs and the substrate can be affected by e-beam exposure, either through direct e-beam irradiation or e-beam induced amorphous carbon contaminant deposition. Therefore, for regular untreated gold, alkanethiol substrates and other two post assembly treated devices, we try to minimize the e-beam exposure of the device. In a typical SEM imaging process before nanomnipulation, a device is exposed to e-beam with current of ~130 pA (EHT of 3KV, aperture of 30 μm, working distance of 6 mm). At a magnification of ~ 20 KX with an exposure area of ~ 3.7 μm × 5.7 μm, if the total exposure time is assumed to be 10 seconds, the overall exposure dose for the device area is 130 pA×10 s/(3.7 μm × 5.7 μm) = 6×10^{-3} C/cm² (3.75 electrons/Å²), which is over 100 times lower than the intentional e-beam exposure dose for surface treatments in section 4.2.5. Also to minimize the e-beam induced amorphous carbon contamination, an oxygen plasma cleaning process is always conducted right before SWNT bundle cutting and nanomanipulation experiments. As it has been found that both intentional e-beam irradiation and e-beam induced carbon deposition would increase the shear stress at the interface, it is expected that both the unintentional e-beam exposure of test devices during imaging and SWNT cutting before nanomanipulation in the SEM would increase the shear stress though the amount is minimized by our experimental procedures. The e-beam irradiation usually takes ~ 17 seconds while the SWNT bundle cutting take ~ 2 minutes. Therefore, the carbon coating mainly takes place during the cutting process. This ~2 minute carbon deposition should is much shorter compared to the intentional carbon depositions with deposition times of 30 or 60 minutes.
4.3.5. Sensitivity of the testing technique relative to the measured experimental parameters

To better understand the limitations of this developed testing technique, the sensitivity of the measurements relative to the measured dimensions like gap, gap elongation, contact length, axial slack is studied. According to the equation (4-8), the calculated shear stress is proportional to the gap elongation minus the axial slack for the complete-partial slip case and the ratio between them is:

\[
\frac{\tau}{u_G-u_s} = \frac{EA}{bL_c(L+L_c/2)}
\]  

(4-15)

The sensitivity of the shear stress versus gap elongation or axial slack is 8 MPa/nm for a typical gap of 500 nm and contact length of 300 nm. Now let us see how much uncertainty exists in the measured axial slack and gap elongation. Due to the high aspect ratio, the SWNTs buckle at quite a low strain. The critical strain for SWNT buckling can be calculated as following by assuming the tube bundle as a both ends fixed beam after nanomanipulation:

\[
\varepsilon_{cr} = \frac{4\pi^2EI}{EA L^2} = \frac{\pi^2R^2}{L^2}
\]  

(4-16)

Where \(E\) is the Young’s modulus of SWNTs, \(I\) is the area moments of inertia, \(A\) is the cross section area, and \(R\) is the radius of the tube bundle, and \(L\) is length of the bundle in the gap. If the radius of the bundle is 5.6 nm/2=2.8 nm, and the length \(L\) is 500 nm, the critical strain would be 0.03%. This means an axial slack of 0.15 nm in 500 nm long SWNT bundle in the gap will cause the tube bundle to buckle. The axial slack is obtained as the curve length \(S\) of a buckled SWNTs minus the originally taut length \(L\). The curve length \(S\) is calculated as:

\[
S = \int_0^L \sqrt{1 + \left(\frac{dy}{dx}\right)^2 + \left(\frac{dz}{dx}\right)^2} \, dx
\]  

(4-17)
where \( y(x) \) is the coordinates of the tube bundle at -20 degree view as shown in figure 3.5a and \( z(x) \) is the coordinates of the tube bundle at 70 degree view as shown in figure 3.5b. For numerical calculation,

\[
S_{i+1} = S_i + \sqrt{1 + \left( \frac{y_{i+1} - y_i}{x_{i+1} - x_i} \right)^2 + \left( \frac{z_{i+1} - z_i}{x_{i+1} - x_i} \right)^2}
\]  

(4-18)

The curve length \( S \) is calculated in a ‘for-end’ loop function with the integer \( i \) from 1-1000, and \( x_0=0, x_{1000}=L \). From equation (4-17), it is clear that the uncertainty of the axial slack comes from the deviations between the tube curve points \( \hat{y}_i \) and the fitted line points \( y_i \) for the -20 degree view, the deviations between the real tube curve points \( \hat{z}_i \) and the fitted line points \( z_i \) for the 70 degree view and the uncertainty of the measured originally length \( L \). For an SEM image at -20 degree view shown in figure 4.11a, the corresponding tube curve points \( \hat{y}_i \) is plotted by the red line with square markers standing for each \( \hat{y}_i \) in figure 4.11b, while a 7th polynomial fitting line has the fitted line points \( y_i \) relative to \( x_i \). For this fitting, the norm of residuals in \( y(x) \) is:

\[
\Delta y = \sqrt{\sum (y_i - \hat{y}_i)^2} = 3.7 \text{ nm}
\]

(a) *SEM of a tube curve at -20 degree view*
(b) CNT curve fitting

*Figure 4.11 A CNT curve and fitted line for a 20 degree view*

For an SEM image at 70 degree view shown in figure 4.12a, the corresponding tube curve points $\hat{z}_i$ is plotted by the red line with square markers standing for each $\hat{z}_i$ in figure 4.12b, while a 7th polynomial fitting line has the fitted line points $z_i$ relative to $x_i$. For this fitting, the norm of residuals in $z(x)$ is:

$$\Delta z = \sqrt{\sum (z_i - \hat{z}_i)^2} = 4.8 \text{ nm}$$
(a) SEM of a tube curve at -20 degree view

(b) CNT curve fitting

Figure 4.12 A CNT curve and fitted line for a 20 degree view
According to equation (4-17), $\Delta y$ and $\Delta z$ can result in change of the curve length $S$. If $\Delta s_y, \Delta s_z$ stands for the uncertainty amount of $S$ resulting from $\Delta y$ and $\Delta z$ respectively, then the overall uncertainty $\Delta s = \Delta s_y + \Delta s_z$. For the Matlab loop calculation with the integer $i$ from 1-1000, if in each loop, the deviation in $y_{i+1} - y_i$ is $\Delta y/1000$, then $\Delta s_y$ is calculated to be 0.13 nm for an accumulated 3.7 nm uncertainty of the fitted line $y(x)$. Similarly, if in each loop, the deviation in $z_{i+1} - z_i$ is $\Delta z/1000$, then $\Delta s_z$ is calculated to be 0.07 nm for an accumulated 4.8 nm uncertainty of the fitted line $z(x)$. Therefore, the uncertainty in the axial slack due to the error in the line fitting is 0.2 nm.

According to equation (4-17), the axial slack is also related to the measured length $L$. The SEM images of a device after nanomanipulation are taken at magnification of 50KX with a pixel size of ~ 2 nm. By taking the test 1 for electron-beam irradiated gold surfaces for an example, a 2 nm change in the original tube length will result in a change of 0.26 nm in the axial slack. As for the gap elongation, the uncertainty depends on the imaging resolution. A typical SEM image extracted from the manipulation video has a pixel size around 4 nm, so the best resolution is ~ 4 nm. Therefore, overall a 5 nm uncertainty in the gap elongation minus the axial slack gives a ~ 40 MPa difference in the shear stress (25% change compared to the calculated 163 MPa shear stress value) based on the 8 MPa/nm sensitivity. For other experimental parameters like gap $L$ and contact length $L_c$, the calculated shear stress is not that sensitive to these two parameters compared to gap elongation and axial slack. Also the relationship between the shear stress and gap $L$ and contact length $L_c$ is not linear. To get an idea of how the uncertainty in these two parameters affects the shear stress, take the first test for the untreated gold for an example. A change of 5 nm in the gap $L$ (343 nm instead of 338 nm) leads to a shear stress of 99 MPa.
compared to the original 100 MPa (1% change in the stress stress). Also a change of 5 nm in contact length \( L_c \) (385nm instead of 380 nm) gives a shear stress of 98 MPa compared to the original 100 MPa (2% change in the stress stress). It is clear that the shear stress is not that sensitive to the measured gap and contact length compared to the axial slack and gap elongation. Therefore, overall the uncertainty in all the measured experimental parameters contribute to a ~28% scatter in the shear stress for this technique.

Besides these measured experimental parameters, uncertainty in many other facts, such as young’s modulus, the effective contact width, the cross section area of the tube bundle will all cause uncertainty in the shear stress. However without the knowledge of the exact uncertainty of the above parameters, it is hard to conclude the resultant error in shear stress. I will discuss the how the shear stress is related to the above assumed parameters here. As shown in equation (4-15), shear stress is proportional to the extensional rigidity of the nanotubes \( E_A \), therefore, the uncertainty in shear stress is proportional to the uncertainty in \( E_A \). As for the effective contact width, as it is discussed in section 4.3.3, how many tubes in the bundle contacts with the substrate has a great effect on the shear stress value. The assumption of a semicircular cross section results in 8.5 times higher shear stress compared to the current assumption of 34 tube bundle contacting with the substrate. Apart from the number of tubes contacting the substrate, the shear stress is also inversely proportional to the contact width of each tube. A lower contact width relative to the current 50% of the diameter leads to larger shear stress. In fact, we are really measuring the shear force per unit length based on the experiment in concert with the theoretical model. The contact width of the tube bundle is used to convert the shear force per unit length to the shear stress.
The roughness of the surface affects how the SWNTs contact the surface and the effective contact area. The variation in the effective contact area can directly affect the shear stress results. In our current model, this roughness effect is not taken into consideration.
Conclusions and recommendations for future

5.1. Conclusions

A novel and effective technique to determine the shear stresses between a dielectrophoretically assembled SWNT bundle and a nanofabricated cantilever has been developed. The measurements were conducted in a SEM chamber using a Zyvex nanoprobe to push one of the two cantilevers with a small SWNT bundle suspended over the cantilever surfaces. This nanomanipulation of the cantilever causes the nanotube bundle to slide with respect to the surface. After testing, the axial slack of the bundle provides the input to a theoretical model that is used to estimate the shear stress at the interface. Before discussing the final conclusions on the shear stress data for each substrate, I would like to make it clear that all the shear stress values obtained are based on several assumptions in section 4.1. Therefore they are not absolutely numerically accurate.

For a gold cantilever surface, the shear stress was determined to be 87 MPa. This shear stress value is higher than that for graphite, silicon or silica surfaces previously reported in the literature. Gold cantilever surfaces were modified by chemical functionalization with alkanethiols to study the shear stress between SWNTs and different surfaces. For the self-assembled 2-phenylethanethiol surface, the shear stress was determined to be 7.2 MPa with an estimated work of adhesion of 0.5 J/m². On a self-assembled 2-aminoethanethiol surface, an average shear stress of 142 MPa was obtained. These results indicate that through simple modification of the Au surface, the interaction energies and associated shear stresses between SWNTs and the Au cantilever can be tuned in either direction, and in total by at least a factor of 20. It should be possible to further tune interaction energies and shear stresses in either direction, as required by select applications, through judicious choices of surfaces and materials.
Besides chemical functionalization, the gold cantilever/SWNT interactions have been modified through post-assembly physical treatments that have previously been shown to improve electrical or mechanical connections between nanotubes and various substrates. Post-assembly N\textsubscript{2} annealing, e-beam irradiation and e-beam induced carbon deposition were used to modify the interactions between SWNTs and untreated Au cantilevers. For N\textsubscript{2} annealed devices, the SWNTs either break or partially break, which suggests a shear stress higher than 309 MPa on average by assuming the SWNTs break at a critical strain of 5.3%. For e-beam irradiated gold surfaces, an average shear stress of 202 MPa is obtained based on 3 independent tests and another two tests suggest a shear stress higher than 311 MPa on average by assuming the SWNTs break at a critical strain of 5.3%. For e-beam induced carbon deposited gold surfaces, a shear stress of 200 MPa is obtained with 60 minute deposition and an average shear stress of 109 MPa is obtained with 30 minute deposition based on 2 independent tests. The above results demonstrate that by using N\textsubscript{2} annealing, e-beam irradiation or e-beam induced carbon deposition the shear stress can be increased by factors of 2 to at least 3 times.

This measurement technique can also be used for other materials by modifying the cantilever surface through different methods, such as metal layer deposition on the cantilevers or simply making the entire cantilever out of other materials. Further, instead of using SWNTs, the one-dimensional element under test can be MWNTs or other types of nanowires. This method of combined measurements and modeling using well controlled materials provides a way to determine the interfacial stress between a large number of quasi-one-dimensional elements (e.g., nanotubes, nanowires and nanofibers etc.) and a wide range of surfaces.
5.2. Recommendations for the future

In the future, it will be possible to further tune the interaction energies and shear stresses by systematically varying the nature of the alkanethiol end group. For example, we predict that the introduction of a larger aromatic end group like a naphthalene ring or an anthracene ring will lead to enhanced pi-pi stacking and increased shear stresses as compared to the 2-phenylethanethiol surface. Even finer control can be achieved by systematically varying the length of the carbon spacer between the thiol function and the associated end group. In this way, it may be possible to tune shear stresses to within 1 MPa, as potentially required for different applications. It has been reported in the literature that there is no simple correlation between adhesion and friction/shear stress, but that friction/shear stress does correlate with adhesion energy hysteresis [80], an idea that might be tested with properly designed and characterized nanotube-end group interactions.

It is also recommended that more work be done to look deeper into the effect of the three physical treatments on the shear stress. With the current preliminary results showing an increased shear stress through physical treatments of the devices, more data points are required to confirm the consistency of the testing results. Also it will be very interesting to study how the shear stress can be tuned by varying the surface treatment times, temperatures, doses, or thicknesses for the three methods.

With reported shear stress on silicon dioxide by AFM manipulation in the literature, it is also interesting to investigate the shear stress between SWNTs and silicon dioxide surfaces using this developed technique. Another silicon dioxide or silicon film (native oxide layer on top) can be
deposited on the original gold cantilevers with an adhesion layer in between to modify the surface for further tests. Comparing the results with the reported shear stress in the literature would provide an interesting comparison between the axial shear stress and the shear stress measured perpendicular to the nanotube axis using the AFM methods.
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Appendix 1

clear;
clc;
I=imread('B14C8A6D6_aft zyvex_D70_82_dot.tif');
I=im2double(I);
figure(1)
imshow(I);
I = imcrop;% need to crop the image here before going forward
imtool(I);% to view the pixel range
figure(2)
imcontour(I,[0.1]);%to check the pixel value on cnt
[y,x]=find(I<0.1);%check the pixel value at the cnt position, and get the position information by
using'find'
y=-y;
x=x-min(x);
a=range(x);
L=503;% the original gap or length of suspended taut CNT is 1000nm
x=x/a*L;
y=y/a*L;
%y=y/sin(80/180*pi);% for 70 degree side view
figure(3)
%plot(x,y);% to check the plot shape of cnt
plot(x,y,'--rs','LineWidth',2,'MarkerFaceColor','g','MarkerSize',10); % for sensitivity analysis
y1=y_mid-(min(y)+max(y))/2;
y2=y_mid+L/2;
%z_mid=(min(z)+max(z))/2;
%z1=z_mid-L/2;
%z2=z_mid+L/2;
axis([0 L y1 y2]);% for C14A1D1 mid part
%axis([0 L -130 -130+L]);
xlabel('x/nm','FontSize',18);
ylabel('z/nm','FontSize',18);
set(gca,'fontsize',18);
set(gca,'linewidth',3);
Reference


