2014

Assembly and mechanical characterization of suspended boron nitride nanotubes

Rachel Waxman
Virginia Commonwealth University

Follow this and additional works at: https://scholarscompass.vcu.edu/etd
Part of the Engineering Commons

© The Author

Downloaded from
https://scholarscompass.vcu.edu/etd/3493

This Thesis is brought to you for free and open access by the Graduate School at VCU Scholars Compass. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of VCU Scholars Compass. For more information, please contact libcompass@vcu.edu.
ASSEMBLY AND MECHANICAL CHARACTERIZATION OF SUSPENDED BORON NITRIDE NANOTUBES

A Thesis submitted in partial fulfillment of the requirements for the degree of M.S. at Virginia Commonwealth University

by

RACHEL WAXMAN
B.Sc. in Mechanical Engineering, Virginia Commonwealth University, 2011

Director: DR. ARUNKUMAR SUBRAMANIAN
Assistant Professor, Department of Mechanical and Nuclear Engineering,
School of Engineering,
Virginia Commonwealth University

Virginia Commonwealth University
Richmond, Virginia
August 2014
ACKNOWLEDGMENTS

I would like to acknowledge and thank those who provided funding and support for this project. The Department of Mechanical and Nuclear Engineering at Virginia Commonwealth University’s School of Engineering supported my first year and a half of study via a teaching assistantship. The Nuclear Regulatory Commission’s fellowship provided support for my last year. Collaborators included Sandia National Laboratories’ Center for Integrated Nanotechologies in Albuquerque, New Mexico and the National Institute of Aerospace in Hampton, Virginia, which works closely with NASA Langley Research Center, also in Hampton. Much of my training occurred at Sandia, and the materials used in this study were provided by Dr. Cheol Park at NIA. I appreciate all support from these sources, as well as from my advisor, Dr. Arunkumar Subramanian. I would also like to thank labmates Naveen Palapati and Adrienne Muth for their collaboration on this project.
# Contents

**Abstract** xiii  

1 **Introduction** 1  
1.1 Background ......................................................... 1  
1.2 Synthesis ........................................................... 2  
1.3 Assembly ............................................................ 4  
1.4 Properties .......................................................... 5  
1.5 Applications ....................................................... 7  

2 **Methods** 13  
2.1 Materials ............................................................ 13  
2.1.1 Chips .............................................................. 13  
2.1.2 Boron nitride nanotubes ......................................... 14  
2.2 Dielectrophoretic assembly ........................................ 15  
2.3 Stiffness and Young’s Modulus ................................... 19  
2.3.1 Stiffness measurements ......................................... 19  
2.3.1.1 Atomic force microscopy .................................... 19  
2.3.1.2 AFM force-displacement curves ............................. 21  
2.3.2 Beam model ....................................................... 25  
2.3.3 Tip stiffness ....................................................... 26
3 Results

3.1 Imaging ............................................................... 30
   3.1.1 SEM images ..................................................... 30
   3.1.2 AFM images ....................................................... 32
   3.1.3 Three-dimensional AFM images ............................... 36

3.2 Measurements .......................................................... 37
   3.2.1 Nanotube diameter .............................................. 37
   3.2.2 Pure bending ..................................................... 38
   3.2.3 Bending plus tension ........................................... 40
   3.2.4 Discussion ........................................................ 42

4 Conclusions ............................................................. 44

References ................................................................. 45

Vitae ................................................................. 51
List of Figures

1.1 Structure of a BNNT [33]. ................................................................. 1
1.2 Theoretical band structures (single layer): a) carbon, b) h-BN [11]. ........... 2
1.3 Stacked structures: a) graphite, b) boron nitride [11]. .............................. 2
1.4 SEM images of BNNS, where $R_{BF_3}/R_{H_2}$ (sccm) = (a) 5/10; (b) 3/10; (c) 2/30 [30]. 5
1.5 Fabrication process for BNNT-DNA hybrid [34]. .................................... 5
1.6 SEM images of BNNT (d=43nm; l=9.75µm): (a) at rest; (b) in first resonance mode; (c) in second resonance mode—with analytical fit superimposed [22]. .... 6
1.7 Frequency response of BNNT at fundamental mode, with Lorentzian curve fit in solid line [22]. ................................................................. 7
1.8 Young’s Modulus (E) versus (a) outer diameter and (b) length [22]. ............ 7
1.9 TEM images of individual multiwalled BNNTs of different diameters: (a) “thick” and (b) “thin” [6]. ................................................................. 8
1.10 Force-displacement curves for (a) thick and (b) thin BNNTs. Insets display starting and deformed NTs [6]. ................................................................. 8
1.11 Images of BNNTs with Fe$_3$O$_4$ uniformly bonded to their surfaces (a) low magnification TEM; (b) bright-field SEM; and (c) HAADF-STEM image [9]. .......... 8
1.12 Magnetic BNNT-Fe$_3$O$_4$ composite’s migration over a period of 8min [9]. .... 9
1.13 Schematic for a nano-FET, with a single NT used as a channel [12]. .......... 9
1.14 Temperature-dependent two-terminal I-V data for BNNT FET [14]. .......... 9
1.15 Humidity sensors and BNNT sensor setup schematic [31].

1.16 (a) I-V in static 85% RH at room temperature; (b) I-H with bias voltage of 10V;
(c) I-V of single Au-BNNT at various RH values at room temperature; (d) I-V of single BNNT at various RH values at room temperature; (e) Response and recovery measured by switching RH from 54% to 85%—inset shows 4 cycles; (f) $I_{\text{current}}/I_{\text{initial}}$ of Au-BNNT at 90% RH and room temperature—applied voltage of 10V [31].

1.17 (a) pH-dependent photoluminescence; (b) absorption spectrum for BNNT/biotin-fluorescein [8].

2.1 Sample chip: Si with nitride layer and Au electrodes [19].

2.2 Schematic of BNNT fibril growth via PVC method [18].

2.3 Translation and rotation of nanotube in electric field via DEP [28].

2.4 Schematic of an atomic force microscope.

2.5 Schematic of AFM force-displacement bending test: (a) Determining tip sensitivity; (b) Force-displacement test [21].

2.6 AFM-generated force-displacement curve on gold electrode used to calibrate tip sensitivity: Chip A2, electrode 23.

2.7 AFM-generated force-displacement curve on suspended boron nitride nanotube: Chip A2, electrode 23.

2.8 Partially processed force-displacement data showing gold signal versus NT signal: Chip A2, electrode 23.

2.9 Partially processed force-displacement data showing gold signal versus NT signal: Chip A2, electrode 128.

2.10 Sample AFM tuning curve.

2.11 Sample AFM tuning curve, with relevant Q factor data marked.
3.1 SEM: Chip A1, electrode 74. .................................................. 30
3.2 SEM: Chip A1, electrode 211. ................................................ 30
3.3 SEM: Chip A2, electrode 23. ............................................... 31
3.4 SEM: Chip A2, electrode 89. ............................................... 31
3.5 SEM: Chip A2, electrode 105. ........................................... 31
3.6 SEM: Chip A2, electrode 128. ........................................... 31
3.7 SEM: Chip A4, electrode 5. ............................................. 32
3.8 SEM: Chip A4, electrode 11. ........................................... 32
3.9 SEM: Chip A6, electrode 7. ............................................. 32
3.10 SEM: Chip A6, electrode 42. ......................................... 32
3.11 AFM image of electrode ends and gap. ......................... 33
3.12 2D AFM: Chip A2, electrode 22. .................................. 34
3.13 2D AFM: Chip A2, electrode 23. .................................. 34
3.14 2D AFM: Chip A2, electrode 60. .................................. 34
3.15 2D AFM: Chip A2, electrode 128. ................................. 34
3.16 2D AFM: Chip A4, electrode 4. .................................. 35
3.17 2D AFM: Chip A4, electrode 4: smaller window. .......... 35
3.18 2D AFM: Chip A4, electrode 5. .................................. 35
3.19 2D AFM: Chip A4, electrode 6. .................................. 35
3.20 3D AFM: Chip A2, electrode 89. .................................. 36
3.21 3D AFM: Chip A2, electrode 89. .................................. 36
3.22 3D AFM: Chip A4, electrode 4. .................................. 36
3.23 3D AFM: Chip A4, electrode 5. .................................. 36
3.24 Height trace for Chip A2, electrode 19. ...................... 37
3.25 AFM section: Chip A2, electrode 19. ......................... 37
3.26 SEM image: Chip A2, electrode 19. ......................... 37
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.27</td>
<td>Force-displacement curve: Chip A2, electrode 19.</td>
</tr>
<tr>
<td>3.28</td>
<td>Force-displacement curve: Chip A2, electrode 20.</td>
</tr>
<tr>
<td>3.30</td>
<td>Force-displacement curve: Chip A2, electrode 22.</td>
</tr>
<tr>
<td>3.31</td>
<td>Force-displacement curve: Chip A2, electrode 23.</td>
</tr>
<tr>
<td>3.32</td>
<td>Force-displacement curve: Chip A2, electrode 23.</td>
</tr>
<tr>
<td>3.34</td>
<td>Force-displacement curve: Chip A2, electrode 22: bending plus tension device.</td>
</tr>
<tr>
<td>3.35</td>
<td>Force-displacement curve: Chip A2, electrode 23: bending plus tension device.</td>
</tr>
<tr>
<td>3.36</td>
<td>Height trace for Chip A2, electrode 23.</td>
</tr>
<tr>
<td>3.37</td>
<td>Zoomed in height trace for Chip A2, electrode 23.</td>
</tr>
<tr>
<td>3.38</td>
<td>AFM section: Chip A2, electrode 23.</td>
</tr>
<tr>
<td>3.39</td>
<td>SEM image: Chip A2, electrode 23.</td>
</tr>
<tr>
<td>3.40</td>
<td>Young’s modulus versus BNNT diameter.</td>
</tr>
</tbody>
</table>
List of Tables

2.1 DEP parameters for corresponding chips. ............................................. 18
2.2 Centrifuge parameters for corresponding chips. .............................. 18
2.3 NSC19 cantiliver specifications from MikroMasch [13]. .............. 27
2.4 Sample AFM tip stiffness calculation—voltage values in V; frequency values in kHz. 29
3.1 Summary of results from successful devices. ................................. 40
# List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>degrees Celcius</td>
</tr>
<tr>
<td>2D</td>
<td>two-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>three-dimensional</td>
</tr>
<tr>
<td>AC</td>
<td>alternating current</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>Ag</td>
<td>silver</td>
</tr>
<tr>
<td>Au</td>
<td>gold</td>
</tr>
<tr>
<td>BN</td>
<td>boron nitride</td>
</tr>
<tr>
<td>BNNS</td>
<td>boron nitride nanosheet</td>
</tr>
<tr>
<td>BNNT</td>
<td>boron nitride nanotube</td>
</tr>
<tr>
<td>B₃N₃H₆</td>
<td>borazine</td>
</tr>
<tr>
<td>C</td>
<td>carbon</td>
</tr>
<tr>
<td>c-BN</td>
<td>cubic boron nitride</td>
</tr>
<tr>
<td>Cd</td>
<td>cadmium</td>
</tr>
<tr>
<td>Cl</td>
<td>chloride</td>
</tr>
<tr>
<td>CINT</td>
<td>Center for Integrated Nanotechnologies</td>
</tr>
<tr>
<td>CNT</td>
<td>carbon nanotube</td>
</tr>
<tr>
<td>Co</td>
<td>cobalt</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
</tr>
<tr>
<td>DEP</td>
<td>dielectrophoresis</td>
</tr>
<tr>
<td>E</td>
<td>Young’s modulus</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>DNA</td>
<td>deoxyribonucleic acid</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>iron oxide</td>
</tr>
<tr>
<td>FET</td>
<td>field-effect transistor</td>
</tr>
<tr>
<td>GPa</td>
<td>gigapascal</td>
</tr>
<tr>
<td>H</td>
<td>hydrogen</td>
</tr>
<tr>
<td>h-BN</td>
<td>hexagonal boron nitride</td>
</tr>
<tr>
<td>I</td>
<td>first moment of inertia</td>
</tr>
<tr>
<td>in</td>
<td>inch</td>
</tr>
<tr>
<td>k</td>
<td>stiffness</td>
</tr>
<tr>
<td>kHz</td>
<td>kilohertz</td>
</tr>
<tr>
<td>L</td>
<td>length</td>
</tr>
<tr>
<td>mm</td>
<td>milimeter</td>
</tr>
<tr>
<td>MPa</td>
<td>megapascal</td>
</tr>
<tr>
<td>MPCVD</td>
<td>microwave plasma chemical vapor deposition</td>
</tr>
<tr>
<td>N</td>
<td>nitrogen</td>
</tr>
<tr>
<td>NASA</td>
<td>The National Aeronautics and Space Administration</td>
</tr>
<tr>
<td>Ni</td>
<td>nickle</td>
</tr>
<tr>
<td>NIA</td>
<td>National Institute of Aerospace</td>
</tr>
<tr>
<td>nm</td>
<td>nanometer</td>
</tr>
<tr>
<td>NS</td>
<td>nanosheet</td>
</tr>
<tr>
<td>NT</td>
<td>nanotube</td>
</tr>
<tr>
<td>Q factor</td>
<td>quality factor</td>
</tr>
<tr>
<td>RH</td>
<td>relative humidity</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>Si</td>
<td>silicon</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
</tbody>
</table>
TEM  transmission electron microscope
TPa  terapascal
V    volt
ABSTRACT

ASSEMBLY AND MECHANICAL CHARACTERIZATION OF SUSPENDED BORON NITRIDE NANOTUBES

A Thesis submitted in partial fulfillment of the requirements for the degree of M.S. at Virginia Commonwealth University

by

RACHEL WAXMAN

B.Sc. in Mechanical Engineering, Virginia Commonwealth University, 2011

Director: DR. ARUNKUMAR SUBRAMANIAN

Assistant Professor, Department of Mechanical and Nuclear Engineering, School of Engineering, Virginia Commonwealth University

This study details the dielectrophoretic assembly and mechanical characterization of boron nitride nanotubes on silicon chips with gold electrodes. The chips were fabricated from 4in round silicon wafers with a 100nm-thick low stress silicon nitride insulating layer on the top and bottom. The electrodes were patterned using photo- and electron-beam lithography and dry etching, and the wafers were cut into 4 x 6mm chips.

The boron nitride nanotubes studied were obtained from NIA and were synthesized via a unique pressurized vapor/condensor method, which produced long, small-diameter BNNTs without the use of a catalyst. These nanotubes were studied due to their desirable mechanical and electrical properties, which allow for unique applications in various areas of science, engineering, and tech-
nology. Applications span from magnetic manipulation to the formation of biocomposites, from nano-transistors to humidity and pH sensors, and from MRI contrast agents to drug delivery.

The nanotubes and nanotube bundles characterized were suspended over gaps of 300 to 500nm. This study was unique in that assembly was performed using dielectrophoresis, allowing for batch fabrication of chips and devices. Also, stiffness measurements were performed using AFM, eliminating the reliance of other methods upon electron microscopes, and allowing for imaging and measurements to occur simultaneously and at high resolution.

It was found that DEP parameters of \( V = 2.0V_{pp} \), \( f = 1 \text{kHz} \), and \( t = 2 \text{min} \) provided the best results for mechanical testing. The nanotubes tested had suspended lengths of 300nm, the width of the electrode gap, and diameters of 15–65nm. Chips were imaged with both scanning electron microscopy and atomic force microscopy. Force-displacement measurements with atomic force microscopy were used to find stiffness values in the range of 1–16N/m. These stiffness values, when plugged into a simple double-clamped beam model, indicated Young’s moduli of approximately 1–1600GPa. Within this wide range, it was shown that a decrease in diameter strongly correlated exponentially to an increase in Young’s modulus.

Work in this study was divided between assembly and characterization. Therefore, a lot of time was spent working to optimize dielectrophoresis parameters, followed by SEM and AFM imaging. Parameters that were adjusted included DEP voltage and time, pre-DEP sonication times, as well as adding a centrifuging procedure to attempt to better separate nanotube bundles in solution. Another method discussed but not pursued was the use of surfactants to agitate the solution, thus separating the nanotubes. The reason this material in particular was so difficult to separate was twofold. First, the small size of the nanotubes—individual BNNTs have diameters on the order of \(~5\) nanometers—generates very strong nanoscale van der Waals forces holding the nanotubes together. Larger nanotubes—with diameters on the order of 50 to 100nm or more—suffer less from this problem. Also, the dipoles created by the boron-nitrogen bonds cause attraction between adjacent nanotubes.
The results shown in this thesis include DEP parameters, SEM and AFM images, and force-displacement curves leading to nanotube stiffness and Young’s modulus values. The force-displacement tests via AFM are also detailed and explained.
Chapter 1

Introduction

1.1 Background

As nanotechnology becomes increasingly prevalent in engineering, research has focused on one-dimensional nanomaterials, such as nanotubes and nanowires. Due to their high aspect ratios, they offer unique material properties and have potential applications in many areas, including electromechanical components and atomic force microscopy (AFM) tips [10].

Boron nitride nanotubes are formed when boron and nitrogen form polar covalent bonds in single-layer, honeycomb structures, and then are rolled into tubes. This structure is shown in Figure 1.1. This is similar to how carbon atoms are arranged in graphene sheets, and then rolled into carbon nanotubes (CNTs). Because of their similar structures, CNTs and BNNTs are often compared. There are indications that BNNTs can match—and even rival—the high strength and versatility of CNTs.

Figure 1.1: Structure of a BNNT [33].
CNTs have received a lot of attention due to their desirable electrical, thermal, and mechanical properties. Their electrical properties—including whether they are metallic or semiconducting—depend upon diameter and chirality. In contrast, BNNTs are wide band gap semiconductors, regardless of structure or diameter. Therefore, electronic properties of the two materials are extremely different. Theoretical band structures are shown in Figure 1.2. CNTs and BNNTs also differ in their multilayer interactomic spacing and in-plane lattice constants, as shown in Figure 1.3 [11].

1.2 Synthesis

Synthesis of BNNTs can occur via a number of methods. The arc-discharge method utilizes two electrodes: an anode built by inserting a hexagonal boron nitride (h-BN) into a hollow tungsten electrode; and a cathode made from rapidly cooled, pure copper. As a result of the arc-discharge, the h-BN is evaporated, depositing a grey product onto the copper. Contained in that powder are single-walled BNNTs. Other cathodes have been used (such as hafnium diboride and tantalum), as well as different environments (nitrogen).

A few different synthesis methods exist using lasers. Laser heating involves heating a single
crystal cubic boron nitride (c-BN) with a laser in a diamond anvil cell in high pressure nitrogen environments. Oven-laser ablation uses high-purity h-BN and nanoscale nickel and cobalt powders. The target mixture is heated in a long quartz tube by a furnace. A laser is focused on the target at an oven temperature near 1200°C. The ablated product flows in gas and is collected on a water-cooled copper collector. Changing the carrier gas in this method can significantly change the end products: inert argon and helium result in mainly single-walled BNNTs, while nitrogen produces mainly double-walled NTs.

As mentioned previously, CNTs and BNNTs have very similar structures. Because of this, BNNTs can be synthesized from CNTs via substitution reactions. As shown in Equation 1.1, the carbon atoms in CNTs are replaced by boron and nitrogen atoms. B₂O₄ powder is covered in CNTs in an open sintered graphite crucible in an environment of flowing nitrogen at 1500°C for 30min. Once cooled, the substance changes from black CNTs to grey BNNTs.

\[
\text{B}_2\text{O}_3 + 3\text{C (CNTs)} + \text{N}_2 \rightarrow 2\text{BN (BNNTs)} + 3\text{CO} \quad (1.1)
\]

A technique that tends toward high yield but low purity is ball-milling. Hardened steel balls mill boron powder in a 300kPa ammonia gas environment. The large amounts of mechanical energy exerted on the boron powder results in morphological and chemical changes in the material. Annealing then takes place at 1200°C for 16h in a tube furnace under nitrogen gas flow. The powder is converted into tubules, resulting in BNNTs with a yield of 75–85%.

The most commonly used method of synthesizing nanotubes and nanowires of various materials is chemical vapor deposition (CVD). BNNTs can be grown from the precursor B₃N₃H₆ (borazine). The chemical reaction is shown in Equation 1.2.

\[
3(\text{NH}_4)_2\text{SO}_4 + 6\text{NaBH}_4 \rightarrow 2\text{B}_3\text{N}_3\text{H}_6 + 3\text{Na}_2\text{SO}_4 + 18\text{H}_2 \quad (1.2)
\]

Successful catalysts for this method include Co, MgO, FeO, SnO, Ni, NiB, and Ni₂B, the last
two being the most effective. In the Ni and Ni$_2$B experiments, a substrate coated with the catalyst is placed in the center of a tube-furnace reactor at approximately 1000°C and is then exposed to B$_3$N$_3$H$_6$-containing carrier gas for 30min. Multi-walled BNNTs form as white deposits on the substrate. Other methods exist, but these are the most commonly used [26].

1.3 Assembly

When researching BNNTs, it is very easy to find information on characterization techniques, but there are very few papers on methods of assembly. Much of this has to do with the limitations of mass BNNT production [25]. However, there are three basic assembly methods discussed in literature, all different from the method used in this study.

The most common method for assembling BNNTs onto chips is via random deposition. Sonicated BNNT solutions are dispersed onto a chip, with NTs landing in arbitrary locations. Chips are then imaged with SEM and AFM to find and map the NTs. Once their locations are known, electrodes are designed on top of the NTs. In this type of device, the NT is not suspended, but rather sitting on the chip surface, with metal contacts on top of its ends. This device can be used for electrical measurements, as the chips surface will be insulating. As far as mechanical tests, this design is limited. Hardness can be measured, depending upon NT/bundle diameter, but bending and stiffness are not measurable, as no segment of the NT is suspended.

Another BNNT assembly method found in literature is as-grown assembly. In this setup, the material synthesis is combined with the assembly process. BNNS (boron nitride nanosheets) are grown vertically-aligned via microwave plasma CVD (MPCVD) on a silicon substrate, from a gas mixture of BF$_3$—N$_2$—H$_2$. The gas flow rates of BF$_3$ and H$_2$ ($R_{BF_3}$ and $R_{H_2}$), and the ratio of $R_{BF_3}/R_{H_2}$ help control the NS growth. Figure 1.4 shows SEM images of BNNS grown for 60min at different flow rate ratios [30].
A more unique method with very specific applications is DNA-mediated assembly. A high concentration of BNNT solution is used. The BNNTs are bonded to thiol-modified DNA, as shown in Figure 1.5. The NTs order themselves nematically based on a system’s desire to minimize its surface energy. The use of thiol-modified DNA allows pre-defined localization due to thiol’s bonding tendencies [34].

### 1.4 Properties

Mechanical properties of BNNTs have been studied in many ways to date. A Young’s modulus of $1.22 \pm 0.24\text{TPa}$ was measured by Zettl et al. They utilized thermal vibration amplitude measurements of cantilevered multi-walled BNNTs in a transmission electron microscope (TEM). This value is similar to CNTs [4].

Electric-field-induced resonance was used by Yu et al. in a TEM to find an average elastic modulus of $722\text{GPa}$ for individual BNNTs with diameters between 24 and 94nm. Figure 1.6
shows SEM images of a 43nm-diameter, 9.75µm-long BNNT first at rest, and then in its first and second harmonic modes. The dotted lines show the shape of the analytical modes, offset from the actual images so as to be visible. Figure 1.7 shows a frequency response curve for a BNNT at its fundamental mode, including a solid-line Lorentzian fit.

Figure 1.8 shows Young’s Modulus (E) versus (a) outer diameter and (b) length. Elastic modulus was found using the electric-field-induced resonance method inside a TEM, combined with classic beam mechanics. The formula can be seen in Equation 1.3 [22].

An integrated TEM-AFM system was developed by Goldberg et al. to see modulus values of 0.5–0.6TPa with diameters of 40–100nm. Representative “thick” and “thin” BNNTs are shown in Figure 1.9. Sample force-displacement curves are shown in Figure 1.10 [6]. While demonstrating high stiffness, this last method also suffered buckling, indicating low toughness for high diameter BNNTs. In situ TEM bending tests of thin BNNTs (diameters less than 10nm) showed
Figure 1.7: Frequency response of BNNT at fundamental mode, with Lorentzian curve fit in solid line [22].

Figure 1.8: Young’s Modulus (E) versus (a) outer diameter and (b) length [22].

compressive/bending strengths of \( \sim 1200\) MPa and indicated strain energy density of \( \sim 400 \times 10^6 \) J m\(^{-3}\) [10].

1.5 Applications

The motivation for the characterization of BNNTs is their potential for applications in many
fields of science and engineering, including chemical, electrical, mechanical, and medical. In order for the materials to be used, they must first be fully understood—mainly their mechanical and electrical properties.

In the electromechanical arena, Fe$_3$O$_4$ (iron oxide) nanoparticles were uniformly bonded via an ethanol-thermal process to the surface of BNNTs for the purpose of characterization and magnetic manipulation. TEM and SEM images of the NTs can be seen in Figure 1.11. Figure 1.12 shows how the nanoparticles in the solution were attracted to the sidewall of the vial when placed next to a magnet [9].

In electrical engineering, nanotubes have been used as the channel of field-effect transistors (FETs). The general set up can be seen in Figure 1.13. In the past, this has been done with CNTs [12]. BNNTs have been studied for their electrical transport properties to achieve the same setup.
It has been found that while transport in CNTs occurs via tunneling, in BNNTs, transport occurs across Schottky barriers. This is illustrated in Figure 1.14 [14].

Electrochemists have investigated using BNNTs as part of a humidity sensor. A single NT was assembled onto an alumina ceramic plate, between two nickel electrodes. Gold nanoparticles were deposited onto the BNNT surface via direct-current magnetron sputter. In this setup, the resistance of the NTs changes with relative humidity (RH). The setup can be seen in Figure 1.15. A currently-available humidity sensor was used in parallel with the BNNT sensor in order to compare results. Detailed results are shown in Figure 1.16 [31]
Another chemical application for BNNTs is their potential for hydrogen storage. CNTs can be metallic or semiconducting, depending upon their geometry and chirality; this affects their compatibility with hydrogen. BNNTs, on the other hand, are always semiconducting; this gives much more consistent compatibility. Also, the polar covalent bond of B-N leads to dipole moments, which are favorable to hydrogen absorption. Research has shown that metal-doped BNNTs maybe be even better for hydrogen storage, due to inherent defects [25].

Studies have also been completed for utilizing CVD-synthesized BNNTs as a pH sensor. BNNTs were combined with a biotin-fluorescein powder and put into solution in tetrahydrofuran (THF). Biotin is a binder to attach fluorescein, a tag for photoluminescence and fluorescence, to the BNNTs. The solution was ultrasonicated to ensure combination. Here, the fluorescence changed with pH. This change was enhanced by anchoring the NTs with silver nanoparticles. In the spectra, the location (wavelength) of the peak stays the same, but the intensity increases with pH, as seen in Figure 1.17. [8].
Figure 1.16: (a) I-V in static 85% RH at room temperature; (b) I-H with bias voltage of 10V; (c) I-V of single Au-BNNT at various RH values at room temperature; (d) I-V of single BNNT at various RH values at room temperature; (e) Response and recovery measured by switching RH from 54% to 85%—inset shows 4 cycles; (f) $I_{\text{current}}/I_{\text{initial}}$ of Au-BNNT at 90% RH and room temperature—applied voltage of 10V [31].

Figure 1.17: (a) pH-dependent photoluminescence; (b) absorption spectrum for BNNT/biotin-fluorescein [8].
Biologists have found that BNNTs have a strong potential for functionalization—the adding of chemical functional groups to their structure. This alters material properties (such as changing solubility or band gap tuning). It also allows for the making of composites for mechanical applications, or use in molecular biology by controlling certain interactions [25]. In the biomedical field, research has been conducted using BNNTs in MRI contrast [3], targeted magnetic drug delivery [5], enhanced low-voltage electropermeabilization, which is related to cell-membrane-permeability [15], and immobilization of proteins [32].
Chapter 2

Methods

2.1 Materials

2.1.1 Chips

The chips used in this study were made from silicon, with a 100nm-thick low stress silicon nitride insulating layer on top and bottom. Chips of 4mm by 6mm were cut from 4in wafers. The labeling system for the chips involves a wafer number, a die number, and a chip number. Each die contains six equally-sized chips. Gold electrodes were patterned on the chip surface using photo- and electron-beam lithography and dry etching. Electrodes were 100nm thick—85nm of gold and 15nm of chromium for adhesion. Electrode gaps were between 300nm and 500nm. A partial SEM image of a sample chip is shown in Figure 2.1 [19].

Figure 2.1: Sample chip: Si with nitride layer and Au electrodes [19].
2.1.2 Boron nitride nanotubes

The boron nitride nanotubes used in this study were synthesized by Dr. Cheol Park’s lab at NIA, in collaboration with NASA Langley Research Center, the Thomas Jefferson National Accelerator Facility (Jefferson Labs), and the Air Force Office of Scientific Research. The method used was the pressurized vapor/condenser (PVC) method. It produces long, small-diameter BNNTs without the use of a catalyst.

![Figure 2.2: Schematic of BNNT fibril growth via PVC method [18].](image)

The process, shown in Figure 2.2, involves the forced condensation of pure boron vapor at elevated pressure. The vapor is produced by heating a boron target in high pressure nitrogen gas at room temperature. The velocity profile of the boron vapor is shown in Figure 2.2A. A cooled
metal wire traverses the boron plume and acts as a condensor, forming boron droplets, as shown in Figure 2.2B. The droplets move along the velocity profile, as in Figure 2.2C, and interact with the nitrogen gas, forming BNNTs, as in Figure 2.2D. From here, clusters of BNNTs grow (Figure 2.2E) and then form into a BNNT fibril, due to the fluid flow (Figure 2.2F). This process produces BNNT fibrils and clusters that look like fine-grained cotton balls, approximately 1mm in diameter and 10cm in length. Production occurs at approximately 80% yield, by boron mass [18]. The NTs used in this study were much smaller (on the order of microns in length).

## 2.2 Dielectrophoretic assembly

Many methods of nanoassembly were discussed in Chapter 1. In this study, assembly was performed via dielectrophoresis (DEP). The principle of DEP uses a non-uniform electric field to move particles. When placed in the field, the particles experience both force and torque, resulting in motion. The net torque is shown in Equation 2.1, and the net force is shown in Equation 2.2, for particles with zero net charge [20].

\[
T = P \times E \quad (2.1)
\]

\[
f = (\nabla \cdot P)E \quad (2.2)
\]

Note that \(T\) represents torque, \(P\) polarity, \(E\) electric field, and \(f\) force. For particles with net charge (\(\sigma_f\)), Equation 2.3 applies.

\[
f = (\nabla \cdot P)E + \sigma_f E \quad (2.3)
\]

More specifically, for this study, the particles were electrically neutral BNNTs suspended in ethanol. The ultrasonicated suspension was dropped onto an array of nanoelectrodes experiencing
an AC voltage, or electric field. The force experienced by the nanotubes is shown in Equation 2.4.

\[ F_{DEP} = \Gamma \varepsilon_2 \text{Re}\{K(\varepsilon_1, \varepsilon_2)\} \nabla E_0^2 \]  

(2.4)

The following variable definitions apply: \( \varepsilon_2 \) is the permittivity of the suspension, \( K(\varepsilon_1, \varepsilon_2) \) is a complex polarization factor, \( E_0 \) is the applied (non-uniform) electric field, and \( \Gamma \) is a geometric factor, in this case given by Equation 2.5

\[ \Gamma = \frac{\pi r^2 l}{6} \]  

(2.5)

for a nanotube of radius \( r \) and length \( l \). The complex polarization factor is defined by Equation 2.6, with \( \varepsilon_1 \) representing the permittivity of the BNNT. In general, the force is directly proportional to AC voltage. Sharper tips and smaller electrode gaps also tend to increase force. The relationship between force and voltage frequency is a bit more complicated: they are directly proportional to a point, but force becomes negative (repulsive) beyond a certain frequency.

\[ K(\varepsilon_1, \varepsilon_2) = \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_2} \]  

(2.6)

As shown in Figure 2.3, the non-uniform electric field both pulls the nanotube closer to the electrodes by translation, and also rotates the nanotube to align with the field [28].

The variables tested in this study included voltage and duration. Voltage values ranged from 0.2–2.0\( V_{pp} \) (volts, peak-to-peak). Times used varied from 2–3\( \text{min} \). Frequency was held constant at 1kHz based on past experiments with other materials.

The BNNTs obtained from NIA were in powder form. A seed solution was made by dissolving a small amount of nanoparticles in ethanol. That seed solution was used to make multiple dilute solutions over a period of multiple months. Nine drops of seed solution were added to a vial of ethanol to create the dilute solutions. These dilute solutions were used for a one day’s worth of
DEP experiments.

The steps followed in DEP remained consistent for the non-centrifuged experiments (for chips A1 and A2). The dilute solution was sonicated for 30min. During that time, the chip was placed on the probe station and contact was made from a function generator: positive bias on the large shared electrode, and negative bias on the gold edge electrode. This edge electrode formed the border of the chip, and was capacitively coupled to all of the right side, individual electrodes. Because of the chip design, this grounded all the individual electrodes simultaneously. Once sonication time was done, two small pipettes of dilute solution were dropped onto the chip. Once DEP time was over, contact was broken. The excess dilute solution was poured back into the vial, and the chip was rinsed in ethanol to remove any excess, non-chip-bound material. In Table 2.1, the chips used and their corresponding DEP parameters are listed, with an asterisk (*) indicating the usage of centrifuging.

For the chips utilizing centrifuged solutions, the pre-DEP steps were altered slightly. All variables named as <var> correspond to columns in Table 2.2. The solution was sonicated for <Sonic1> in the cleanroom, pipetted <PipeVol> from sonication vial to centrifuge tube, and then transported across campus to a lab in the chemistry department for centrifuging. The centrifuge tube was then sonicated again for <Sonic2> in the chemistry lab, and then placed in the centrifuge. Centrifuge
parameters included <Accel> and <time>; all centrifuging was performed at room temperature (24°C). This sent the heavier bundles of NTs to the tube’s bottom and walls. After centrifuging, the clearer portion of liquid <Vol2>—containing smaller, less visible bundles—was pipetted back into a clean sonication vial. Before DEP, the centrifuged solution was sonicated again for <Sonic3>. Centrifuge parameters for chips A3–A6 and B1, B2, and B4 are provided in Table 2.2.
For the starred items, see below for alterations made to the procedure.

At this point, SEM images showed that centrifuging was successful—the bundles deposited after this procedure were much smaller than those without centrifuging. However, the yield was far too high—too many NTs were being deposited on each electrode location. For the last two chips, B2 and B4, the solution was diluted to try to decrease NT concentration. The centrifuge parameters were followed again, as in B1. Then, 1mL of the final solution was added 20mL of ethanol. This was sonicated for 30min, then divided into two vials, each containing 15mL of diluted, sonicated BNNT solution. SEM imaging from these chips showed that NTs were deposited on the chips, but failed to bridge the electrode gaps.

2.3 Stiffness and Young’s Modulus

2.3.1 Stiffness measurements

2.3.1.1 Atomic force microscopy

Atomic force microscopy (AFM) was developed in 1986 by IBM and Stanford University. It is a high-resolution scanner able to sense interactomic forces between single atoms, and use those forces to output a height-profile scan of micro and nanomaterials. AFM imaging is based on sensing the deflection of a cantilever on the surface of a material of interest. As the AFM scans a sample, the interatomic forces cause the cantilever to deflect. The deflection data is used to generate the height profile of a surface [2].

Typical AFMs consist of a cantilever with a sharp tip or probe usually made out of silicon, a laser that is reflected off the cantilever, and a sensor used to detect reflection of the laser off the cantilever [1]. An alternative option to the laser setup is to embed a piezoelectric strain sensor in the AFM cantilever. The deflection will cause a measurable current change, which can be detected and converted back into deflection. Depending on the sharpness of the probe and the force being measured, an AFM can have nanometer scale resolution [24]. Figure 2.4 shows a schematic of a
typical AFM using a laser for detection. The dotted lines show how the reading on the photodiodes change with position as the tip scans the sample surface.

![Schematic of an atomic force microscope](image)

Figure 2.4: Schematic of an atomic force microscope.

The AFM can be operated in a variety of modes. In contact mode, the tip of the cantilever is in contact with—or very close to—the sample as it scans. A feedback loop moves the scanner across the sample and the vertical deflection of the cantilever is measured. Contact mode can be configured to act in constant height mode, where cantilever deflection is held constant, or constant force mode, where cantilever deflection is varied. In non-contact mode, the cantilever oscillates above the sample surface without making contact. The atomic force between the sample and the probe decreases the oscillation frequency of the probe and is measured. A feedback loop moves the probe vertically as the material is scanned. In tapping mode, the cantilever is oscillated with amplitude greater than that used in non-contact mode. As the probe nears the sample, the interatomic forces decrease the amplitude of the oscillation and a feedback circuit vertically adjusts the probe. The tapping of the material in this way minimizes the damage between the sample and the tip [29].
2.3.1.2 AFM force-displacement curves

Since the AFM uses mechanical contact to image samples, it is ideal for performing mechanical characterization. The force-displacement tests performed in this study were set up similarly to a macro-scale beam bending test. The NT was deposited suspended across the electrode gap. The cantilever probe tip was then brought into contact with the NT at its longitudinal center. The stage was raised to deflect both the cantilever and the NT. Before this is done, the tip is calibrated by performing the same procedure on a sufficiently hard surface. On this hard surface, all of the deflection is in the cantilever—the surface does not deflect. This tells the software how to convert the voltage signal it receives into a nm deflection. This procedure is shown in Figure 2.5 [21].

To calibrate tip sensitivity, a force-displacement test was performed on the gold electrodes. This surface was hard enough to know that all of the deflection was absorbed by the tip. The curve generated by the software is initially in units of displacement versus displacement: this is cantilever deflection versus piezo (stage) deflection. On a hard surface, after adjusting for sensitivity, the slope of this curve is unity (1): the piezo and cantilever deflect at the same rate. An example is shown in Figure 2.6. Note that in this figure, a dummy value for tip stiffness was used, based on manufacturer’s specifications: $k_c = 0.6$N/m. Because of this, the slope of the gold curve is not unity (1), but rather 0.6.
Figure 2.5: Schematic of AFM force-displacement bending test: (a) Determining tip sensitivity; (b) Force-displacement test [21].

Figure 2.6: AFM-generated force-displacement curve on gold electrode used to calibrate tip sensitivity: Chip A2, electrode 23.
The graph shows two lines: one for approach, and one for return. Note that the x axis displays to piezo stage deflection, while the y axis displays to cantilever force, which is just scaled cantilever deflection. Starting from zero (0) on the x axis, the process followed by the AFM is as follows: First, the stage moves up, approaching the cantilever probe tip. At this point, the stage is moving, but the cantilever is not, hence the horizontal line. When the stage brings the sample close enough to the tip, the cantilever is snapped to the sample by interatomic van der Waals forces. This corresponds to the vertical drop in the line at the end of the horizontal line: the cantilever is moving, but stage is not. Next, the piezo stage moves up, moving the cantilever with it. On the gold surface, the piezo and cantilever move at the same rate, causing a slope of unity (1), or the dummy cantilever stiffness value. When the tip is on the NT, or another softer surface, the slope is different, indicating that the piezo stage and the cantilever are moving at different rates.

At this point, tip stiffness was input into the software. As stiffness was not known until the tuning curve data was processed, a default value of unity (1), or a dummy value of 0.6 (based on manufacturer specifications) was used. The user then had a choice of displaying a displacement-displacement curve (as described above) or force-displacement (with a false force value based upon incorrect tip stiffness). Next, the test was performed on the suspended BNNT. The indication that the tip was placed correctly on a NT was that the slope of the curve changed: the stiffness of the system (the NT plus the tip) was different from the stiffness of the tip alone. This is illustrated in Equation 2.7 in the next section. A sample curve with a NT signature is shown in Figure 2.7.
Figure 2.7: AFM-generated force-displacement curve on suspended boron nitride nanotube: Chip A2, electrode 23.

Figure 2.8: Partially processed force-displacement data showing gold signal versus NT signal: Chip A2, electrode 23.

Figure 2.8 shows the data on the same plot, so the slopes can be easily compared. Figure 2.9 shows the same result, from a different location. Note that these NT slopes do not give actual nanotube stiffness values until data has been processed; the change in slope is merely an indicator that the AFM tip was testing something other than the hard gold electrodes. The raw data was processed using the model in the next sections. The reason for the NT line being shorter than
the gold line is that the length of the deflection test—the amount of movement of the piezo stage during the curve generation—is limited in the NT case. If the NT is deflected too far, it will hit the chip surface, thus eliminating the suspended beam.

Figure 2.9: Partially processed force-displacement data showing gold signal versus NT signal: Chip A2, electrode 128.

2.3.2 Beam model

Force-displacement measurements were taken using AFM. Suspended nanotubes were treated as doubly-clamped beams. The AFM applied deflection near the center of the beam length-wise. AFM cantilever tip deflection was compared to nanotube deflection (piezo stage deflection). Cantilever tip stiffness was calculated using resonance (described in the next section), and cantilever deflection was converted to applied force. The slope of the cantilever force versus nanotube deflection plot gave the system stiffness. Using the stiffness equation for springs in series shown in Equation 2.7, the nanotube stiffness can be ascertained.

\[
\frac{1}{k_{sys}} = \frac{1}{k_c} + \frac{1}{k_{nt}}
\]  

(2.7)

In the equation, \( k \) is stiffness, and subscripts \( sys, c, \) and \( nt \) indicate system, cantilever, and
nanotube, respectively. Then, using bending beam model equations and measured system dimensions, that stiffness can be converted to Young’s modulus. In general, Young’s modulus is related to deflection as shown in Equation 2.8.

\[ EI = \frac{d^2z}{dx^2} = -M \]  

(2.8)

where \( I \) is the first moment of inertia (a geometric property, defined for an annulus in Equation 2.9, where \( r_o \) is outer radius and \( r_i \) is inner radius—a wall thickness of 1nm was assumed for \( \sim 3-4 \) BN walls) and \( z \) is the beam’s deflection.

\[ I = \frac{\pi}{4} (r_o^4 - r_i^4) \]  

(2.9)

Assuming the load is applied at the center of the beam, Equation 2.10 has been developed as an approximation to convert stiffness to Young’s modulus.

\[ E = \frac{k_{nt}L^3}{192I} \]  

(2.10)

where \( L \) is suspended beam length [27].

2.3.3 Tip stiffness

In order to extract nanotube stiffness from measured system stiffness (as described in Equation 2.7), AFM cantilever tip stiffness must be known. Manufacturers provide specifications which include this value, but the margin of error is relatively high, considering the small scale. Because of this, tip stiffness must be measured to obtain a more exact value. This is done via tuning curves.

The tips used in this study were MikroMasch NSC19 AL-BS cantilevers. Their listed specifications can be found in Table 2.3. The tips had a typical probe tip radius of 8nm and were made from aluminum-coated n-type silicon [13].

Before tapping-mode imaging can take place, the software connected to the AFM calibrates
Table 2.3: NSC19 cantilever specifications from MikroMasch [13].

<table>
<thead>
<tr>
<th>Cantilever</th>
<th>Resonance Frequency, kHz</th>
<th>Force Constant, N/m</th>
<th>Length l ± 5, µm</th>
<th>Width w ± 3, µm</th>
<th>Thickness t ± 0.5, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>19 Series</td>
<td>25</td>
<td>0.05</td>
<td>125</td>
<td>22.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

the tip by obtaining a tuning curve. A sample is shown in Figure 2.10. The amplitude versus frequency plot contains a resonance frequency, a maximum amplitude (voltage), and a frequency spread. The software chooses a drive frequency, or an operating frequency, close to but offset from the resonance frequency. This balances sensitivity with control, as the tip’s behavior is somewhat unpredictable at exactly resonance frequency.

![Sample AFM tuning curve](image)

Figure 2.10: Sample AFM tuning curve.

The tuning curve is used to extract stiffness information from the tip. First, a quality factor, or Q factor ($Q_f$), is calculated. The relevant information is shown in Figure 2.11: $V_{\text{max}}$, $V_{\text{max}}/\sqrt{2}$, $f_1$ and $f_2$ (the two frequencies at which $V = V_{\text{max}}/\sqrt{2}$), and $f_{V_{\text{max}}}$, or $f_{\text{res}}$. 
The relevant equations for calculating Q factor are shown in Equations 2.11 through 2.14 [23].

\[
V_{\text{max}} = V(f_{\text{res}}) \quad (2.11)
\]

\[
\frac{V_{\text{max}}}{\sqrt{2}} = V(f_1) = V(f_2) \quad (2.12)
\]

\[
\Delta f = f_2 - f_1 \quad (2.13)
\]

\[
Q_f = \frac{f_{\text{res}}}{\Delta f} \quad (2.14)
\]

From Q factor, tip stiffness was calculated using a website [16] based upon a journal article [17]. On the website, one enters the Q factor, geometry, and relevant information about medium (in this case, air). The output is a stiffness value in N/m. For the graph shown, for example, the data obtained is shown in Table 2.4. All voltage values are in V; all frequency values are in kHz. The geometry of the tip was characterized in Table 2.3.
Table 2.4: Sample AFM tip stiffness calculation—voltage values in V; frequency values in kHz.

<table>
<thead>
<tr>
<th>$V_{\text{max}}$ (V)</th>
<th>$f_{\text{res}}$ (kHz)</th>
<th>$V_{\text{max}}/\sqrt{2}$</th>
<th>$f_1$</th>
<th>$f_2$</th>
<th>$\Delta f$</th>
<th>$Q_f$</th>
<th>$k_{\text{tip}}$ (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4999</td>
<td>102.9118</td>
<td>0.3535</td>
<td>102.6782</td>
<td>103.1737</td>
<td>0.4955</td>
<td>207.6928</td>
<td><strong>2.590</strong></td>
</tr>
</tbody>
</table>

Note that the expected value for tip stiffness was in the range of 0.05 to 2.3N/m, with an expected average of 0.5N/m. The calculated value of 2.59N/m not only varies greatly from the average, but it is not even in the given range. This emphasizes the importance of independently calculating tip stiffness.
Chapter 3

Results

3.1 Imaging

3.1.1 SEM images

The following images show SEM images for some of the progression of chips with changing DEP parameters. Figures 3.1 and 3.2 are from chip A1. As stated in Table 2.1, chip A1 had DEP parameters of $2.0V_{pp}$, 1kHz, and 3min.

Figure 3.1: SEM: Chip A1, electrode 74.

Figure 3.2: SEM: Chip A1, electrode 211.

These chips had large bundles of nanowires, most of which were not suspended over the elec-
trode gap. After these results, the DEP time was decreased from 3 minutes to 2 minutes, in hopes of seeing less deposition. Figures 3.3 through 3.6 are from chip A2.

Figure 3.3: SEM: Chip A2, electrode 23.  
Figure 3.4: SEM: Chip A2, electrode 89.

Figure 3.5: SEM: Chip A2, electrode 105.  
Figure 3.6: SEM: Chip A2, electrode 128.

After centrifuging, many of the larger bundles were broken up. Figures 3.7 and 3.8 show deposition on chip A4, which had DEP parameters of 1.0V$_{pp}$, 1kHz, and 2min.
Figures 3.9 through 3.10 show deposition on chip A6, which had DEP parameters of $0.75V_{pp}$, 1kHz, and 2min, and which also utilized a centrifuged solution.

3.1.2 AFM images

Figure 3.11 shows a sample AFM scan of an empty electrode pair and the electrode gap. The window of the scan is $10\mu m$. The scale bar on the right shows how color relates to height. The software does not necessarily start at zero height—the default is to center “zero”; this figure has a range of approximately -100nm to +100nm, meaning a total possible height profile of 200nm.
Figures 3.12 to 3.19 show AFM images of NTs deposited on electrodes. The images from A2 (Figures 3.12 through 3.15) were used for the force displacement curves generated to characterize the BNNTs. Note that the red targets on these images indicate the location of the mechanical bending test. The images from A4 represent DEP after centrifuging.
Figure 3.12: 2D AFM: Chip A2, electrode 22.

Figure 3.13: 2D AFM: Chip A2, electrode 23.

Figure 3.14: 2D AFM: Chip A2, electrode 60.

Figure 3.15: 2D AFM: Chip A2, electrode 128.
Figure 3.16: 2D AFM: Chip A4, electrode 4.

Figure 3.17: 2D AFM: Chip A4, electrode 4: smaller window.

Figure 3.18: 2D AFM: Chip A4, electrode 5.

Figure 3.19: 2D AFM: Chip A4, electrode 6.
3.1.3 Three-dimensional AFM images

Because AFM images are height profiles, a three-dimensional image can be obtained based on the scan. Figures 3.20 and 3.21 show 3D AFM images from chip A2—the main chip used for force-displacement measurements, while Figures 3.22 and 3.23 show 3D AFM images from chip A4, after centrifuging. Note the larger bundles on A2, and the smaller NTs on A4 (after centrifuging).

Figure 3.20: 3D AFM: Chip A2, electrode 89.  
Figure 3.21: 3D AFM: Chip A2, electrode 89.  
Figure 3.22: 3D AFM: Chip A4, electrode 4.  
Figure 3.23: 3D AFM: Chip A4, electrode 5.
3.2 Measurements

3.2.1 Nanotube diameter

An important dimension in the beam model is NT diameter, which was obtained using AFM scans. From 2D scans, a section can be taken—a horizontal line is drawn on the image, and the software produces a height trace. An example is shown in Figure 3.24, from chip A2, electrode 19. The line traced for the AFM profile is shown in blue in Figure 3.25. The large bump on the height trace is the nanotube. Note that the diameter (maximum height minus minimum height) is approximately 40nm. The SEM image is shown in Figure 3.26.

![Figure 3.24: Height trace for Chip A2, electrode 19.](image)

![Figure 3.25: AFM section: Chip A2, electrode 19.](image)

![Figure 3.26: SEM image: Chip A2, electrode 19.](image)
3.2.2 Pure bending

Linear force-displacement curves result from devices operating in small deformation mode, meaning deflection is equal to or less than the nanotube radius. This is indicative of pure bending. At least seven successful bending devices were found on chip A2: one each on electrodes 19 through 22, two on electrode 23, and one on electrode 26. Processed force-displacement curves for these electrodes are shown in Figures 3.27 through 3.33.

Figure 3.27: Force-displacement curve: Chip A2, electrode 19.
Figure 3.28: Force-displacement curve: Chip A2, electrode 20.
Figure 3.29: Force-displacement curve: Chip A2, electrode 21.
Figure 3.30: Force-displacement curve: Chip A2, electrode 22.
Figure 3.31: Force-displacement curve: Chip A2, electrode 23.

Figure 3.32: Force-displacement curve: Chip A2, electrode 23.

Figure 3.33: Force-displacement curve: Chip A2, electrode 26.

The data from these nanotubes is listed in Table 3.1. Note that all NTs have a suspended length of 300nm, the width of the electrode gap.
Table 3.1: Summary of results from successful devices.

<table>
<thead>
<tr>
<th>Elec</th>
<th>(d) (nm)</th>
<th>(k_{nt}) (N/m)</th>
<th>(E) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>41.5</td>
<td>3.73</td>
<td>20.09</td>
</tr>
<tr>
<td>20</td>
<td>39.6</td>
<td>1.48</td>
<td>9.18</td>
</tr>
<tr>
<td>21</td>
<td>45</td>
<td>0.98</td>
<td>4.11</td>
</tr>
<tr>
<td>22</td>
<td>15</td>
<td>11.85</td>
<td>1539</td>
</tr>
<tr>
<td>23</td>
<td>22</td>
<td>15.94</td>
<td>615</td>
</tr>
<tr>
<td>23</td>
<td>26</td>
<td>9.15</td>
<td>209</td>
</tr>
<tr>
<td>26</td>
<td>65</td>
<td>6.70</td>
<td>9.15</td>
</tr>
</tbody>
</table>

### 3.2.3 Bending plus tension

When nanotube deformation far exceeds the nanotube radius, non-linear force-displacement curves result. These plots indicate bending is not the only mechanism at work—there is also tension in the nanotube. This is due to its one-dimensional structure. The stretching component of the nanotube’s strain results in stress-stiffening, which leads to a non-linear curve [7].

Figures 3.34 and 3.35 show what this looks like. The beginning of the graphs show a small amount of linear deformation. The non-linearity that follows indicates tension. This is generally indicative of a smaller diameter nanotube. The height trace for electrode 23 is shown in Figure 3.36. Figure 3.37 shows a zoomed in window of the NT being characterized, with the scale adjusted to show an approximate diameter of \(~5.5\)nm (zoom window shown in dotted lines in Figure 3.36). Figures 3.38 and 3.39 show the corresponding AFM image, with the trace profile again highlighted in blue, and SEM image.
Figure 3.34: Force-displacement curve: Chip A2, electrode 22: bending plus tension device.

Figure 3.35: Force-displacement curve: Chip A2, electrode 23: bending plus tension device.

Figure 3.36: Height trace for Chip A2, electrode 23.

Figure 3.37: Zoomed in height trace for Chip A2, electrode 23.
3.2.4 Discussion

Note the trend from Table 3.1: in general, as diameter decreases, Young’s modulus increases. Figure 3.40 illustrates this point more clearly, displaying an exponential trend ($R^2 = 0.95$).

Figure 3.40: Young’s modulus versus BNNT diameter.
One concern when performing bending tests is slippage. In some cases, it is required that beams be clamped top-side, meaning something holds the beam in place from the top. In this case, the NTs are small enough in diameter that it might not be an issue: van der Waals forces are significantly higher than other materials, many of which having diameters in the range of hundreds of nanometers or more. As a precaution, before force-displacement tests were conducted on the suspended NTs, a cycle was run on the nanotube on the electrode. This gave no useful data for mechanical characterization, but it served to reinforce the nanotube’s contact on the electrode, making slippage less likely. Even with all of this, however, slipping is still possible—and might explain some of the lower Young’s modulus values found in the larger nanotube bundles. This could possibly help explain the trend found in Figure 3.40.

Some of the larger bundles (not included in this study) indicated slipping might be present: Young’s modulus values were found to be in the range of hundreds of MPa to single GPa, which is lower than literature suggests for BNNTs, and lower than the smaller diameter bundles indicated in this study. This small Young’s modulus indicates that in those cases, true material properties might not be observed due to slippage. This effect could be lessened or even avoided by trying top-side clamping, or by working harder to separate the nanotubes.
Chapter 4

Conclusions

This study detailed dielectrophoretic assembly of boron nitride nanotubes onto silicon chips with gold electrodes. DEP parameters, including different attempts to separate large bundles of BNNTs, have been listed and an attempt was made at optimizing them. Enough devices were formed in order to perform mechanical tests to characterize the materials.

Imaging via scanning electron microscopy and atomic force microscopy was used to evaluate the success of the assembly process. It was found that DEP parameters of $V = 2.0V_{pp}$, $f = 1\text{kHz}$, and $t = 2\text{min}$ provided the best results for mechanical testing. Centrifuging of the solution was also attempted to break up larger bundles, but an adequate balance was never completely achieved.

The NTs tested had suspended lengths of 300nm, the width of the electrode gap, and diameters of 15–65nm. AFM cantilevers were calibrated for stiffness using quality factor calculations from their tuning curves. Force-displacement measurements were converted into stiffness values via the series spring equation, and then a simple doubly-clamped beam model was used to convert stiffness values and geometry into Young’s moduli. Stiffness values were found to be in the range of 1–16N/m, indicating Young’s moduli of approximately 1–1600GPa. A trend was shown indicating that a decrease in diameter strongly correlates to an increase in Young’s modulus, with an exponential relationship.
Future work related to this project could focus on better assembly parameters, resulting in smaller BNNT bundles, and single nanotubes. The DEP parameters have been optimized, but more effort could be spent on breaking up the larger bundles, which are present (and harder to separate) due to the high van der Waals forces from small diameters, and due to dipole bonds between nanotubes. Centrifuging had some success in separating NTs, but based on SEM images of A6, it was too violent: the NTs were no longer able to bridge the electrode gap. Centrifuging parameters can be adjusted to help this, or other tactics can be employed. One possibility is the use of a surfactant (in place of centrifuging) and decreased sonication times. This might help break up the nanotube bundles without damaging the materials.
Bibliography


[33] Chunyi Zhi, Yoshio Bando, Chengchun Tang, and Dmitri Golberg. Boron nitride nanotubes. 

[34] Chunyi Zhi, Yoshio Bando, Wenlong Wang, Chengchun Tang, H. Kuwahara, and Dmitri 
Golberg. DNA-mediated assembly of boron nitride nanotubes. *Chemistry–an Asian Journal, 
VITAE

EDUCATION

• PhD, Mechanical and Nuclear Engineering, May 2017 (expected)
  Virginia Commonwealth University, Richmond, Virginia

• MS, Mechanical and Nuclear Engineering, August 2014, GPA: 3.82
  Thesis: “Assembly and mechanical characterization of suspended boron nitride nanotubes”
  Virginia Commonwealth University, Richmond, Virginia

• BS, Mechanical Engineering, May 2011
  GPA: 3.95; Major GPA: 4.0
  Virginia Commonwealth University, Richmond, Virginia

HONORS AND SOCIETIES

• Virginia Commonwealth University: Graduate
  Teaching Assistantship, 2012-2013

• Virginia Commonwealth University: Undergraduate
  Jamie Knight Scholarship
  Engineering GPA 4.0

• American Society of Mechanical Engineers Member
• Tau Beta Pi Member
• Phi Kappa Phi Member

SERVICE

• Promotion and tenure committees
  Tenure committee, Associate Professor Dr. Jayasimha Atulasimha (2012)
  Promotion committee (Professor), Associate Professor Dr. Hooman Tafreshi (2014)

RESEARCH EXPERIENCE

• Virginia Commonwealth University: Graduate
  Laboratory of Integrated Nanosystems, January 2012–August 2014
  – Assembled and characterized various nanomaterials using AFM, SEM, and TEM
• Sandia National Laboratories, Center for Integrated Nanotechnologies
  Visiting graduate research assistant, June–August 2012
  – Assembled and characterized $\alpha$-MnO$_2$ nanowires; performed lithiation experi-

• Virginia Commonwealth University: Undergraduate
  Biofluid Dynamics and Multiphase Transport Laboratory, January–May 2011
  – Performed fluid dynamics calculations for aerosol drug delivery; rapid prototyped
  small-scale dryers for nebulizers and designed and performed experiments
  Smart Materials Laboratory, 2010–2011
  – Designed and performed energy harvesting experiments with piezoelectric mate-
  rials; created a viscosity sensor from piezoelectric probes
  Integrated Systems Laboratory, May–August 2010
  – Performed electrochemistry experiments on polymer smart materials

INSTRUMENTATION, TECHNIQUES, AND COMPUTING EXPERIENCE

• Nanomaterial characterization
  AFM
  SEM
  TEM
  Probe station
  Glove box
  Signal generator and oscilloscope

• Programming and computing
  LaTeX
  MATLAB & Simulink
  Labview
  SigmaPlot
  Autodesk Inventor
  Solidworks
  ANSYS

• Other
  Rapid prototyping
  Cyclic voltammetry
PRESENTATIONS

- “Feasibility of using piezoelectric probes to measure viscosity in Newtonian fluids.” (September 2010) ASME 2010 Conference on Smart Materials, Adaptive Structures and Intelligent Systems, Philadelphia, PA, USA

PUBLICATIONS


PUBLICATIONS IN PROGRESS


TEACHING EXPERIENCE

- Virginia Commonwealth University, Richmond, VA
  Teaching Assistant, 2009–2011, 2012–present
  – Courses: Engineering Mathematics, Numerical Methods

53
• A Plus Success and Henrico County Public Schools
  Tutor, 2011–2012
  – Title I afterschool program for K-5th-graders; taught reading skills and comprehension in small groups

• College of William and Mary Summer Program for Gifted Children
  Teacher’s Assistant, Summers 2002 and 2005
  – Assisted with interactive experiments to ensure student success and safety

WORK EXPERIENCE

• SpectraQuest, Inc., Richmond, VA
  Applications engineer, May–September 2011
  – Designed equipment to train technicians in vibration analysis; worked with 2D and 3D engineering drawings and machine shop coordination; assisted with PHP and SQL website database and design

• Mechanical Engineering Department, VCU, Richmond, VA
  Student office worker, 2009-2011
  – Provided office support for department chair and administrative assistant with student filing, travel and purchase reimbursements, and laboratory orders

• Monticello Shell Auto Center, Williamsburg, VA
  Automotive mechanic, VA state inspector, Sales associate, 2005-2008
  – Performed automotive repairs and maintenance and VA state inspections; maintained shop customer records and provided office support