The Development and Characterization of Tunable Alumina-Carbon Nanotube Composite Structures

Michael DeFord

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Richard Vanfleet, Advisor

Department of Physics and Astronomy

Brigham Young University

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ABSTRACT

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Michael DeFord
Department of Physics and Astronomy, BYU
Bachelor of Science

Carbon nanotubes (CNTs) are versatile nanostructures that exhibit incredible material properties. One application of interest is the development of CNT composite materials where the CNTs act as a temporary scaffolding or a permanent skeleton for other materials that have been deposited onto the CNTs. This allows for the unique geometric properties of CNTs, such as high aspect ratio or the ability to be grown in any desired pattern using lithography, to be utilized with some of the desirable properties of other materials. In particular, we present a method for building CNT-alumina composites using atomic layer deposition (ALD). We also report a measurement of the Young's modulus of the resulting CNT-alumina composites and demonstrate the ability to tune the modulus by altering the thickness of the alumina layer. These methods can be generalized to other ALD compatible materials as well.

Keywords: Carbon Nanotube, Atomic Layer Deposition, Dual Deflection, CNT, ALD, DD

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Chapter 1

Introduction

1.1 Micro-electromechanical Systems (MEMS) and Carbon Nanotube (CNT) composites

As science and technology advances, the methods and materials we use to manufacture technology must advance as well. Sometimes all that stops theoretical advances in science from becoming fully realized technologies is the lack of materials with appropriate properties. Indeed, as technology becomes more advanced, the exact properties required of the materials we use become stricter and manufacturing methods must become more sophisticated as well.

Many areas of technology and electronics require components to continue getting smaller and smaller. One example is the field of Micro-electromechanical Systems or MEMS. MEMS are tiny integrated devices that combine mechanical and electrical components. These systems can be as small as a few micrometers across. As a result, MEMS can be found in most, if not all, modern electronics. However, the size and functionality of these systems are severely limited by the physical properties of the materials that we can use on these scales. Therefore, the development of new materials that are compatible with MEMS manufacturing techniques can potentially impact a wide

range of disciplines and subjects.

One method for developing new materials that are compatible with MEMS processes is by forming composites with materials that are already in use. Carbon nanotubes (CNTs) are one such material. CNTs are a subject of great interest for MEMS devices and are extremely tough and versatile [1]. This provides an excellent jumping off point for the development of new composites that expand the capabilities of MEMS devices.

1.1.1 Carbon Nanotubes (CNTs)

CNTs are extremely versatile nano-structures with properties that make them ideal for MEMS applications. CNTs share the basic chemical form of graphene, a hexagonal lattice of carbon atoms in 2D sheets [2]. The only major difference is that where graphene has parallel layers lying flat and loosely bonded together, CNTs have individual tubes, each one like a sheet of graphene that was rolled into a cylinder. There are also two major kinds of CNTs, single-walled CNTs which have only a single layer as the name implies, and multi-walled CNTs (MWCNTs) which have many concentric layers in a single tube [2].

There are a handful of important properties that CNTs have that make them so useful for MEMS processes. The first is that CNTs are deposited, or grown, from a specially prepared substrate using a Chemical Vapor Deposition (CVD) process. A thin film of iron is deposited onto an appropriate substrate and heated in a furnace. Under these conditions, H_2 is introduced to reduce the oxygen that has bonded to the iron film. This reduced iron forms nanoparticles on the surface of the substrate. Carbon rich gasses are then introduced to the furnace at high temperatures and react with the iron nanoparticles to form the CNTs. This growth method is excellent for MEMS applications because photolithography techniques can be used to deposit the initial iron substrate in any arbitrary 2D pattern and the subsequent CNT growth will follow that same pattern [1]

Another property that makes CNTs extremely useful in MEMS applications is their extreme

aspect ratio. An individual CNT can be on the order of 10 nm or less in diameter [3] and CNTs can be grown to heights of over a millimeter [1, 4]. That's an aspect ratio of over 10^5. In practice, CNTs are generally used in micro-scale structures, however that still results in aspect ratios up to 10^3. A secondary property of this extreme aspect ratio is that thick growths of CNTs, called forests, also have extremely high surface areas.

CNTs have a host of other beneficial properties that are, in general, less relevant to the details of this work and have been illuminated in numerous other works [5]. One additional property that will be relevant is that pristine, unmodified CNTs are generally chemically neutral [6]. This can be an essential property for some applications, but it also poses a barrier to the development of composite materials as will be discussed in the next section.

Finally, there are two basic methods for creating a CNT composite material. The first is common in macroscopic materials synthesis, adding powdered CNTs to macroscopic materials like cement or concrete to increase their tensile strength when hardened [7]. This particular method has no application to MEMS. The other method is more relevant to MEMS, and uses the structure of the CNTs as a foundation for the material.

This second method involves coating the individual CNTs with thin films of a second material. This produces individual tubes with a carbon core and a deposited outer shell while the forests are now micro-structures made of this composite. This approach allows the composite to take advantage of the structure and geometry of the CNTs while also introducing or reinforcing properties associated with the second material. Properties affected could include electrical, mechanical, or chemical properties or a combination thereof.

1.1.2 Atomic Layer Deposition (ALD)

As mentioned above, the method of interest for manufacturing CNT composites is to deposit thin films of a second material throughout the CNT forest, coating each nanotube completely and

conformally. Unfortunately, several of the properties that make CNTs ideal for MEMS applications make this kind of deposition difficult to achieve. Specifically, the high aspect ratio and high surface area of CNT forests, along with their chemical neutrality, provide barriers to the successful creation of these composites. Atomic Layer Deposition (ALD) is a deposition method (a form of CVD) that provides a solution.

ALD is a cyclic process of deposition that takes advantage of self-limiting chemical reactions to deposit a single atomic layer, or less, of a given material during a single cycle [8]. A self-limiting chemical reaction occurs when the products of a reaction do not continue to react with the original reactants. It works by exposing a chemically active substrate to a gaseous precursor chemical that reacts with the surface. Each chemically active site, called a nucleation site, is reacted with until none remain. Regardless of how much of the precursor gas is left, no more reactions can occur, effectively ending the process. However, this is only the first half of the ALD cycle.

After each of these reactions takes place, the nucleation site where the reaction occurred has been altered. In general, it will have either lost or gained one or more atoms that have changed its chemical nature. At this point the precursor gas can be pumped out and replaced with a second precursor gas that is reactive with the products of the first reaction. For each nucleation site that was affected in the first half of the process cycle, there is now at least one nucleation site where the second precursor can react. Generally, when this second reaction is finished it will leave behind one layer of the desired deposition material and, crucially, it will leave behind new nucleation sites for the first precursor. Therefore, while this single cycle has deposited just one "atomic layer", it can be repeated until the film deposited is the desired thickness. Thanks to the thin layers deposited every cycle, there is direct correlation between cycle number and film thickness and films can be deposited with incredible precision.

This cyclic process of self-limiting reactions make ALD ideal for depositing on substrates with high aspect ratios, high surface areas, and complex shapes that other deposition methods may

struggle with [3, 8]. This is because regardless of how much precursor is used or how long each part of the substrate is exposed, each cycle will only react with each available site once. This ensures that each layer is uniform and complete, even if the precursors need time to diffuse or react. ALD can even deposit around corners and onto complex shapes without sacrificing film quality. This seems like a perfect solution to the difficulties associated with CNT composites but there is one more problem to tackle: chemical functionalization.

1.1.3 Chemical Functionalization

ALD is fundamentally a chemical process and requires that the substrate be chemically reactive with the precursors involved. As mentioned previously, pristine, unmodified CNTs do not generally satisfy this criteria because they are very stable chemically and not very reactive. This provides a significant barrier to the use of ALD in manufacturing these composites. Overcoming this issue requires the application of a chemical pretreatment, a process called functionalization, that chemically activates the surface of the CNTs to allow for effective ALD.

When ALD is performed on pristine, untreated CNTs, there is still some deposition. When CNTs are grown they accrue material defects across their surfaces: imperfections such as missing a carbon atom in the hexagonal lattice. While these nanoscopic defects don't effect the majority of macroscopic properties, they do provide nucleation sites for the chemical reactions of the ALD process to occur. This results in the growth of small beads of the deposited material at each of these sites. If the deposition is thick enough, these beads can spread and connect to each other to form conformal films as before. Depending on the growth rate and the density of defects on the CNTs this process can take 10's or 100's of cycles before a complete conformal layer is formed.

To solve this problem, chemical functionalization can be employed [6]. Specifically, highly reactive chemicals such as O_2 plasma [4] or ozone [3] can be used to treat the surface of the CNTs. This treatment opens up new defect sites on the surface of the CNTs. These defect sites can then act

as viable nucleation sites for the ALD process.

1.2 Overview of Work

We report on the development of a process for manufacturing a CNT-alumina composite material. The Young's modulus of this composite is variable depending on the thickness of the alumina film deposited. The Young's modulus is a measure of how elastic a material is, how much it will bend or stretch when a stress is applied to it. We also report a set of measurements of the Young's modulus for the material via dual deflection as a demonstration of the tunability of its mechanical properties.

The purpose of this work is to explore the possibilities of new and novel materials for a variety of MEMS applications. While CNT composites have been investigated previously [1, 3, 4] it can be exceptionally difficult to measure their mechanical properties accurately. This work provides a framework for producing consistent composites along with a measurement of the Young's modulus of the composite. It can also act as a framework for creating new composites using other materials.

Hereafter, this work includes a detailed technical description of the process for producing a CNT-alumina composite structure. It is followed by a brief description of the method used to measure the Young's modulus of the material [2]. In the final sections we summarize the results of the measurements and discuss possible next steps.

Chapter 2

Methods

2.1 Methods Overview

This chapter contains detailed technical explanations of the development of the CNT-alumina composite, followed by a description of the Dual Deflection (DD) method used to measure the Young's modulus of the composite. Here we provide an overview of the steps in light detail for context.

The first step in the production of the CNT-alumina composite is the growth of the CNTs. The CNTs were grown on silicon wafers with a thin film of alumina and a thin film of iron pattered on top using photolithography. The pattern used in this work is an array of dots, when grown this produces an array of cylindrical CNT posts. This pattern is used to facilitate the measurement of the Young's modulus using the DD method as described below. The growth process is performed in a heated Chemical Vapor Deposition (CVD) furnace with C_2H_4 (Ethylene) and H_2 flowing. Following growth, the CNTs need to be functionalized to prepare them for the deposition of the alumina.

The CNTs are placed under vacuum and ozone is introduced into the chamber. Once the surface of the CNTs have been functionalized, ALD can be used to deposit thin films of alumina directly

onto the surfaces of the CNTs. This is also done under vacuum by introducing alternating chemical precursors. The first precursor is Trimethyl Aluminum (TMA) vapor which reacts with the surface of the CNTs leaving an aluminum atom and two methyl groups attached to the surface. After the remaining TMA vapor is pumped out of the chamber, water vapor is introduced which reacts with the methyl groups of the TMA reaction. This strips away the unnecessary atoms and leaves behind a single layer of alumina (Al2O3). This can be repeated cyclically to deposit films of arbitrary thickness.

To measure the Young's modulus of the resulting CNT-alumina composite we use the Dual Deflection (DD) method. This method leverages small deflection Euler Beam Theory to calculate the Young's modulus based on the modulus and geometry of a known wire. We can bend the composite posts by using a small thin wire and record the deflections of both the wire and the post (hence the Dual Deflection moniker). Since the physical properties of the wire are known we can use the measured deflections to calculate the Young's modulus of the composite.

2.2 Carbon Nanotube Growth Parameters

CNTs are grown from thin film layers of iron on the order of 10 nm or less in thickness. At high temperatures this thin layer of iron forms nanoparticles that serve as the foundations for CNT growth. However, these thin films of iron can diffuse into the substrate if not prepared properly which disrupts the growth. The substrate we use is a silicon wafer coated with a thin film of sputtered alumina with a nominal thickness of 50 nm. This thin layer of alumina acts like an insulator that keeps the extremely thin iron layer from diffusing into the silicon. 4 nm thin films of iron were used in this work.

These thin films of iron are deposited on the substrate via thermal evaporation. Photolithography is used to control where the iron is deposited and, therefore, where the CNTs will grow. The iron is

deposited in 40 micrometer diameter circles in a square array 400 micrometers apart. When the CNTs are grown these circles become cylindrical posts that can be used to measure the Young's modulus using the DD test see Fig. 2.1.

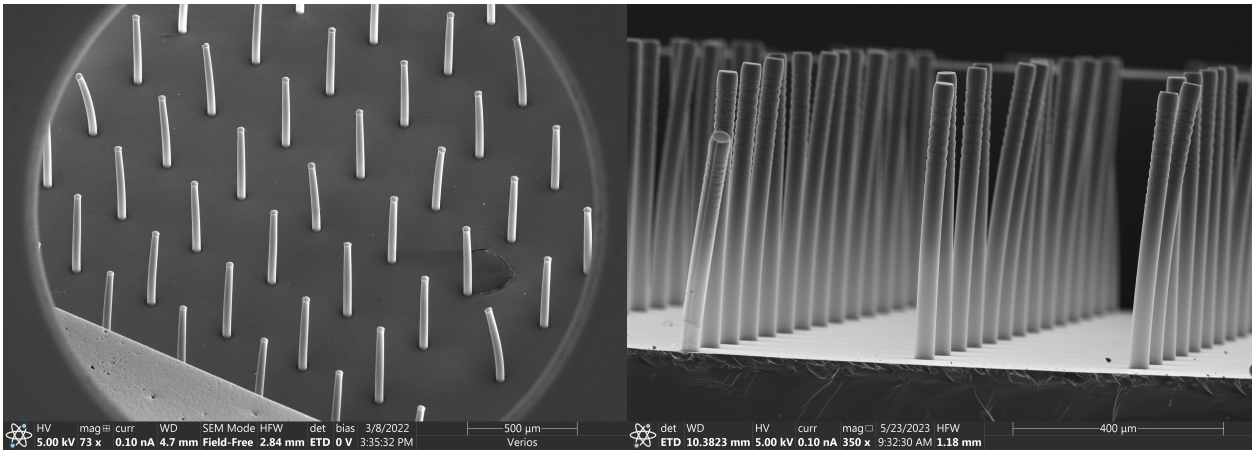


Figure 2.1 Example images of cylindrical CNT posts as grown from the silicon substrate described in the text.

When substrate preparation is complete, growth is performed in a high-temperature furnace. When the samples have been heated to the process temperature in a hydrogen atmosphere, ethylene is introduced and the CNT deposition begins. CNT growth was performed at 750 C. Following this process the height of each CNT post is measured using an optical microscope and recorded for use in the DD test.

2.3 Alumina Deposition

To ensure high quality deposition via ALD, the CNTs must be functionalized prior to deposition. Functionalization with ozone improves the quality of the deposition by significantly increasing the areal density of nucleation sites on the surface of the CNTs. Without functionalization, the nucleation sites are so far apart that small beads are formed rather than a continuous conformal film and many cycles of ALD are required before those beads coalesce. Ozone treatment allows for

conformal deposition within 15-25 ALD cycles. This is demonstrated in Fig. 2.2

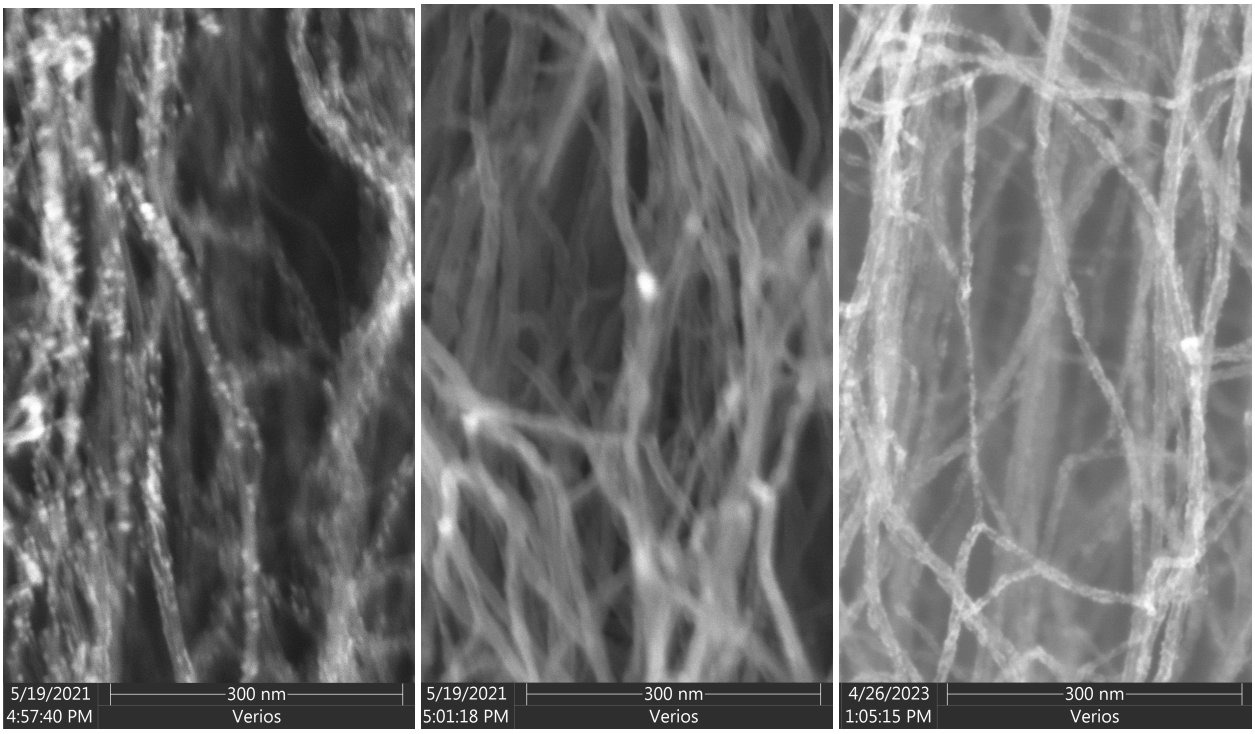


Figure 2.2 Comparison of ALD alumina deposition on CNTs with and without ozone functionalization at 200k times magnification. Left: No ozone treatment - 25 cycles ALD, bright points correspond to isolated nucleation sites. Middle: Ozone functionalized - 25 cycles ALD, the same ALD process has deposited smooth conformal layers because of increased nucleation site density. Right: Ozone functionalized - 15 cycles ALD, beaded but almost coalesced

Once the CNTs have been functionalized, the deposition of alumina can begin. TMA is introduced into the chamber, given enough time to diffuse into the CNT forest, purged with ultra-high purity nitrogen, and then followed by water vapor, and another purge. This is performed in a low-pressure chamber heated to 300 C and repeated until the desired thickness is deposited.

The functionalization of the CNTs and the deposition of the alumina is performed using a Lesker ALD-150LX deposition system. The samples were functionalized with ozone at room temperature. The ozone was introduced into the chamber at 200 SCCM with a concentration of approximately 10% ozone in pure O2. These were split into four groups: a control set with no deposition, and other sets with 15 cycles, 25 cycles, and 100 cycles respectively. These cycle numbers were chosen

specifically to target pristine CNTs, nonconformal beaded growth (15 cycles, see Fig 2.2), and two very different thicknesses of conformal growth (25 and 100 cycles). The dose time parameters for the deposition cycles were the same for all samples: 50 ms TMA, 120 s purge, 50 ms water, 120 s purge.

2.4 Measurement of Young's Modulus via Dual Deflection

The Young's modulus of the alumina-CNT composite material is measured using a process we call Dual Deflection (DD). This method uses Euler Beam Theory to model the composite posts as cantilevers to calculate the Young's modulus from the force required to bend, or deflect, them. This force is applied using the edge of a 20 micron diameter Stablohm 650 wire [9] mounted perpendicular to the post. Using the known material and geometric properties of the Stablohm wire combined with the distance the post and wire deflect, the force applied can be calculated and thereby the Young's modulus. For a more in depth description of the process see S. Roberts' "Mechanical Characterization of Carbon Nanotube based Neural Probes" [2].

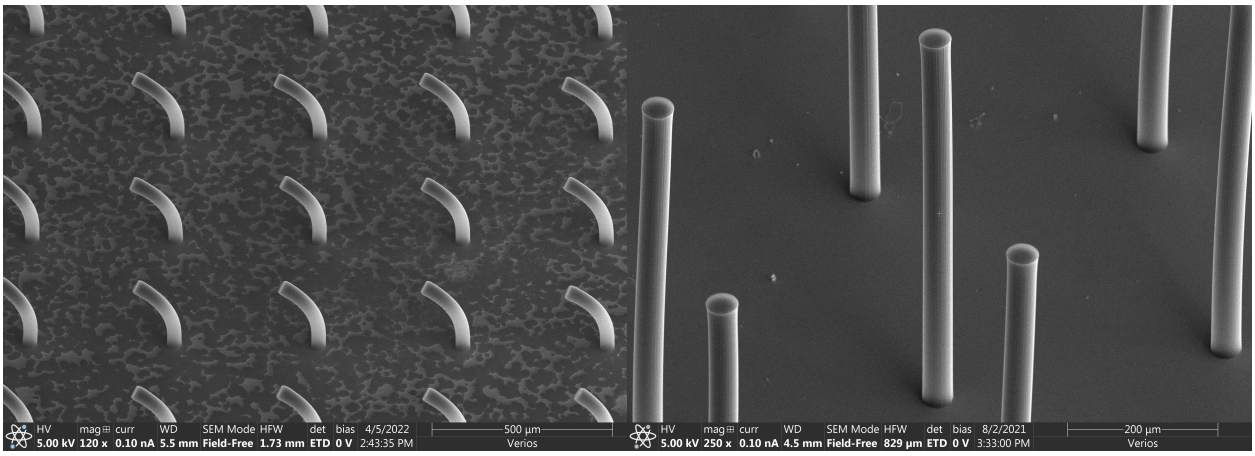


Figure 2.3 Left: Unusable array of "bent" posts. Right: An ideal straight post in array.

DD provides an excellent method for measuring the properties of microscopic structures but it does come with some drawbacks. In order for the assumptions of small deflection Euler Beam

Theory to apply, both the CNT posts and the Stablohm wire must be as close to perfectly straight as possible. The CNT growth pattern does not provide additional support to the posts as they grow and often the posts will not grow straight. Typical "bent" growth and an example of the ideal CNT post are shown in Fig. 2.3 above. This frequently makes testing and accumulating data a slow and arduous process as samples often have few, if any, sufficiently straight posts for testing.

Chapter 3

Results

3.1 Young's Modulus

The Young's modulus of the CNT-alumina composite correlates positively with thickness of the deposited alumina layer. The average Young's modulus for composites with 0, 15, 25, and 100 cycles of ALD are shown in Table 3.1 along with both the propagated error and the standard deviation of each alumina thickness. The error range provided with the average modulus is strictly due to the inaccuracies inherent in any physical measurement, especially at the microscale.

Number of Cycles	Average Modulus (MPa)	Standard Deviation (MPa)
0	$4.15 \pm .511$	2.59
15	10.4 ± 1.13	3.06
25	16.0 ± 1.33	3.10
100	364 ± 33.9	73.48

Table 3.1 Results of Young's modulus testing on composites of each number of ALD cycles with propagated experimental error. Note that the standard deviation of each batch of measurements is significantly larger than the error on all treatments.

Statistically speaking, that range should include the "true" average of the measurements taken if every measurement was exact with no opportunity for error. In contrast, the standard deviation is a measure of how spread out the measurements of different posts were i.e. a standard deviation of 2 MPa the the measured Young's modulus for around 68% of posts would fall within 2 MPa of the average assuming an approximately normal distribution of moduli. I've provided both the error and the standard deviation to provided a clear picture of the expected variations in the moduli of the composites.

As noted above there is a great deal of variability in the specific modulus of any given composite post. This could provide a barrier to some potential applications if the desired modulus or stiffness must be extremely precise or reproducible. However, the 40 micron composite posts are also particularly small and sensitive structures; applications with larger structures might have more consistent results. In addition, due to the stringent requirements of the DD test, the sample sizes for these tests have been extremely limited, additional testing with larger sample sizes would significantly increase the precision of the reported values.

Keeping the above in mind, this work has demonstrated that CNT-alumina composites of a desired modulus can be produced across significant ranges and that modulus can be tuned by precisely controlling the number of ALD cycles and thus the thickness of the alumina film. The Young's modulus of the composites increase almost 100 times between bare CNTs and CNTs with 100 cycles of alumina, an alumina layer less than 10 nm thick, and incremental increases in modulus are demonstrated by comparing the moduli of 0, 15, and 25 alumina cycle composites. This can also be seen in the boxplots of Fig. 3.1 which compare the measurements of each treatment directly. By taking advantage of the precision of ALD to deposit exact thicknesses of alumina, composites can be produced with targeted moduli within that range. Greater moduli are also likely achievable simply by increasing the alumina layer thickness.

Additionally, the current results are sufficient to begin developing a model for how the Young's

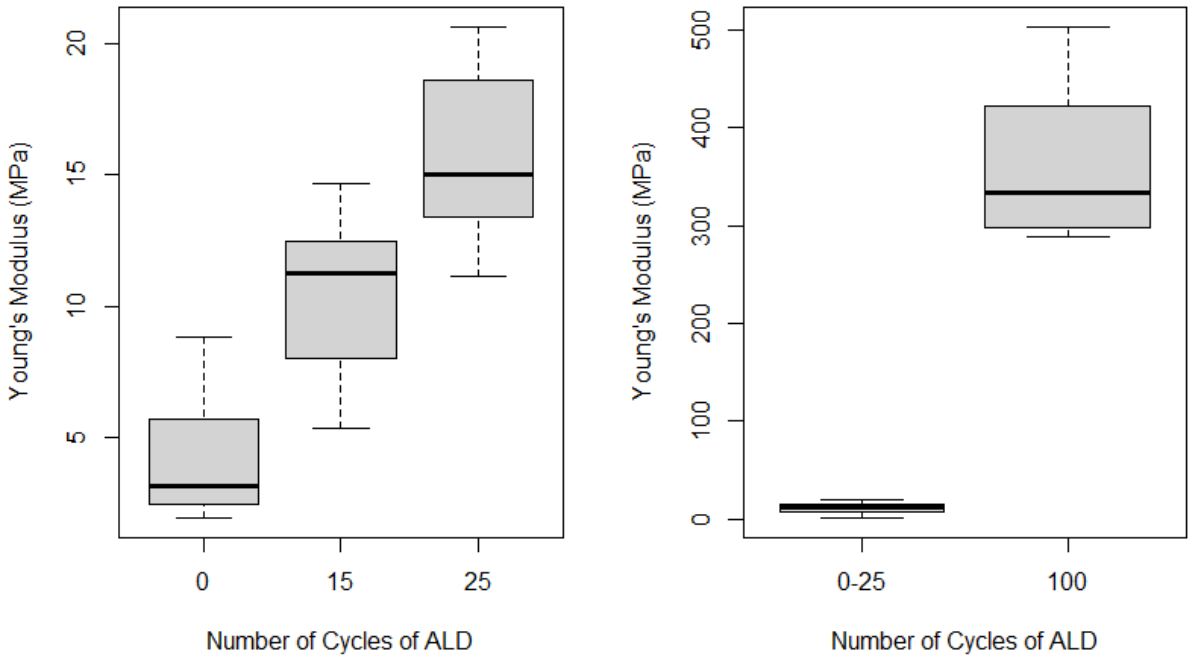


Figure 3.1 Boxplots showing variability of moduli. There is significant overlap between the lower cycle count composites (left). Contrast the significant difference between the lower counts and the 100 cycle composites (right)

modulus of the composite changes with ALD cycles. Considering the small incremental changes in the first three smaller cycle counts (0, 15, and 25 see Fig. 3.1) and the multiple magnitudes difference between those and the 100 cycle samples (also Fig. 3.1) modeling the relationship between cycle count and modulus as an exponential is the obvious first step. Plotted in Fig. 3.2 are the Young's modulus measurements for each cycle count versus the number of cycles. They are plotted on a log 10 y axis scale to make the relevant data more clear. Exponential lines of best fit have been calculated using linear regression and strongly support a exponential model. This is made even more clear if the data point corresponding to the pristine CNTs is removed. This makes sense as in the earliest cycles the deposited alumina would be in isolated beads and have little effect on the macroscopic properties of the CNTs. There is likely a transition point where the alumina coalesces

sufficiently to provide a measurable effect and follows an exponential relationship from there on as demonstrated by the second plot in Fig. 3.2 which has a nearly perfect exponential fit.

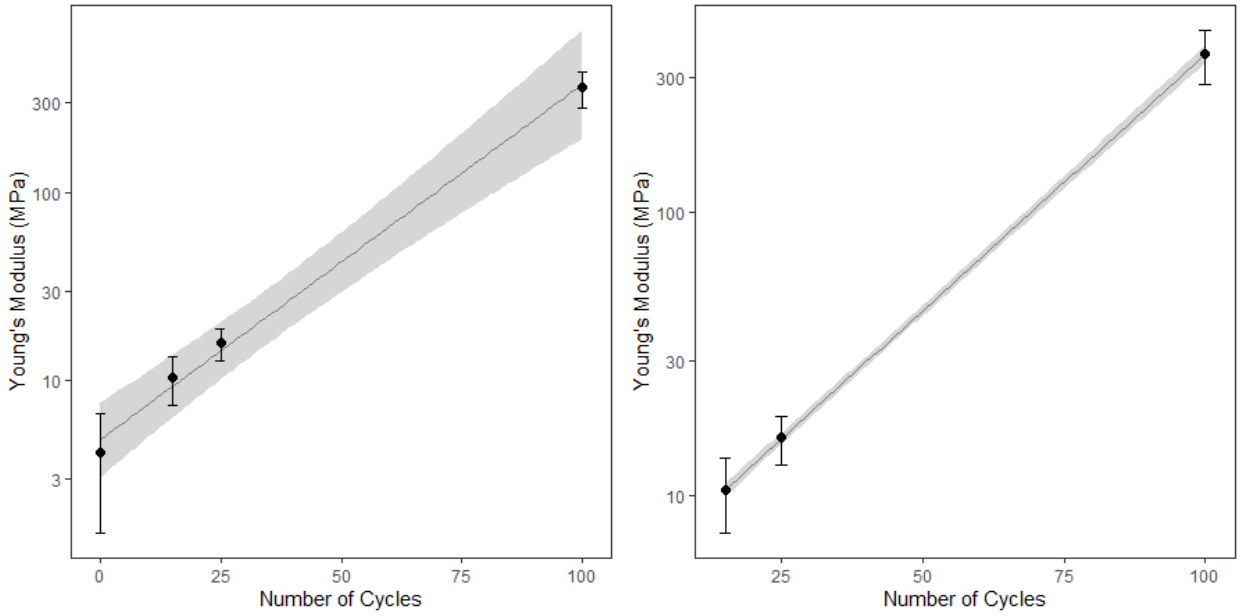


Figure 3.2 Plots of the measured Young's moduli vs ALD cycles on a log 10 y scale with an exponential linear regression fit. The error bars in this case are the standard deviation. The grey areas around the fit line show the standard error for the linear regression. This means that they can be used as a rough estimation of the quality of the fit, the narrower the grey band, the better calculated fit. The right plot has omitted the 0 cycle data point and the fit is exceptionally good.

There are many exciting directions this research could be expanded in. Larger samples of the current composites would help refine the accuracy of the values reported herein. Additional testing should also be performed to explore the upper limits as more alumina is deposited as well as fill in the data between 25 and 100 cycles. Doing so would define the range of possible moduli as well as provide data to model the relationship between alumina thickness and Young's modulus. In addition, tests of other material properties, such as electrical conductivity or tensile strength, could be performed to achieve a similar goal: tunable properties on a versatile material platform. Finally, there are many ALD processes for other materials (such as SiO_2 [10] and Fe_2O_3 [11]) with which new composite materials could be developed that would also provide similarly tunable properties.

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