Advanced Techniques for Carbon Nanotube Templated Microfabrication

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Advanced Techniques for Carbon Nanotube Templated Microfabrication

Jason Matthew Lund

A dissertation submitted to the faculty of
Brigham Young University
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

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ABSTRACT

Advanced Techniques for Carbon Nanotube Templated Microfabrication

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Doctor of Philosophy

Carbon nanotube templated microfabrication (CNT-M) is a term describing a grouping of processes where carbon nanotubes (CNTs) serve a structural role in the fabrication of a material or device. In its basic form, CNT-M is comprised of two steps: produce a template made from carbon nanotubes and infiltrate the porous template with an additional material. Vertically aligned carbon nanotube (VACNT) templates can be grown to heights ranging from microns to millimeters and lithographically patterned to a desired form. Deposition of an existing thin film material onto a CNT template will coat all template surfaces and can produce a near solid material with dimensions on the millimeter scale with resulting material properties coming primarily from the thin film. Progress within CNT-M falls broadly within one of two categories: control of the CNT template’s properties and form, or control of infiltration and new materials.

Three-dimensional CNT templates were developed to allow patterned multilayer VACNT structures. In one embodiment, VACNTs were grown below an existing, patterned and capillary-formed VACNT structure by reusing the original catalyst in combination with newly deposited catalyst to create a CNT-based microneedle array on a VACNT support. In another embodiment, VACNTs were mechanically coupled from the initial stages of growth to create a smooth, low porosity surface on which a secondary, patterned CNT forest was grown using standard film deposition and lithographic techniques.

A microfabrication compatible thermal barrier was produced using CNTs as a sacrificial template for silicon oxide. The resulting thermal barrier exhibited a thermal conductivity that could be tuned across 2 orders of magnitude based on the degree to which the sacrificial template was removed. Carbon infiltrated carbon nanotubes (CI-CNTs) were produced that exhibited a Young’s modulus ranging from 5 GPa to 26 GPa based on controlled process parameters. Porosity, centroid position, and the second moment of area was calculated from SEM images of CI-CNT structures using an automatic pore identification technique. The porosity results suprisingly show little to no porosity gradient across the width of the structure and a nearly linear increase in porosity from the top to bottom. This work advances the understanding of existing CNT-M processes and demonstrates novel techniques for producing future CNT templates.

Keywords: carbon nanotubes, CNT, CVD, MEMS, 3D MEMS, ICCNT, VACNT, Porosity, CI-CNT, Carbon Infiltration, CNT Template, CNT-M, Nanoinjection, Initially Coupled CNT, microfabrication
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Example of porosity profile obtained with developed pore identification. Shows unexpected porosity distribution.
**NOMENCLATURE**

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<td>CNT</td>
<td>Carbon nanotube</td>
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<tr>
<td>CI-CNT</td>
<td>Carbon infiltrated carbon nanotube</td>
</tr>
<tr>
<td>CNT-M</td>
<td>Carbon nanotube templated microfabrication</td>
</tr>
<tr>
<td>VACNT</td>
<td>Vertically aligned carbon nanotube</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>$R_q$</td>
<td>Root mean square (RMS) surface roughness (nm)</td>
</tr>
<tr>
<td>$R_{sa}$</td>
<td>Surface area difference (%)</td>
</tr>
<tr>
<td>G</td>
<td>Carbon nanotube growth</td>
</tr>
<tr>
<td>S</td>
<td>Ultrasonically sprayed carbon nanotubes</td>
</tr>
<tr>
<td>I</td>
<td>Carbon infiltration</td>
</tr>
<tr>
<td>ICCNT</td>
<td>Initially coupled carbon nanotubes</td>
</tr>
<tr>
<td>PI</td>
<td>Propidium iodide</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>$R_{tot}$</td>
<td>Thermal resistance across silicon substrate and thermal barrier (KW$^{-1}$)</td>
</tr>
<tr>
<td>$R_s$</td>
<td>Thermal resistance across silicon substrate (KW$^{-1}$)</td>
</tr>
<tr>
<td>$R_b$</td>
<td>Thermal resistance across thermal barrier (KW$^{-1}$)</td>
</tr>
<tr>
<td>$k$</td>
<td>Thermal conductivity (W m$^{-1}$ K)</td>
</tr>
<tr>
<td>$h_b$</td>
<td>Height of thermal barrier (m)</td>
</tr>
<tr>
<td>$h_s$</td>
<td>Height of silicon substrate (m)</td>
</tr>
<tr>
<td>$q$</td>
<td>Power per unit area (W/m$^2$)</td>
</tr>
<tr>
<td>$A$</td>
<td>Area (m$^2$)</td>
</tr>
<tr>
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<td>Laser power (W)</td>
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<tr>
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<tr>
<td>$P_{transmitted}$</td>
<td>Transmitted laser power (W)</td>
</tr>
<tr>
<td>$E$</td>
<td>Young’s modulus (GPa)</td>
</tr>
<tr>
<td>$E_{eff}$</td>
<td>Young’s modulus of carbon infiltrated carbon nanotubes (GPa)</td>
</tr>
<tr>
<td>$E_c$</td>
<td>Young’s modulus of chemical vapor deposited carbon (GPa)</td>
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<tr>
<td>$E_{cntf}$</td>
<td>Transverse Young’s modulus of carbon nanotube forest (GPa)</td>
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<tr>
<td>$E_{corr}$</td>
<td>Corrected Young’s modulus of carbon infiltrated carbon nanotubes (GPa)</td>
</tr>
<tr>
<td>$k$</td>
<td>Mechanical stiffness, slope of force-displacement curve (Nm$^{-1}$)</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Porosity</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Fraction of volume occupied by carbon nanotube forest</td>
</tr>
<tr>
<td>$x'$</td>
<td>Normalized x-axis of the CI-CNT material cross-sections</td>
</tr>
<tr>
<td>$y'$</td>
<td>Normalized y-axis of the CI-CNT material cross-sections</td>
</tr>
<tr>
<td>$C$</td>
<td>Theoretical centroid (µm)</td>
</tr>
<tr>
<td>$C'$</td>
<td>Calculated centroid (µm)</td>
</tr>
<tr>
<td>$\bar{x}$</td>
<td>Theoretical x centroid (µm)</td>
</tr>
<tr>
<td>$\bar{x}'$</td>
<td>Calculated x centroid (µm)</td>
</tr>
<tr>
<td>$\bar{y}$</td>
<td>Theoretical y centroid (µm)</td>
</tr>
<tr>
<td>$\bar{y}'$</td>
<td>Calculated y centroid (µm)</td>
</tr>
<tr>
<td>$I$</td>
<td>Theoretical second moment of area (µm$^4$)</td>
</tr>
</tbody>
</table>
\( I' \quad \text{Calculated second moment of area (\(\mu m^4\))}

\( L_{gap} \quad \text{Span across three-point bending supports (m)}

\( P \quad \text{Force applied in three-point bending tests (N)}

\( t \quad \text{Thickness of samples in the direction of the applied force in three-point bending tests (N)} \)
CHAPTER 1. INTRODUCTION

1.1 Background

Carbon nanotube templated microfabrication, or CNT-M, is a term coined by researchers at Brigham Young University [1] to describe a large category of processes where carbon nanotubes (CNTs) serve a structural role in the fabrication of a material or device. In its basic form, CNT-M is comprised of two steps: produce a template made from carbon nanotubes and infiltrate the porous template with an additional material. The template can be comprised of single, double, or multi-walled CNTs (SWCNT, DWCNT, MWCNT) [2] that can exhibit any chirality [3, 4] or level of defectivity and is typically produced as vertically aligned carbon nanotubes (VACNT) [5, 6]; or in other words, as a CNT “forest” (Figure 1.1). CNT forests are commonly grown from a thin film catalyst in a chemical vapor deposition (CVD) reactor, meaning the desired 2D profile of the forest can be patterned directly into the catalyst via standard lithographic techniques.

![Wide view of patterned VACNTs.](image1.png)

Figure 1.1: SEM images of vertically aligned carbon nanotubes.
Infiltration in CNT-M refers, primarily, to the process of depositing a thin film coating on all surfaces of the CNT template and is commonly performed via thin film deposition techniques such as electroplating, physical vapor deposition (PVD), chemical vapor deposition (CVD), and their respective variants. A natural consequence of thin film infiltration on a porous substrate, and an important point to keep in mind when considering a CNT-M approach, is that the resulting structure will always retain some level of porosity as shown in Figure 1.2.

1.2 Motivation

Thin films can exhibit very unique and desirable properties but are nonetheless confined to thicknesses below 1000 nm. This limitation may be imposed by the application of use, such as electronic or optical devices that are driving for ever smaller features. The time it takes to produce a thicker film with deposition or growth rates in the range of 10 nm/min may be time or cost pro-
hbitive. Or, in some cases, thin films remain thin if stress prevents the material from reaching a certain thickness without cracking or peeling. Knowing that the spacing between CNTs in a forest can range from 30 nm to 200 nm, a conformal coating of less 100 nm on a 500 µm CNT template can effectively produce a bulk material that was previously confined to the realm of thin films. This opens possibilities to create micro- to meso- scale devices via microfabrication with an ever expanding field of thin film materials to choose from. Examples of CNT-M produced devices using CVD carbon as the infiltration material are shown in Figure 1.3 [7–11].

There is ongoing research into ways to take advantage of CNTs in microfabrication which investigates new strategies to infiltrate VACNTs and new materials with which to infiltrate them [12–
15]. With respect to the CNT template, teams are now able to simultaneously grow VACNTs at different and defined rates [16]. With capillary forming [17] researchers are collapsing patterned VACNTs into repeatable three-dimensional structures. It is possible to grow centimeter tall VACNTs [18, 19], grow on a variety of substrates [20, 21], and to tune the properties of the CNTs produced [22–25]. The technologies related to CNTs are maturing and inching ever closer to adoption in the commercial space.

1.3 Objective

The aim of this research is to advance the capabilities and understanding of CNT-M techniques and key to that advancement is the development of strategies for producing more complex, three-dimensionally formed CNT templates. To integrate any CNT template or CNT templated material with existing microfabrication processes it must be patternable and able to support patterned materials. To lower the barrier of entry to these technologies, an understanding of the unique fabrication challenges associated with CNT-M development and insight into the properties expected is important. This work sets out to address these items in order to push microfabrication forward and to make CNT-M adoption more appealing for academic and industrial researchers alike.

1.4 Outline

Chapter 2 explores methods to create complex, three dimensional CNT structures from multilayer, patterned VACNTs. Chapter 3 investigates an alternative three-dimensional CNT template applied to the development of lance arrays for the injection of DNA into thousands of cells simultaneously and addresses the topic of adhesion of VACNTs to the surface. In chapter 4, a MEMS compatible thermal barrier layer is developed using CNT-M techniques and the unique challenges to CNT-M development are examined. Chapter 5 looks at the porosity and mechanical properties of carbon infiltrated CNT structures to isolate the true contribution of the infiltration material on the apparent material properties.
CHAPTER 2. THREE-DIMENSIONAL VACNT TEMPLATES BY INITIALLY COUPLED CARBON NANOTUBE GROWTH

2.1 Introduction

Carbon nanotube templated microfabrication, or CNT-M [1], is a term that describes a large category of processes where carbon nanotubes (CNTs) [2] serve a structural role in the fabrication of a material or device. CNT-M is comprised of two basic steps: produce a template made from carbon nanotubes and infiltrate the porous template with an additional material. Work focused on chemical vapor infiltration (CVI) of CNT structures primarily uses vertically aligned carbon nanotubes (VACNTs) [5, 6], that may or may not have been patterned, as the CNT template [7–15, 26, 27].

Catalytic chemical vapor deposition (CVD) using a thin film catalyst is a powerful and flexible method of producing CNT forests. To produce CNTs, the catalyst film must form into nanoparticles from which the CNTs are grown. These nanoparticles generally stay confined to regions where the initial film was deposited, thus allowing one to pattern the two-dimensional arrangement of the CNT forest by patterning the initial film with standard lithographic techniques. Differently sized particles produce CNTs of different diameters, which will grow at different rates [28].

During the initial stages of growth, individual CNTs are not interacting mechanically with their neighbors and wander randomly as their length increases. VACNTs are possible due to crowding effects [29], because neighboring CNTs will eventually meet and be mechanically coupled by van der Waals forces. At this stage in the growth there is a balance of forces and the entire field of CNTs will continue to grow, but together, at an average rate and in a primarily vertical direction [30]. For CNT-M technologies to mature, progress must be made both on the infiltration of new materials and on methods to controllably produce complex structures. Presented here is a
strategy to manufacture three-dimensional CNT templates via lithographically defined, multilayer VACNTs. The methodology and a discussion of the present challenges and properties are discussed below.

2.2 Challenges in depositing patterned films on VACNTs

The primary challenges to lithographically patterned thin films on a CNT forest are the porosity, roughness, and fragility. In terms of fragility, VACNTs are easily collapsed or removed from the substrate through interaction with fluids [17, 31], meaning that any photoresist or developer would deform or damage the CNT forest. Through shadow masking it is possible to selectively deposit films onto a CNT surface, but the roughness and porosity of the surface necessitate extremely thick depositions before the film will be contiguous. Figure 2.1 shows an example of a 1 µm thick, electron beam evaporated, aluminum oxide (Al₂O₃) deposited on a CNT forest that was under constant rotation. Despite the thickness of the alumina, the surface appeared to retain some amount of porosity and a high degree of roughness as shown in Figure 2.1.
2.3 Patterned films on VACNTs via initial coupling

The key to addressing surface roughness and porosity lies in how the plane of forest growth is defined. As discussed above, the initial growth of CNTs is independent and randomly oriented. At some point enough CNTs are coupled together to grow as a collective, with the plane defining forest growth appearing 2 µm to 10 µm below the uppermost CNTs. This means that the surface roughness of a VACNT forest is defined before “forest growth” even begins. In theory, a plane that mechanically linked all of the CNTs from the earliest stage of growth could significantly reduce the surface roughness of the forest. To define precisely this plane, powdered CNTs, prepared in a solution, were ultrasonically sprayed onto a thin film catalyst (iron supported by aluminum oxide) that had been prepared for growth. The sprayed CNTs were relatively short (<15 µm), landing in generally horizontal, random orientations on the surface, forming a CNT mesh held together by the same van der Waals forces described above. Growth of CNTs beneath another film is only possible if gases are able to penetrate the layer to accesses the catalyst [32]. Sprayed CNTs were chosen for this novel process in part because of the natural permeability of the layer, in part to retain a purely CNT structure, and the experience of the research group in using sprayed CNTs [33]. And indeed, standard CVD growth of this CNT coated catalyst film results in VACNTs that lift the sprayed CNT layer as they grow. This process is depicted as steps (1) - (3) in Figure 2.2. The resulting structure, shown in Figure 2.3, is an average CNT forest, with the expected height and porosity, but with a smooth, low porosity upper surface. This type of CNT forest grown beneath a film that mechanically links CNTs in the early growth stages will be referred to as initially coupled carbon nanotubes, or ICCNTs, throughout this work.

With, potentially, the challenges of porosity and roughness addressed, the ICCNTs remain vulnerable to fluids and capillary forces. To address this, the ICCNTs were reinforced with 5 min of CVD carbon which locks the CNTs together at points of contact. The light carbon infiltration was chosen to retain a highly porous, primarily CNT, structure while providing enough strength for the structure to survive lithographic processes.

Standard photolithography, film deposition, and liftoff steps proceeded normally on the lightly infiltrated ICCNTs as depicted in steps (4) - (7) of Figure 2.2. Once the new, patterned,
Figure 2.2: Diagram of process to produce stacked VACNTs with a lithographically patterned top layer. Where ICCNT refers to initially coupled carbon nanotubes. (1) Prepare standard CNT growth catalyst film stack (iron on alumina) on silicon substrate. (2) Ultrasonically spray CNTs onto the prepared catalyst. (3) Growth of VACNTs that lift the sprayed CNTs above them. (4) Light CVD carbon infiltration to reinforce the structure. (5) Spin, expose, and develop photoresist using standard processes on the top surface of the structure. (6) Deposit the same CNT catalyst film stack on top of the ICCNT forest. (7) Standard liftoff procedure to leave a patterned catalyst layer. (8) Growth of VACNTs on ICCNT support resulting in a highly porous, three-dimensional CNT template.

CNT growth catalyst was prepared it was returned to the atmospheric CVD furnace for CNT growth, resulting in the stacked VACNT layers shown in Figure 2.4. There are no fixed rules on what level of porosity and roughness are acceptable for lithography and thin film deposition on such a surface. Clearly the ICCNT surface does not have the same roughness and flatness of a silicon wafer. However, this structure appears capable of supporting thin films and the experimental processes proves it is possible, but it is an open question as to what limitations ICCNTs, in their current embodiment, will present in lithography and film deposition. Surface roughness results, process variants, and development challenges are addressed below.
2.4 Results and discussion

There are three basic processes in ICCNT production: ultrasonically spraying CNTs (spray), CNT growth (grow), and light carbon infiltration (infiltrate). Seven combinations of these pro-
cesses were produced: G, GI, GIS, GS, S, SG, SGI. G refers to VACNTs grown from a standard catalyst. GI are grown VACNTs that were lightly infiltrated with CVD carbon. GIS samples are GI samples onto which CNTs were sprayed onto the surface. GS are VACNTs that are exposed to CNT spraying without carbon infiltration reinforcement. S refers to CNTs sprayed onto the catalyst films but without a subsequent CNT growth step. SG samples are ICCNTs as described above where VACNTs are grown beneath a sprayed layer of CNTs. SGI samples are SG samples that were lightly infiltrated with CVD carbon. With the exception of GS samples, the surface of each of these process combinations was measured via atomic force microscopy (AFM) to quantify their RMS surface roughness (Rq) and surface area difference (RsΔ), which measures the percentage increase in surface area compared to the projected area of the scan. AFM measurements were taken with 100 µm x 100 µm (1 × 10⁴ µm²) and 2 µm x 2 µm (4 µm²) scan areas and the results are given in Table 2.1. GS samples were not measured by AFM because the CNT spray process significantly altered the VACNTs, creating interesting structures (see Figure 2.5) that no longer had a planar upper surface.

### 2.4.1 AFM results

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>2 µm x 2 µm</th>
<th>100 µm x 100 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rq (nm)</td>
<td>RsΔ (%)</td>
</tr>
<tr>
<td>G</td>
<td>123.1</td>
<td>325</td>
</tr>
<tr>
<td>GI</td>
<td>148.2</td>
<td>298</td>
</tr>
<tr>
<td>GIS</td>
<td>43.35</td>
<td>59</td>
</tr>
<tr>
<td>S</td>
<td>39.9</td>
<td>87</td>
</tr>
<tr>
<td>SG</td>
<td>45.39</td>
<td>90</td>
</tr>
<tr>
<td>SGI</td>
<td>43.61</td>
<td>68</td>
</tr>
</tbody>
</table>

AFM measurements on the 100 µm x 100 µm scan area showed that G and GI samples had a lower roughness than an ICCNT (SGI) structure which seems to contradict what is seen when vi-
Figure 2.5: Example of GS sample showing deformed VACNTs caused by ultrasonic spray deposition of CNTs onto the as grown CNT forest.

Figure 2.6: Comparison of AFM linescan profiles of G and SGI samples in Figure 2.6.

usually comparing VACNT and ICCNT structures, see Figures 2.7 and 2.8. Looking at the surface area difference ($R_{sa}$), the G and GI samples have a lot of surface area present on vertical surfaces, and more than the SGI counterpart. One piece of information that is lost in a RMS roughness value is the lateral scale of the roughness, whether it is high or low frequency. A large wave may have a larger calculated roughness than a structure with higher frequency roughness such as that seen on the CNT forests. This is shown in the comparison of AFM linescan profiles of G and SGI samples in Figure 2.6.

Measurements over a 2 µm x 2 µm scan area exhibit the expected trend of roughness and surface area difference on the order most relevant to thin film deposition and lithography. The surprising roughness results over the larger area are possibly caused by sampling effects, where the
Figure 2.6: Example AFM profiles from the 100 µm x 100 µm scans of G (CNT growth only) and SGI (Spray, Growth, Infiltrate) samples. These profiles show the calculated roughness for SGI samples is dominated by lower frequency waviness compared to the G sample, which appears rougher in the profile.

regions of the CNT forest measured had larger scale height variation. The precise location of each scan on the sample and the total height of each sample were not recorded, which is unfortunate as this could have provided further insight into the unexpected trends. Additional replication of samples and more measurements per samples at different scales will be needed to determine if the higher level of waviness in the ICCNT type samples (SG, SGI) is intrinsic or within the natural variation of VACNT growth. The smaller scan area, isolated from large scale waviness, seems to indicate that the ICCNTs are indeed smoother, less porous, and better suited to supporting patterned thin films. It should be noted that GIS samples also exhibit a low roughness, indicating that this is another alternative for producing multilayer CNT templates. However, the GIS sample would need undergo an additional carbon infiltration to bind the sprayed CNTs prior to any processes involving fluids.
2.4.2 Thin film catalyst on ICCNTs

It was possible to grown patterned VACNTs on an ICCNT layer, but a slight modification to the catalyst film stack was required. The standard alumina diffusion barrier on silicon used in this study was 30 nm thick while the successful growth on ICCNTs used a 140 nm thin film. Initially 30 nm was attempted but yielded no VACNT growth. No intermediate thicknesses were attempted.
2.4.3 Patterned ICCNT

In an attempt to produce even more complex CNT templates with ICCNTs, the initial catalyst on the silicon substrate was also patterned following steps (1) - (3) in Figure 2.9. What is seen in the resulting structure, see Figure 2.10, is that even with gaps in the underlying CNT forest the sprayed CNT layer can remain contiguous. Steps (4) - (7) in Figure 2.9 were not experimentally performed but are theoretically possible. It appears, in patterning the ICCNTs, that the sprayed CNT layer is fairly well adhered to the substrate and if the gap between VACNTs is large enough, the sprayed CNT layer will rip apart. This is seen at the bottom edge of the patterned features in Figure 2.10. Potential strategies to expand the gap that can be bridged by the initially coupled plane include: reducing the adhesion of the film to the substrate surface and increasing the strength of the film. One could increase the bonding between CNTs or use longer CNTs in the sprayed layer. Or the sprayed CNTs could be replaced with an alternate film that is stronger but retains gas permeability.

2.5 Regrowth of the initial catalyst

It is possible for the initial catalyst on the silicon substrate to be used for CNT growth multiple times; either quick cycles in the same CVD run or after it has been removed, cooled, and returned to the CVD furnace. A catalyst may stop being active if it completely diffuses into the substrate or if it is sealed off from access to the hydrocarbon gas. In the case of this work, the second CNT growth was only ever attempted after a short carbon infiltration. It is suspected that no CNTs grew again from the base catalyst in step (7) of Figure 2.2 either because the catalyst had already been coated in CVD carbon, isolating it from future reactions, or the catalyst diffused into the substrate during the high temperature carbon infiltration step. Some method of neutralizing the catalyst needs to take place to prevent parasitic CNT growth below the ICCNT layer.

2.6 Methodology

This section outlines in detail the processes used in this work. While these protocols are important in understand and replicating what has been developed, it is hoped that readers will
Figure 2.9: Diagram of process to produce stacked VACNTs with a lithographically patterned top layer. Where ICCNT refers to initially coupled carbon nanotubes. (1) Prepare standard CNT growth catalyst film stack (iron on alumina) on silicon substrate. (2) Ultrasonically spray CNTs onto the prepared catalyst. (3) Growth of VACNTs that lift the sprayed CNTs above them. (4) Light CVD carbon infiltration to reinforce the structure. (5) Spin, expose, and develop photoresist using standard processes on the top surface of the underlying structure. (6) Deposition the same CNT catalyst film stack on top of the ICCNT forest. (7) Standard liftoff procedure to leave a patterned catalyst layer. (8) Growth of VACNTs on ICCNT support resulting in a highly porous, three-dimensional CNT template.

recognize that there are many possible variations to produce the same or similar three-dimensional CNT templates.

2.6.1 Catalyst preparation

30 nm of aluminum oxide was deposited onto a single crystal silicon substrate in a Denton Vacuum electron beam evaporator at $7.3 \times 10^{-8}$ bar with a rate of $0.4 \text{ nm s}^{-1}$ from a graphite crucible. The 4 nm thick iron catalyst film was deposited via thermal evaporation from an alumina coated tungsten basket heater at $3.8 \times 10^{-8}$ bar. The prepared wafer was coated in a protective layer of AZ 3312 photoresist, soft baked on a hotplate at 110 °C for 60 s, and diced into 1.5 cm squares with a Disco Dad 320 Automatic Dicing Saw at a rate of $5 \text{ mm s}^{-1}$ before the resist was
stripped with acetone and IPA. The same procedure and equipment were used for depositing aluminum oxide and iron on top of a CNT structure, except the alumina thickness was increased to 140 nm and no additional dicing was performed.

2.6.2 Catalyst patterning

Liftoff techniques were used to pattern the iron/alumina film stack, both on the silicon wafer and CNT structures. Prior to iron or alumina deposition, the substrate was coated with AZ
3312 positive photoresist using a Laurell Spin Processor (WS-400A-6NPP-LITE) at 2750 rpm for 60 s, and 6000 rpm for an additional 2 s. The resist was soft baked on a hotplate at 110 °C for 60 s and then allowed to cool for 120 s. Exposure through the chrome mask was performed with a MA 150 CC Karl Suss Mask Aligner for 8 s at 50 µm of separation after 10 s of hard contact. For the post exposure bake, the sample was returned to the 110 °C hotplate for 60 s before being allowed to cool again for 120 s. The photoresist was developed for 60 s in AZ 300 MIF, rinsed with water, and dried with a nitrogen gun. The patterned photoresist was then placed into a plasma etcher (Technics Planar Etch II) for 30 s at 250 W with a 10 sccm flow of oxygen at $4 \times 10^{-4}$ bar for a descum process to remove residual organics. After deposition of the the alumina and iron layers, the actual liftoff occurred when the sample was submerged in NMP and placed in an ultrasonic cleaner for 5 min before it was rinsed with acetone, rinsed with IPA, and dried with a nitrogen gun.

### 2.6.3 CNT spraying

To spray CNTs they were first prepared in a solution compatible with an ultrasonic sprayer fed by a syringe pump. 11 mg of powdered multi-walled carbon nanotubes (SigmaAldrich CAS Number:308068-56-6) were added to 80 mL of NMP (N-Methyl-2-pyrrolidone, CAS number:
872-50-4) in a glass beaker. The MWCNTs were dispersed in the NMP using a 500 W ultrasonic processor for 20 min. The dispersed CNTs were centrifuged in a Sorvall RC-5C Plus centrifuge with a SS-34 rotor at 4 °C for 1 h at 1200 rpm. The centrifuged solution was decanted into polypropylene vials for storage prior to ultrasonic spraying. The CNT spray system used a syringe pump with a 20 mm diameter syringe to feed the CNT solution into the ultrasonic spray head which was mounted on a motorized, computer controlled xy stage above a hotplate on a z stage. The CNT solution was pumped to the ultrasonic head which sprayed out onto the hotplate. The ultrasonic head settings and its height above the hotplate determined the area sprayed in a single pass. The hotplate (230 °C) heated the sample to quickly evaporate any solvent (NMP) but leave the CNTs intact on the surface. Without the hotplate, surface tension played a larger role during the evaporation of the NMP, resulting in rings of sprayed CNTs rather than a uniform coating.

For this system the standard spray pattern used a series of back and forth passes where the pass length, inter-pass spacing, and speed are user defined. To ensure a uniform coating the spray program was designed to avoid the spray resting on a region of interest, such as when the spray head is changing directions or at the end of each cycle. The spray head moved at a rate of 1000 \( \frac{\text{step}}{\text{s}} \), and was placed 25 mm above the sample surface. The CNT solution was fed into the ultrasonic spray head at a rate of 0.25 mL/min using a syringe pump. The thickness of the sprayed CNT layer was controlled by setting the number of rasters for the program, set to 100 for this work.

2.6.4 CNT growth

Vertically aligned CNTs were grown, following the process shown in Figure 2.12, from an iron/alumina film stack at 750 °C in an atmospheric pressure, 25 mm, quartz tube furnace (Lindberg Blue M™, 1200 °C) with a 30 cm heated zone. Samples were positioned 15 cm into the heated zone on a rectangular quartz tray such that the samples were centered vertically in the tube. The temperature ramp from room temperature to growth temperature occurred under 230 sccm of hydrogen to reduce the iron thin film, allowing the catalyst nanoparticles to form. At growth temperature, 250 sccm of ethylene gas flow was added and held until the desired growth height was reached, typically around 100 \( \mu \text{m} \) after 100 s. The hydrogen and ethylene flow was then replaced.
with 220 sccm of argon flow and held for 2 min to purge the reactor before turning off the heaters and allowing the furnace to cool below 200 °C for sample removal.

Figure 2.12: Diagram and description of the CNT growth process in an atmospheric thermal CVD furnace. (A) Ramp temperature under hydrogen flow until growth temperature $T_1$ (750 °C) is reached. (B) CNT growth for specified time at temperature $T_1$. (C) Argon replaces hydrogen and ethylene to purge and settle the system. (G) Heaters are turned off and the clamshell furnace is opened to cool the system. Samples are removed at temperatures below 200 °C.

### 2.6.5 Carbon infiltration

CVD carbon infiltration was performed, following the process shown in Figure 2.13, at 900 °C in an atmospheric pressure, 25 mm single zone quartz tube furnace (Lindberg Blue M™, 1200 °C) with a 30 cm heated zone. Samples were positioned 15 cm into the heated zone on a rectangular quartz tray such that the samples were centered vertically in the tube. The temperature ramp from room temperature to carbon infiltration temperature occurred under 220 sccm of argon. At infiltration temperature, 463 sccm of hydrogen and 250 sccm of ethylene replaced the argon to begin the carbon infiltration. After 5 min of carbon infiltration hydrogen and ethylene were exchanged for 220 sccm of argon for a 2 min settle and the following cooldown, when the furnace
heaters were turned off and the clamshell opened to cool the furnace.

![Diagram of carbon infiltration process](image)

Figure 2.13: Diagram and description of the carbon infiltration process in an atmospheric thermal CVD furnace. (D) Ramp furnace under argon until carbon infiltration temperature $T_2$ (900 °C). (E) Ethylene and hydrogen replace argon to perform carbon infiltration for a specified time at temperature $T_2$. (F) Argon replaces hydrogen and ethylene to purge and settle the system. (G) Heaters are turned off and the clamshell furnace is opened to cool the system. Samples are removed at temperatures below 200 °C.

In the case where a carbon infiltration step is intended to come directly after a CNT growth step both steps are performed sequentially in a single CVD process as show in Figure 2.14. This process is a simple combination of those described in Figures 2.12 and 2.13 with the exception that it isn’t necessary to cool the furnace between the growth and infiltration steps. GI, GIS, and SGI samples were processed this way.

### 2.6.6 AFM measurements

The surface of the various CNT-M structures were characterized via AFM using a Veeco Dimension V scanning probe microscope with silicon AFM tips in tapping mode. AFM measurements were taken at two different scales; one with a 100 µm x 100 µm ($1 \times 10^4 \text{ µm}^2$) scan area and the other with a 2 µm x 2 µm (4 µm²) scan area. Parameters presented in these tables include $R_q$, $R_m$, and $R_g$. 
Figure 2.14: Diagram and description of the CNT growth and carbon infiltration process in an atmospheric thermal CVD furnace. When the carbon infiltration directly follows CNT growth, the steps are performed sequentially during one CVD run. (A) Ramp temperature under hydrogen flow until growth temperature $T_1$ (750°C) is reached. (B) CNT growth for specified time at temperature $T_1$. (C) Argon replaces hydrogen and ethylene to purge and settle the system. (D) Ramp furnace under argon until carbon infiltration temperature $T_2$ (900°C). (E) Ethylene and hydrogen replace argon to perform carbon infiltration for a specified time at temperature $T_2$. (F) Argon replaces hydrogen and ethylene to purge and settle the system. (G) Heaters are turned off and the clamshell furnace is opened to cool the system. Samples are removed at temperatures below 200°C.

the RMS roughness, and $R_{sa}$, which represents the percentage surface area difference between the actual and projected surface area. Results for each sample type are presented in Table 2.1.

2.7 Conclusion

This work has resulted in the development of initially coupled vertically aligned CNTs, a process that enables the deposition of well defined thin film materials on top of a CNT forest. The $R_{sa}$ has been reduced by about 80% compared to the normal VACNT surface, and small scale roughness, $R_q$, was reduced by 65%. The process has demonstrated the ability to create stacks of multilayer CNT forests with a patterned top layer and theoretically stacks where both CNT forests are structured. And it was observed that three times the thickness of alumina was needed to support CNT growth on top of the ICCNT layer. Future work in this area can include proving the theory of Figure 2.9 and in exploring the maximum gaps possible while retaining a contiguous and smooth top surface. To enable wider adoption for applications and combinations with new materials, it is critical to characterize the structural and material properties of thin films.
deposited onto ICCNTs. This work did confirm the possibility of creating increasingly complex CNT structures using microfabrication compatible processes.
CHAPTER 3. CNT-BASED MICRONEEDLE ARRAYS PRODUCED VIA CARBON NANOtube TEMPLATED MICROFABRICATION

3.1 Introduction

New materials and processes for microelectromechanical systems (MEMS) are in demand to extend capabilities, improve performance, and reduce cost. Carbon nanotube templated microfabrication (CNT-M) is a term encompassing microfabrication techniques in which carbon nanotubes (CNTs) or, more specifically, vertically aligned carbon nanotubes (VACNTs) are critical to the device or device fabrication. Song et al. [1] first introduced the term to describe a process wherein patterned VACNTS were partially infiltrated with silicon and subsequently oxidized to simultaneously convert the silicon to silica and remove the CNTs from the structure. Porous oxide structures without volume expansion from the silicon to silica conversion were achieved [34] by using atomic layer deposition (ALD) to directly deposit alumina onto VACNTs, after which the CNTs were removed by oxidation. Hutchison et al. [26] demonstrated the novel use of patterned CNTs as a framework for high aspect-ratio MEMS by infiltrating the porous, as-grown CNTs with silicon to create mechanical devices. Other filler materials such as silicon nitride, carbon, and more were suggested as viable options. Jones et al. [11] investigated a coronary stent made from carbon infiltrated CNTS. Measurements by Hanna et al. [27] indicate that the mechanical properties of infiltrated CNTs are dominated by the filler material. Moulton [35] studied the effect of iron catalyst thickness on feature definition and wall straightness and developed an iron border technique for improving wall straightness of high aspect-ratio features.

CNT-M as a term was created by the research group at Brigham Young University. However, significant additional published work can be applied to, or added under the umbrella of, CNT-M. Capillary forming [17, 31] is a technique by which a CNT forest is collapsed to a denser form and, with proper design of the catalyst shape, more complex 3D structures are possible. Field emission properties of a CNT forest can be improved by plasma etching [36] which changes the
surface structure from a tangled mat to a set of needle-like bundles. Catalyst is reused to grow a stack of independent VACNT forests on top of each other [37] in a process that the authors refer to as “regrowth”.

In this work, these techniques are combined and demonstrated as part of CNT-M through the fabrication of a nanoinjection device. Nanoinjection [38] is a pumpless, physical injection method for delivering foreign material into a cell using a solid lance. In this work, the words “lance” and “needle” will be used interchangeably to reference a microscale solid spike, typically with a tapered structure. In nanoinjection a cell is placed in media with the foreign material of interest, such as DNA. Applying a voltage bias attracts DNA to the lance, which is inserted into the cell, and the voltage bias is reversed to repel the DNA. The lance is retracted and the minimal cross-sectional area minimizes damage to the cell and cell membrane. Nanoinjection can be performed on thousands of cells simultaneously using an array of solid lances [39] and was demonstrated using silicon lances made with deep reactive ion etching (DRIE) [40], see Figure 3.1. Work focused on better understanding the nanoinjection process [41, 42] led to attempts to substitute carbon nanotubes for silicon [42] in hopes of reducing cost or creating a lance array whose efficacy is less sensitive to variation. While unsuccessful in fabricating a CNT solid lance array, Toone’s thesis [42] was the foundation on which the CNT nanoinjection device presented here was built. This work will disclose and discuss the microfabrication techniques involved in making a CNT-M lance array, describe its testing, and compare its performance to that of the established silicon lance array.

3.2 Methods and Materials

The fabrication process described here is shown in Figure 3.2. A 100 mm single crystal silicon wafer is coated with >30 nm of aluminum oxide (alumina or Al₂O₃) using a Denton Vacuum e-beam evaporator. The desired pattern is photolithographically defined on the alumina with AZ2020 photoresist. The resulting resist layer is approximately 1 μm thick with 5 μm diameter holes in a square packing pattern at a 10 μm pitch (see Figure 3.3). 4 nm of iron catalyst is thermally evaporated onto the wafer with a Denton thermal evaporator. The photoresist and unwanted iron is removed via liftoff by sonicating the wafer in NMP (N-methyl-2-pyrroldione), rinsing with acetone, rinsing with IPA, and drying with lab nitrogen.
A 30 s, 200 W oxygen plasma de-scum (Technics Planar Etch II) removes residual organics, including photoresist. The wafer is spin-coated with AZ3330 and soft-baked to protect the patterned iron features during dicing. The wafer is diced, using a Disco Dad 320 Automatic Dicing Saw, into 2 cm × 2 cm chips to fit the 1” Lindberg Blue M tube furnace where CNT growth is performed via thermal chemical vapor deposition (CVD). The protective photoresist is removed by rinsing with acetone, rinsing with IPA, and drying with lab nitrogen. Growth 1 occurs at 750 °C with an ethylene (C₂H₄ at 233 sccm) carbon source and hydrogen (H₂ at 230 sccm) carrier gas. VACNTs grow, with base growth mode [43], as defined by the catalyst pattern to a height determined by the growth time (see Figure 3.4). In this work, the target height is approximately 12 µm, typically achieved with 8 seconds of growth.
Figure 3.2: Process for fabricating carbon nanotube based needles. (1) Begin with a silicon wafer coated in >30 nm of alumina. (2) Define needle geometry lithographically. (3) Deposit iron catalyst. (4) Remove photoresist and unwanted catalyst by lift-off. (5) Grow carbon nanotubes by thermal CVD (6) Etch away top surface where CNTs are strongly bound together (7) Condense IPA onto the CNT structures (8) As the IPA dries the CNT needles collapse (9) Deposit a blanket coating of iron catalyst (10) Second CNT growth between and under the original needles (11) Infiltrate the entire structure with CVD carbon

The exposed VACNT pillar array surfaces are etched by oxygen plasma using a Technics Planar Etch II for 22 s at 200 W with 10 sccm oxygen flow at $4 \times 10^{-4}$ bar. The etch removes the intertwined CNTs on the top of each pillar (see Figures 3.5 and 3.6), which is crucial to creating lance points by capillary forming in a subsequent step. The plasma etch also results in a slight pillar diameter reduction because the CNTs are also etched from the sides but the top etches at a faster rate. While the O$_2$ plasma etching is only used to alter the physical structure of the pillars, it is recognized that this type of etch has been shown to alter the surface chemistry of the individual CNTs, making the CNTs more hydrophilic [25].
Figure 3.3: Needle packing pattern and spacing. Needles patterned in a square array to be 5 µm in diameter with a 10 µm pitch.

The etched VACNT pillars are collapsed into a denser needle shape using capillary forming. The sample is inverted and suspended 13 mm over IPA, heated to 44 °C, for approximately 3 seconds. When the chips are removed, the IPA that condensed on the structure dries and capillary forces pull the VACNTs together in tight bundles as shown in Figures 3.7 and 3.8. A second 4 nm layer of iron is thermally evaporated onto the entire chip which is placed back into the growth furnace for a second CNT growth step.

Growth 2 is typically 6 seconds using the same conditions as growth 1 and results in a short, blanket forest underneath the collapsed needles. This is possible because CNTs grow from the both the second blanket of catalyst and the original catalyst beneath the collapsed CNT needles (see Figure 3.9). After growth 2, the furnace temperature is raised to 900 °C to coat and infiltrate the entire sample with CVD carbon for 5 minutes using the same ethylene as during growth (233 sccm) and doubling the hydrogen flow rate (460 sccm). The infiltration step strengthens the bonds between CNTs and between the CNT forest and the substrate. The resulting structure, shown in Figure 3.10, is a CNT-M based needle array. Capillary forming, oxygen plasma etching, and regrowth are discussed in detail below.
3.2.1 Capillary Forming

An ideal single CNT lance should be 1 µm in diameter and 10 µm tall. Moulten et al. [35] showed that high aspect-ratio VACNTs tend to tip or curl. Growing a 1 µm pillar to the desired height with this process is likely to result in non-straight pillars. If that challenge were overcome with careful control of the catalyst and growth conditions, the needles still need to have a sharp tip to ease injection. Capillary forming with CNTs, as described by Volder and Tawfick [17, 31], involves
wetting a VACNT structure with a liquid, typically a fast drying solvent, and allowing it to dry. As the liquid dries the capillary forces draw the CNTs together.

Successful capillary forming in this work is performed by evaporating IPA at 44 °C and allowing it to condense on the inverted chip held approximately 13 mm above the IPA surface. Condensation time is critical because the amount of fluid involved in capillary forming becomes increasingly important as the size of the CNT structures decreases. Initial attempts to form needles from VACNT pillars failed fantastically. For example, the structures in Figure 3.11 were suspended over the IPA for too long and the pillars typically fell over or bundled with neighboring features.
Too little time over the IPA resulted in no noticeable change in the structure. Successful densification results in CNT pillars that show a significant reduction in diameter, remain upright, and show a characteristic tree root structure at the base, see Figure 3.12. For these CNT features and IPA evaporation setup, 3 seconds results in correctly formed CNT needles. However, capillary forming alone fails to produce the desired tip characteristic of needles. Figure 3.13 shows a plume at the top where the pillar fails to collapse because of the orientation and interaction of the topmost CNTs.
3.2.2 Oxygen Plasma Etching

Individual CNTs can grow at vastly different rates based on the catalyst particle size [44]. During initial stages of growth the CNTs grow in somewhat random directions until they hit another nanotube and lock together. Once all of the nanotubes meet another they create an interlocking mesh that stays at the top of the CNT forest. From that point on, the CNT forest as a whole grows at some average rate. SEM data, see Figure 3.14, shows that some CNTs in the forest are growing faster than others.
Because the CNTs interlock, the tips of the pillars resist collapse and result in a structure like that shown in Figure 3.13, where the pillar collapsed but has a plume at the tip. To avoid the plume, the CNTs are etched in an 200 W oxygen plasma for 90 seconds prior to capillary forming. The VACNTs, post-etch, demonstrate a scattering of needle-like points as shown in Figures 3.5 and 3.6. The spots where the needle points form are likely higher density than the surrounding region and therefore etch slower, though this deserves further investigation to understand the etching mechanism. The needle points are more pronounced in a larger area of CNT forest as shown in Figures 3.15 and 3.16.

Figure 3.8: Tip of CNT pillar after capillary forming with IPA
Figure 3.9: Base of CNT lances after growth 2. The original catalyst under the needles tends to grow faster than the surrounding forest.

Beyond removing the top, tangled surface of the CNTs, the plasma etch will reduce the height and diameter of the CNT pillar. The ability to shorten the nanotubes is helpful given the difficulty in growing 12 µm tall nanotubes consistently. The CVD furnace used to synthesize CNTs in this work is designed for growing much taller forests with a tolerance on the order of 10 µm. CNTs that are too tall can be etched to a more appropriate height. Also, the diameter of the pillars is reduced during etching. Since the CNT pillars were already lithographically patterned to be larger than the final diameter, this reduction in diameter is not unfavorable. In fact, it helps result
in a lance closer to the intended diameter. Using a more directional oxygen plasma should reduce sidewall etching if desired. Pairing an oxygen plasma etch with the appropriate capillary forming parameters enables the repeatable creation of densified CNT lances. However, the lances at this stage show poor adhesion to the substrate and proved unsuitable for nanoinjection as shown in Figure 3.17.
3.2.3 Adhesion and Regrowth

For the CNT needles to be a viable nanoinjection array they must be robust enough to be handled and used for injection into cells. CNTs are among the strongest materials known [45], but the CNT lances are not well adhered to the substrate and are easily knocked off. Titanium is a known adhesion promoter [46] but adding titanium between the alumina and iron resulted in fuzzy, poorly defined growth as seen in Figure 3.18. In addition to the poorly aligned CNTs not being well suited for needle creation via capillary forming, the titanium showed no adhesion advantages as the CNT arrays experienced capillary forming issues like those shown in Figure 3.11. Carbon infiltration was attempted as a means of bonding the needles more strongly to the substrate, but
the tens-of-nanometers thick carbon layer was insufficient to prevent needles from being knocked off during the nanoinjection process.

The catalyst for CNT growth can be reused [37] and Figure 3.19 clearly demonstrates a catalyst being used to create multiple layers of CNTs. It was decided to attempt to coat the entire chip, underneath the needles, with a CNT forest that provides more bond sites between the CNT structure and the silicon chip. Carbon coating strengthens the connection between the CNTs and the substrate at each of the bond sites and improves the overall adhesion. Improved adhesion is due to the much larger surface area contacting the substrate compared to only the CNT needles. The
original catalyst underneath the CNT needles was regrown and additional catalyst was deposited between the needles to create a continuous CNT forest between the needles and the substrate as shown in Figures 3.20 and 3.9. While the first and second catalyst layers were both the same thickness, the regrown catalyst grows faster than the second catalyst film. The double hydrogen used during carbon infiltration is critical here because without increasing the hydrogen flow the intrinsic stress in the continuous CNT structure causes it to curl away from the silicon substrate, resulting in self-delamination. The higher hydrogen flow rate reduces the stress in the structure,
allowing it to rest flat against the substrate so the base of the CNTs can be anchor points to the substrate.

3.2.4 Nanoinjection

The CNT-M lance arrays are compared to the silicon lances and evaluated based on performance in nanoinjection testing involving passive diffusion of propidium iodide (PI). PI diffusion
Figure 3.15: CNT forest before oxygen plasma etch.

does not involve the voltage bias that DNA injection does, but provides a method for initially testing injection techniques and materials. Hela 229 cancer cells are incubated at 37 °C with 5.0% CO₂ in Dulbecco’s Modified Eagle Medium (DMEM) with 10% fetal bovine serum (FBS) and gentamicin. Prior to nanoinjection, approximately $2 \times 10^5$ cells are placed in each well of six-well flat-bottom culture plates on top of a glass microscope cover slip with 3 mL DMEM and cultured for approximately 24 hours in an incubator. The cells adhere well to the glass cover slip and the glass is flater than the bottom of the injection molded well which is critical to uniform nanoinjection of all cells with the lance array. After 24 hours of incubation, the DMEM is removed and the cells are rinsed with Hanks balance saline solution (HBSS) and HBSS is added to each well. 0.04 mg of PI per 1 mL HBSS are also added to each well.
The lance array chip is attached to a specialized, 3D-printed, orthoplanar spring device for nanoinjection. The device keeps the lance array parallel to the glass cover slip and maintains approximately 30 N of force during injection. The cell membrane is perforated by lancing the cells with the needle array for 5 seconds. The PI and HBSS is removed from each well and trypsin is added before the wells are placed in the incubator to speed the release of cells adhered to the glass cover slip. Once the cells release from the glass, 1 mL of of DMEM is added to each well to deactivate the trypsin. The solution from each well is placed in fluorescence activated cell sorting (FACS) tubes which are centrifuged at 2000 rpm for 10 minutes. The supernatant is removed and the cells resuspended in the remaining media. An additional 0.25 mL of HBSS is added to each FACS tube and the tubes kept on ice for up to an hour awaiting analysis.
Both negative and positive controls are prepared. The negative control, which gives a baseline for cell viability, is prepared identically except no PI is added to the HBSS in the well and no injection is performed. The positive control, which gives a baseline of PI uptake, does include PI in the HBSS but no injection is performed. Nanoinjection success is evaluated using trait expression and cell viability as measured by flow cytometry using standard cytometric techniques [47–49]. Ten thousand particles or “events” are analyzed from each FACS tube. Forward scatter (FSC-A) measures particle size and side scatter (SSC-A) determines complexity. These values are plotted and appropriate gates drawn to classify each particle as live, dead, or debris (see Figure 3.21). Complexity is used to identify debris and size classifies each cell as live or dead. Different experiments will have different gate values. To compare experiments all cell viability data is normalized.
Figure 3.18: Fuzzy CNT pillars grown with a titanium layer between the alumina diffusion barrier and iron catalyst.

into a indicator using Equation 3.1. To compare the amount of PI expression between experiments the data is normalized into a indicator using Equation 3.2.

\[
\text{Normalized Viability} = \frac{\left( \frac{\text{Live cells in sample well}}{\text{Total cells in sample well}} \right)}{\left( \frac{\text{Live cells in negative control well}}{\text{Total cells in negative control well}} \right)} \tag{3.1}
\]

\[
\text{Normalized PI Expression} = \frac{\left( \frac{\text{Live PI+ cells in sample well}}{\text{Live cells in sample well}} \right)}{\left( \frac{\text{Live PI+ cells in positive control well}}{\text{Live cells in positive control well}} \right)} \tag{3.2}
\]
Figure 3.19: CNT forest grown in multiple steps. Growth was performed six times with a waiting period in argon between each growth. Each growth stage is clearly distinguishable and separated by dark horizontal lines in the CNT forest.

3.3 Results and Discussion

CNT-M based needles need to have properties that are comparable to or better than the silicon lances in one or more categories (cost, biocompatibility, robustness, and efficacy) to be a viable replacement. CNT-M and silicon process both use lithography and the associated equipment. Silicon lances additionally require specialized equipment for DRIE. CNT-M requires an e-beam evaporator and CVD furnace. At the same scale of production CNT-M appears to be the less expensive option. However, at the time of this work, there is no large scale fabrication facility dedicated to CNT-M, while silicon is the MEMS industry standard.

Table 3.1 provides a summary of the cell viability and PI expression results. Data indicates that, with regard to cell viability, the CNT-M and silicon lance arrays perform equally well. In this
work, no specific test for biocompatibility is performed. While the published literature is replete with conflicting reports on the cytotoxicity of CNTs [50, 51], cell viability results indicate that the CNT-M lance array used in this work is no less biocompatible than the silicon version.

The CNT-M lance array did show signs of wear after repeated use on the outer edge where the chip is handled. However, the center region, actually used for injecting cells, appeared to be in good condition, with lances still intact and usable, after more than 20 injections. The robustness of
Figure 3.21: Passive diffusion of PI negative control flow cytometry. Data is gated to identify live cells, dead cells, and debris. Levels for quantifying cells as PI positive are identified.

Table 3.1: Nanoinjection results summary comparing CNT-M to silicon. Values are calculated using Equations 3.1 and 3.2.

<table>
<thead>
<tr>
<th></th>
<th>Silicon</th>
<th>CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell Viability</td>
<td>0.93</td>
<td>0.94</td>
</tr>
<tr>
<td>PI Expression</td>
<td>2.54</td>
<td>3.07</td>
</tr>
<tr>
<td>Durability</td>
<td>Excellent</td>
<td>Good</td>
</tr>
</tbody>
</table>

the CNT-M lance array is sufficient for nanoinjection and compares well with the silicon lances. In terms of efficacy, these experiments suggest that the CNT-M based needles improve PI uptake compared to silicon. Overall, the CNT-M lance array performs equally or better than silicon in the categories of interest in PI injection experiments. However, DNA injections are sufficiently different that they should be performed before definitive conclusions are drawn, but the results here are promising.
3.4 Conclusion

This work has demonstrated an expanded definition of carbon nanotube templated microfabrication through the creation of an anchored CNT lance array that proved a viable substitute for silicon in nanoinjection. Oxygen plasma treatments were shown to modify the CNT structure and when used appropriately can greatly improve capillary forming. Capillary forming was demonstrated on CNT forests with lateral dimensions smaller than 10 µm. Regrowth was introduced as a method for creating unique, 3D CNT structures. The resulting CNT-M lance arrays showed comparable cell viability and a 20% increase in PI expression over its silicon counterpart in a side-by-side injection experiment.
CHAPTER 4. PROCESS DEVELOPMENT OF A MEMS FABRICATED, POROUS SILICA THERMAL BARRIER FILM USING A SACRIFICIAL CARBON NANOTUBE TEMPLATE

4.1 Introduction

Carbon nanotube templated microfabrication (CNT-M) is a novel and flexible technique to fabricate complex structures and composite materials by depositing a thin film material on the exposed surfaces of a porous CNT template [1, 26]. Materials with unique mechanical properties in micro- to milli-scale geometries can be made by infiltrating vertically aligned carbon nanotubes (VACNTs) with amorphous carbon [10, 27]. This same technology can produce cell restraints [10], electrodes, chemical sensors, and filters just by adapting the design of the template or the infiltration material. The novelty and importance of these studies is not to be overlooked, because while the theory of CNT-M is very simple, deposit material on a carbon nanotube template, its execution can present unique challenges: conformal deposition on the CNT template deep into the high aspect ratio pores, potential differences in the properties of the material deposited onto CNTs versus a standard silicon substrate, requirements on height uniformity, and stresses intrinsic to the CNT template.

This work demonstrates the successful adaption of the CNT-M technique to fabricate a, relatively, thick porous oxide film, see Figure 4.1, that exhibits low thermal conductivity and explores the challenges related to applying CNT-M. While natural materials exhibit low thermal conductivity, many of the materials put to use as insulators are engineered for the purpose. There are many strategies for engineering lower thermal conductivities, and doubtless many more unknown to this author, but three are of particular interest to this work: add dopants, add interfaces, and add porosity. Silica aerogels, for example, have a base material of silicon oxide (Si₂O₃) with a nominal thermal conductivity in the range of 1.4 W m⁻¹ K⁻¹, but with the addition of porosity and carbon...
doping (carbon opacification) [52, 53] the thermal conductivity drops by two orders of magnitude (0.014 WmK$^{-1}$). The thermal barrier manufactured by CNT-M in this work produces a silica structure that is inherently porous, carbon doped, and exhibits a thermal conductivity of 0.038 WmK$^{-1}$. The fabrication methods and resulting properties are presented below and followed by a discussion of process challenges and variations.

### 4.2 Process and properties

The fabrication of the thermal barrier, as with any CNT-M process, began with production of a CNT template which, in this case, was unpatterned and fabricated on a single crystal silicon substrate. The silicon wafer was coated with a 4 nm iron catalyst film on a 30 nm aluminum oxide diffusion barrier, see steps (1) through (3) in Figure 4.2. A vertically aligned carbon nanotube (VACNT) forest grown from any viable catalyst film stack will tend to exhibit high porosity and roughness on its top surface. During the initial stages of forest growth the CNTs are growing independently in different directions and at different rates. Once the closely packed CNTs find and interlock with each other the system begins to grow at an average rate as a “forest”. But by the
Figure 4.2: Diagram of fabrication process to produce a porous silica thermal barrier. (1) Start with silicon substrate. (2) E-beam deposition of 30 nm of aluminum oxide. (3) Deposit 4 nm of iron via thermal evaporation. (4) Deposition of CNTs onto the film stack via ultrasonic spraying of CNT/NMP solution. (5) CNT growth via thermal CVD at atmospheric pressure, resulting in a VACNT forest beneath the previously sprayed CNT layer. (6) Silicon deposition via LPCVD. (7) Thermal anneal at 900 °C in an oxygen rich atmosphere to convert the Si to SiO₂ and to burn out the carbon nanotube template.

time “forest” growth begins, the top surface of the CNT structure has already been defined by the initial, individual growth.

If all the CNTs in a forest can be mechanically linked together from the initiation of growth, the surface roughness can be significantly reduced. To this end, CNTs were sprayed on top of the catalyst film stack to form a smooth, gas permeable layer of interlocked nanotubes. This particular
method of mechanically linking CNTs during growth also served to reduce the porosity on the top surface, see Figure 4.3. The sample was then placed in an atmospheric pressure CVD furnace where VACNTs grew below the sprayed CNT layer, pushing them up, until the desired height (typically 100 µm) was reached. See steps (4) and (5) in Figure 4.2.

The completed CNT template was exposed to ozone at atmospheric pressure, which altered its surface chemistry to allow more nucleation sites for, and better adhesion with, the LPCVD silicon, see Figure 4.4. Silicon was deposited via low pressure chemical vapor deposition (LPCVD) for 20 min at 535 °C and $2.6 \times 10^{-4}$ bar using a silane (SiH₄) precursor, resulting in a 30 nm to 40 nm thick coating on the CNT template, see Figure 4.5. The silicon-coated CNT template was then annealed at 900 °C in an oxygen rich environment (lab air supply) which served to oxidize the silicon film and to burn out the internal carbon support [34]. These steps ((6) and (7) in Figure 4.2) result in the final CNT-M produced, porous thermal barrier film as shown in Figure 4.1. With particularly tall samples in this work, the burned-out silica structure exhibited wrinkling as shown in Figure 4.7. It is possible the taller samples received less silicon deposition at the base of the CNT forest, weakening the interface with the substrate. These wrinkled samples were still measured and
Figure 4.4: Comparison showing the effect of ozone priming on the nucleation and uniformity of the LPCVD silicon deposited on a CNT template. Notice the many isolated silicon beads when no ozone treatment is used.

Figure 4.5: Comparison of CNT template before and after silicon deposition.

the tallest point was taken as the layer thickness for calculating the thermal conductivity.

\footnote{See Figure 4.7}
Figure 4.6: Thermal conductivity results for the thermal barrier as a function of measurement power. The maximum uncertainty for measurements on all samples, except P24 and SGI, is 14.5%. P24 sample measurements had a maximum uncertainty of 24.4%, and SGI sample measurements had a maximum uncertainty of 79.1%.

With this process it was possible to produce a porous silica thermal barrier layer, around 100 µm thick, with a thermal conductivity of $2.5 \times 10^{-2} \text{ W m}^{-1}\text{K}^{-1}$ and a Young’s modulus in the range of 25 GPa as shown by sample P14 in Table 4.2 and measured in compression as described below. This sample had CNTs grown under sprayed CNTs, was ozonated, coated with LPCVD silicon, and oxidized for 360 min. Based on work regarding carbon opacification of silica aerogels, it was actually possible that silica structures with a higher carbon content (i.e. less burnout time) would exhibit lower thermal conductivity. To this end, samples were produced to be identical except that the burnout time would vary from 0 min to 360 min as shown in Table 4.1 and visualized in Figure 4.6. In addition to the silica coated templates, one of the samples (sample SGI, which stands for Spray, Grow, Infiltrate) was actually coated with carbon instead. The two extremes of thermal conductivity in Figure 4.6 are sample P14 ($2.5 \times 10^{-2} \text{ W m}^{-1}\text{K}^{-1}$) and sample SGI (10.0 $\text{ W m}^{-1}\text{K}^{-1}$), a lightly carbon infiltrated CNT template. The next highest thermal conductivity is from sample P24 (1.0 $\text{ W m}^{-1}\text{K}^{-1}$); showing that between samples P14 and P24 the thermal conductivity spans nearly two.
Table 4.1: Summary of parameters relevant to the interpretation of Figure 4.6. CVD Si refers to the time of LPCVD silicon deposition. Wrinkled samples exhibit large, wavy deformations as shown in Figure 4.7. All burnout was performed at 900 °C. “SGI” is a sample of CNTs that was grown below a sprayed layer of CNTs but was coated with 70 sec of CVD amorphous carbon rather than LPCVD silicon.

<table>
<thead>
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<th>Sample ID</th>
<th>Height (µm)</th>
<th>Burnout Time (min)</th>
<th>CVD Si (min)</th>
<th>Note</th>
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<tr>
<td>SGI</td>
<td>200</td>
<td>NA</td>
<td>NA</td>
<td></td>
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<tr>
<td>P10</td>
<td>57.9</td>
<td>360</td>
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<td>P11</td>
<td>92.5</td>
<td>360</td>
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<td>P22</td>
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<td>30</td>
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<td>124</td>
<td>NA</td>
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</tr>
</tbody>
</table>

Figure 4.7: Example of “wrinkled” thermal barriers. This likely influences the validity of the thermal barrier measurement. For these samples, the maximum height is taken as the representative height of the sample for the purpose of calculating the thermal conductivity of the film.

orders of magnitude using the same basic process. If one includes the SGI sample with its carbon infiltration, it is possible to tune the thermal conductivity across 3 orders of magnitude.
Figure 4.8: Thermal barrier samples with the same amount of silicon deposition (20 min) but with different amounts of burnout in an oxygen rich atmosphere. The samples are labeled with their name and the time spent in burnout.

Table 4.2: Summary of compression test results, particularly the estimated Young’s modulus of the material. The “Corrected” modulus was included due to a calibration issue with the mechanical testing setup. Measured slopes were multiplied by a factor that brought the silicon reference to expected modulus, additional details given in the mechanical testing methodology. With this correction the estimated Young’s modulus is roughly equivalent to silica with 65.2% porosity. Burnout was performed at 900°C. All samples, except the silicon reference, experienced 20 min of LPCVD silicon.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Burnout Time (min)</th>
<th>k (kN m⁻¹)</th>
<th>Height (um)</th>
<th>Young’s Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Calculated</td>
</tr>
<tr>
<td>P09</td>
<td>360</td>
<td>36.68</td>
<td>95</td>
<td>4.71E-05</td>
</tr>
<tr>
<td>P13</td>
<td>360</td>
<td>40.60</td>
<td>95</td>
<td>4.90E-05</td>
</tr>
<tr>
<td>P14</td>
<td>360</td>
<td>33.60</td>
<td>95</td>
<td>4.03E-05</td>
</tr>
<tr>
<td>P24</td>
<td>NA</td>
<td>38.65</td>
<td>135</td>
<td>6.68E-05</td>
</tr>
<tr>
<td>Silicon</td>
<td>NA</td>
<td>38.98</td>
<td>600</td>
<td>2.98E-04</td>
</tr>
</tbody>
</table>

The uncertainty of the thermal conductivity measurements was calculated from equation 4.9. Thermal barrier heights, \( h_b \), were measured via SEM with an error up to 5 \( \mu \)m. The measured laser power (incident, transmitted, and reflected) has a 5% uncertainty. The laser spot diameter, \( d \), has an uncertainty of 0.1 mm. The uncertainty in temperature comes primarily from the uncertainty in the assumed emissivity of the sprayed CNTs used in the thermal camera, resulting in a 3% uncertainty for temperatures. From this analysis, the maximum uncertainty for measurements on all samples, except P24 and SGI, is 14.5%. P24 sample measurements had a maximum uncertainty of 24.4%, and SGI sample measurements had a maximum uncertainty of 79.1%. The higher level of uncertainty for the P24 and SGI is likely due to the lower temperature differences.
that have a higher sensitivity to temperature errors. The majority of thermal conductivities fall between $3.0 \times 10^{-2} \frac{W}{mK}$ to $1.0 \times 10^{-1} \frac{W}{mK}$, which compares well with the values measured by Syme et. al. [54] ($5.4 \times 10^{-2} \frac{W}{mK}$ to $7.1 \times 10^{-2} \frac{W}{mK}$) on a nearly identical silica structure with a different method of thermal conductivity measurement. One notable difference in the structures used in Syme’s work is that no CNTs were sprayed onto the catalyst prior to CNT growth.

While LPCVD silicon deposition is reasonably uniform on the CNT forest, the conversion to SiO$_2$ can cause a volume change which, in turn, can result in cracking or deformation (e.g. Figure 4.7) [34]. Initially PECVD silicon oxide was considered for producing this thermal barrier, but that process is not well suited for deposition in high-aspect-ratio pores. PECVD silica could only penetrate about 15 µm into the CNT forest from any given side like the sample shown in Figure 4.9. Thermal barriers produced with PECVD had to be under 10 µm tall to have sufficient silica at the base for a robust interface with the substrate. Future development should focus on highly conformal techniques, like ALD, to get a thin silica layer directly onto a tall CNT template. Starting with silica also has the advantage of reducing the burn out temperature of the CNTs to around 500 °C because the silicon doesn’t need to be oxidized.

### 4.3 Methodology

This section details the processes and protocols associated with the production and characterization of the CNT-M structures described above.

#### 4.3.1 CNT catalyst preparation

30 nm of aluminum oxide was deposited in a Denton Vacuum electron beam evaporator at $7.3 \times 10^{-8}$ bar with a rate of 0.4 nm s$^{-1}$ from a graphite crucible. The 4 nm thick iron catalyst film was deposited via thermal evaporation from an alumina coated tungsten basket heater at $3.8 \times 10^{-8}$ bar. The prepared wafer was coated in a protective layer of AZ 3312 photoresist, soft baked on a hotplate at 110 °C for 60 s, and diced into 1.5 cm squares with a Disco Dad 320 Automatic Dicing Saw before the resist was stripped with acetone and IPA.
4.3.2 CNT spraying

Prior to spraying, CNTs were first prepared in a solution compatible with an ultrasonic sprayer and syringe pump. 11 mg of powdered multi-walled carbon nanotubes (SigmaAldrich CAS Number:308068-56-6) were added to 80 mL of NMP (N-Methyl-2-pyrrolidone, CAS number: 872-50-4) in a glass beaker. The MWCNTs were dispersed in the NMP using a 500 W ultrasonic processor for 20 min. The dispersed CNTs were centrifuged in a Sorvall RC-5C Plus
centrifuge with a SS-34 rotor at 4 °C for 1 h at 1200 rpm. The centrifuged solution was decanted into polypropylene vials for storage prior to ultrasonic spraying. The CNT spray system used a syringe pump to feed the CNT solution into the ultrasonic spray head which was mounted on a motorized, computer controlled xy stage above a hotplate on a z stage. The CNT solution was pumped to the ultrasonic head which sprays out onto the hotplate. The ultrasonic head settings and its height above the hotplate determined the area sprayed in a single pass. The hotplate (230 °C) heated the sample to quickly evaporate any solvent (NMP) but leave the CNTs intact on the surface. Without the hotplate, surface tension played a larger role during the evaporation of the NMP, resulting in rings of sprayed CNTs rather than a uniform coating.

For this system the standard spray pattern used a series of back and forth passes where the pass length, inter-pass spacing, and speed were user defined. To ensure a uniform coating the spray program was designed to avoid the spray resting on a region of interest, such as when the spray head was changing directions or at the end of each cycle. An example scanning pattern for the ultrasonic spray head is shown in Figure 4.10. The spray head moved at a rate of 1000 steps s⁻¹, and was placed 25 mm above the sample surface. The CNT solution was fed into the ultrasonic spray head at a rate of 0.25 mL/min using a syringe pump. The thickness of the sprayed CNT layer was controlled by setting the number of rasters for the program, set to 100 rasters for this work.

### 4.3.3 CNT Growth

Vertically aligned CNTs were grown from the iron-alumina film stack at 750 °C in an atmospheric pressure, 25 mm, quartz tube furnace (Lindberg Blue M™, 1200 °C) with a 30 cm heated zone. Samples were positioned 15 cm into the heated zone on a rectangular quartz tray such that the samples were centered vertically in the tube. During the temperature ramp from room temperature to growth temperature 230 sccm of hydrogen was flowing to reduce the iron thin film, allowing the catalyst nanoparticles to form. At growth temperature 250 sccm of ethylene gas flow was added and held until the desired growth height was reached, typically around 100 µm. The hydrogen and ethylene flow was then replaced by 220 sccm of argon flow and held for 2 min to purge the reactor.
Figure 4.10: Example scanning program where the ultrasonic spray head follows the path laid out. Special care is take to avoid the spray head resting over the sample at the end of each pass to maintain uniformity of coating.

before turning off the heaters to allow the furnace to cool back to room temperature for sample removal. This process corresponds to step (5) in Figure 4.2.

4.3.4 LPCVD silicon deposition and oxidation

Prior to silicon deposition, the surface of the CNT template was exposed to ozone for 60 min generated by an Atlas 30 Ozone Generator being fed 6.7 sccm of oxygen at 20 psi and with the current set to 45 %. The ozonation served to improve the conformality of the silicon coating by increasing the number of sites on the CNTs available for nucleation. Silicon was deposited for 20 min at 535 °C and $2.6 \times 10^{-4}$ bar in a 100 mm diameter, low pressure chemical vapor deposition (LPCVD) furnace using a silane (SiH₄) precursor, resulting in a 30 nm to 40 nm thick coating on the CNT template, see Figure 4.5. The silicon-coated CNT template was then annealed at 900 °C in an oxygen rich (lab air supply) environment for 360 min.
4.3.5 PECVD silicon oxide deposition

Plasma enhanced chemical vapor deposition can be used to deposit silicon oxide directly onto a CNT template, thus bypassing the need for oxidizing deposited silicon. The caveats include low penetration depth and a large thickness gradient from the inner structure to the surface. In this study, silicon oxide films were deposited in a PlasmaLab Model DP800 PECVD system at 250°C and $8 \times 10^{-4}$ bar while flowing 10 sccm of silane ($\text{SiH}_4$) presursor and 14.5 sccm of nitrous oxide ($\text{N}_2\text{O}$). The plasma system is capacitively coupled and uses a 13.56 MHz RF source capable of up to 650 W, though silica films are deposited using 22 W. Prior to silica deposition on the desired substrate, the chamber is seasoned for 12 min and a 2 min test run is performed to verify the deposition rate (typically in the range of 30 nm/min to 40 nm/min). The chamber is purged with nitrogen before and after deposition and cleaned after process completion using 30 sccm of tetraflouro methane ($\text{CF}_4$) at $8 \times 10^{-4}$ bar and 22 W RF. The heaters are shut off during the cleaning stage though the chamber can still reach 280°C from the plasma alone. The nominal thickness for PECVD silica films deposited on VACNT structures is usually targeted as 400 nm in attempts to get at least a few nanometers of material on the internal structure of the CNT forest.

4.3.6 APCVD carbon infiltration

Sample SGI was prepared by depositing carbon onto the CNT template rather than silicon. This carbon infiltration took place in the same atmospheric pressure CVD furnace that was used for CNT growth. In fact, for carbon infiltration, the sample was left in the furnace after CNT growth while the temperature and gases were adjusted to produce an amorphous CVD carbon instead of CNTs. Carbon infiltration took place at 900°C while flowing 563 sccm of hydrogen and 250 sccm of ethylene for 70 s. After which the flammable gases were replaced with 220 sccm of argon flow and held for 2 min at temperature to purge the reactor before turning off the heaters to allow the furnace to cool back to room temperature.

4.3.7 Thermal conductivity measurements and calculations

To test the thermal conductivity of the thermal barrier the sample was thermally pasted to a large steel mass to act as a constant temperature heat sink while a laser was used to provide energy
to the top surface of the film and a thermal camera measured the temperature. To catch all of the energy of the laser at the top surface, additional CNTs were sprayed onto the top of the finished porous silica structure. For the purposes of the thermal camera, the emissivity of the sprayed CNTs was assumed to be 0.95 [55,56] and an unheated surface spray coated with CNTs was used to measure the reference temperature of the steel mass. A glass slide was sprayed with CNTs at the same time as the samples to act as a reference for the laser power reflected by and transmitted through the sprayed CNTs. The transmitted and reflected power was recorded at each power level and is shown in Figure 4.11. Transmitted power was measured by placing a power meter behind the CNT coated glass slide with the laser perpendicular to the surface. Reflected power was measured by placing the power meter 90° to the laser with the sprayed CNT glass slide at 45° to the laser and power meter. With these levels measured, the actual power contributing to the temperature on the sample was calculated.

To isolate the thermal conductivity of the thermal barrier, the thermal conductivity of the substrate (600 µm silicon wafer, 30 nm alumina, 4 nm iron) had to be measured and subtracted from the thermal resistance path. CNTs were sprayed onto the substrate and the temperature drop across the substrate with a given laser power and spot size was measured again via thermal camera. A diagram of the test apparatus is given in Figure 4.12. From the thermal resistance diagram the thermal barrier can be isolated, resulting in equation 4.7 to represent it’s thermal conductivity, where $h_b$ is the height of the thermal barrier, $q$ is the power per unit area, and $T_1$ and $T_2$ are the temperatures at the base and top of the thermal barrier respectively.

4.3.8 Mechanical Testing

The mechanical stiffness of the thermal barrier materials was measured by compression using a 3300 Series Instron Universal Testing System fitted with a 5 N Futek load cell, see Figure 4.13. The end effector attached to the load cell was a 10 mm diameter circle and the thermal barrier, still attached to the silicon substrate, was supported by an xy stage. The test was displacement controlled and the head descended at a rate of 60 µm/min until a maximum load of 4 N triggered the end of the test. In addition to the various thermal barriers, a bare silicon wafer was
Figure 4.11: Percent of power transmitted and reflected at a given incident laser power. These levels were used to get the true power absorbed by the sprayed CNTs. There is no clear trend in transmitted and reflected power versus the incident power. This may be due to non-uniformity in the sprayed layer of CNTs, or errors in positioning the sensor and laser.

tested. The data was cut between 10% to 100% of the maximum force to retain a linear region of the data. The stiffness of a material in compression is expressed in equation 4.10. The Young’s modulus can be calculated from the slope of the compression test using equation 4.11. Following these calculations yields the data presented in Table 4.2. The moduli calculated from these equations yields surprisingly low moduli, even for the silicon reference. It is believed that the load cell was miscallibrated at the time of these measurements. Due to the cost and time involved in reproducing samples it was desirable to salvage useful information from these measurements. A
bare silicon chip was tested at the same time as the thermal barrier samples. Knowing that the silicon wafer is expected to have a Young’s modulus around 179 GPa [57], a correction factor was determined by which the calculated modulus could be multiplied to bring the silicon reference sample to the correct modulus. Using the same correction factor for all samples resulted in the “Corrected” Young’s modulus given in table 4.2.

\[ R = \frac{\delta T}{q} \]  
\[ R_{tot} = R_s + R_b \]  
\[ R_b = R_{tot} - R_s \]  
\[ R_b = \frac{T_2 - T_{ref}}{q} - \frac{T_1 - T_{ref}}{q} \]  
\[ R_b = \frac{T_2 - T_1}{q} \]  
\[ k = \frac{h_b}{R_b} \]  
\[ k = \frac{h_b q}{(T_2 - T_1)} \]  
\[ k = \frac{h_b P}{A(T_2 - T_1)} \]  
\[ k = \frac{4h_b(P_{tot} - P_{reflected} - P_{transmitted})}{\pi d^2(T_2 - T_1)} \]  
\[ k = \frac{P}{\delta} = \frac{AE}{h} \]  
\[ E = \frac{kh}{A} \]
Figure 4.12: Diagram of the thermal resistance path during testing using a 532 nm laser as the input power to the system. $R_b$ is the resistance of the thermal barrier, $R_s$ is the combined resistance of the silicon substrate plus the alumina and iron thin films. $T_{ref}$ is the temperature of the large steel mass acting as the heatsink for the system. $T_1$ and $T_2$ are the temperatures at the base and top of the thermal barrier respectively. $h_s$ and $h_b$ are the heights of the thermal barrier and substrate respectively. And $d$ is the diameter of the laser spot.

### 4.3.9 Raman Spectra

Raman spectroscopy is a technique that uses single wavelength laser sources to get a response (Raman shift in cm$^{-1}$) that can provide a fingerprint of the material. Raman is one of the commonly used method to rapidly analyze the unique fingerprint of carbon structures. In this study, a Renishaw Qontor Confocal Raman microscope was used to characterize the porous films that had undergone different amounts of burnout with the objective of seeing a transition where the carbon structure is no longer visible in the Raman spectra. The resulting spectra are seen in Figure 4.14 and show the carbon peaks disappear with as little as 30 min of burnout. It is possible that there is some portion of carbon, not seen in the Raman spectra, that has incorporated with the silica structure.
4.4 Conclusions

This work has demonstrated an interesting and unique application of carbon nanotube templated microfabrication to produce a porous silica layer with promising properties. The thermal barrier does have a rather low thermal conductivity despite not being at the level of bulk aerogels, and despite its porosity the surface is smooth and dense enough that deposition of patterned thin films on its surface is feasible. A surprising result is that within the same basic process, it is possible to create a structure whose thermal conductivity can be tuned across three orders of magnitude: $2.5 \times 10^{-2} \frac{W}{mK}$ for a purely silica structure, $1.0 \frac{W}{mK}$ for a CNT forest coated in silicon, and $10.0 \frac{W}{mK}$ for a lightly carbon infiltrated CNT forest. The high level of tunability within the structure is based on how much of the CNT template is left in the final structure and which material is used to coat the CNT template. A core aspect of most CNT-M processes is that the CNT
Figure 4.14: Raman spectra of the thermal barrier samples that experienced different levels of burnout. Carbon peaks around $1343 \text{ cm}^{-1}$ (D peak) and $1566 \text{ cm}^{-1}$ (G peak) are visible in sample P24 (0 min of burnout). These peaks disappear with as little as 30 min of burnout in an oxygen rich atmosphere.

template is part of the final structure. In pursuing new applications this inclusion has to be planned for, or the consequences of excising the template (high temperature anneal in oxygen and potential carbon doping) will have to be accepted. A critical challenge in the thermal barrier and almost all CNT-M processes is that of conformally coating the template. Materials will naturally deposit differently on a CNT forest than on other planar substrates due to surface chemistry, morphology, and aspect ratios. Understanding how existing thin films interact with the CNTs and how to control that interface will widen the range of material engineering that can be employed using CNT-M.
CHAPTER 5. POROSITY MAPPING IN CARBON INFILTRATED CARBON NANOTUBE FOREST STRUCTURES

5.1 Introduction

In a mechanical watch, the spring-mass (hairspring and balance wheel) system defines the frequency at which the watch operates. Traditionally, hairsprings have been metallic, with new alloys developed to improve performance [58, 59]. More recently hairsprings have been cut from single crystal silicon using deep reactive ion etching (DRIE). A third option, recently launched by the TAG Heuer Institute, is a carbon-carbon (C-C) composite fabricated with carbon infiltrated carbon nanotubes (CI-CNTs). The performance of a hairspring is a combination of its material properties and form. Vertically aligned carbon nanotubes, used as the CNT template, can be lithographically defined, allowing for precise control of the geometry. Additionally, the material properties are transversely isotropic perpendicular to the vertical orientation of the carbon nanotubes, meaning that the form can be defined without special consideration to the orientation of particular features. This type of material has exhibited high strain (≈2.0 %) ideal for flexible mechanisms and has been reported with a maximum Young’s modulus of 11 GPa transverse to the CNTs [8,11,27,60]. This work will study a commercially produced CI-CNT structure that exhibits similar strain but with a maximum Young’s modulus around 26 GPa. Unfortunately, the specific process parameters for achieving these values cannot be disclosed, but the trends and behaviors observed in this study are expected to apply to similarly produced materials.

The very nature of the method of production, using horizontally packed, vertically aligned multiwalled CNTs (MWCNTs) as a template for thin film deposition, suggests that this material will contain some level of porosity. Prior studies on, and calculations of, the mechanical properties of CI-CNT structures have assumed a homogeneous, non-porous material in order to report the apparent, effective Young’s modulus most relevant to practical use [15,27,61]. However, this material
is a composite comprised of two forms of carbon (CNT and CVD carbon) in an inherently porous structure and it is hypothesized that the effective material properties are bounded by some rule of mixtures such as that shown in equation 5.1, where $E_{\text{eff}}$ is the effective Young’s modulus, $E_c$ is the Young’s modulus of the CVD carbon, $E_{\text{cnt f}}$ is the transverse Young’s modulus of a CNT forest occupying some portion of the volume $\varepsilon$, and $\varphi$ is the total porosity in the structure. It is proposed that data relating $E_{\text{eff}}$ to $\varphi$ can be used to determine $E_{\text{carbon}}$, $\varepsilon$, and $E_{\text{cnt f}}$. This work investigates the Young’s modulus and porosity of carbon infiltrated carbon nanotube structures produced with various heights, widths, and levels of porosity in an attempt to determine the properties of the underlying component materials. Presented below is the first in depth study correlating geometry and process parameters (specifically time) to the porosity of CI-CNT structures. Methods of analysis and their limitations are discussed.

$$E_{\text{eff}} = E_c (1 - \varphi - \varepsilon) + E_{\text{cnt f}}$$

(5.1)

### 5.2 Experiment

Intuitively the degree of porosity of the this type of structure should increase as the distance from the nearest outer edge increases, as depicted in Figure 5.1. It was expected that the outer edge of any CI-CNT structure, wide or tall, will exhibit the same porosity. And porosity will increase further into the structure, likely reaching a maximum beyond which there is no carbon deposition. It is also assumed that no material deposition is coming from the base of the CNT forest, where it is attached to the substrate. As the form and degree of porosity in the initial CNT forest is different when viewed from the top or sides, it is possible, or even likely, that the porosity gradient from the sides is different than from the top as depicted in (c) of Figure 5.1.

Samples were produced to vary the parameters most relevant to the porosity map hypothesis: carbon infiltration time, height, and width. The reference condition was 240 min of carbon infiltration on beams that were 200 µm tall and 62.5 µm wide. Infiltration time ranged from 10 min to 360 min, widths ranged from 20 µm to 400 µm, and heights ranged from 100 µm to 340 µm, determined via the duration of CNT growth step. Both CNT growth and carbon infiltration were performed in one of two (CVD1 or CVD2) custom, atmospheric CVD furnaces at the TAG Heuer
Figure 5.1: An example of an intuitive porosity profile in a carbon infiltrated CNT forest where lighter colors correspond to higher porosity. Wider structures are expected to have higher internal porosity as there is more area further from an outer surface as seen in (b). The shape of the porosity gradient may look more like (c) if the material penetrates the top surface more easily the sides. Here it is assumed that no mass diffusion originates from the base of the structure.

Institute. Both CVD furnaces were identical in geometry and used the same flow rates and process times. The growth catalyst was commercially produced, alumina supported thin film iron, and the pattern, including beam geometries tested, is shown in Figure 5.2.

Beams were mechanically removed from the silicon substrate with tweezers and tested via three point bending. The Young’s Modulus was calculated using equation 5.2, where $E$ is the Young’s modulus, $L$ is the span of the test or the engaged length of the beam, $I$ is the second moment of area assuming a solid rectangular cross section, and $k$ is the stiffness of the system, calculated as the slope of the linear region of the force-displacement curve, see Figure 5.19. The Young’s modulus results shown in Figure 5.14 describe CI-CNT beams produced using CVD1, and all other results, mechanical and porosity, were obtained using samples produced in CVD2. Porosity, centroid, and second moment of area values were calculated from binarized scanning electron microscopy (SEM) images acquired across cut and polished cross sections. Detailed descriptions
Figure 5.2: Pattern of the iron catalyst used in this study. Red bars indicate which samples were cross-sectioned for SEM imaging to study the impact of beam width. Teal bars indicate samples that were cross-sectioned to study the impact of time and height. Blue ovals are beam samples used for mechanical testing.

The results and calculations are given below.

\[ E_{eff} = k \frac{L^3}{48I} \]  

(5.2)

5.3 Results and Discussion

A method, shown in Figure 5.23, was developed to automatically identify and isolate pores in SEM images of cross-sectioned Cl-CNT materials, the assumption being that a well prepared cross-section will accurately represent the 3D porosity in the structure. The resulting binary im-

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age, depicting pores as white pixels, enabled the calculation of a variety of geometric properties including: porosity ($\varphi$), cross section centroid ($C$), and the second moment of area ($I$), with the last being critical to determining the correct Young’s modulus of the carbon material. Combining variables $k$, $L$, and the boundary condition constants into a single variable, $\eta$, that can be considered a known value for a given sample, the Young’s modulus is shown to be inversely proportional to $I$, see equation 5.4. This means that an overestimated second moment of area will result in an under-valued Young’s modulus. Taking the theoretical second moment of area for a given geometry, if the material is assumed to be homogeneously porous, the true second moment of area of the cross section will be equal to the theoretical value scaled by its solidity ($1 - \varphi$). In this case, the porosity alone could be used to calculate the correct $I_{corr}$ and Young’s modulus ($E_{corr}$) using equations 5.5 and 5.6 respectively.

$$E_{eff} = k \frac{L^3}{48I}$$  \hspace{1cm} (5.3)

$$E_{eff} = \eta \frac{1}{I}$$  \hspace{1cm} (5.4)

$$I_{corr} = I(1 - \varphi)$$  \hspace{1cm} (5.5)

$$E_{corr} = \eta \frac{1}{I_{corr}} = \eta \frac{1}{I(1 - \varphi)}$$  \hspace{1cm} (5.6)

5.3.1 Simple Model of Total Porosity

Consider a CNT forest to consist of square unit cells like those shown in Figure 5.3, where the forest can have unit cells of different sizes, $s$, and the radius of the CNT is $r_i$. Formalizing this simple hypothesis leads to equation 5.7 which describes the porosity in a given unit cell, where $r$ is the radius of solid material including the initial CNT ($r_i$) and $s$ is the size of the unit cell, and $A_c$ is the area occupied by material. If the rate of deposition, or film growth, is the same on all unit cells, then some cells will fill faster than others. Assuming that there is an equal number of cells of different sizes we can generate a plot for porosity versus time, as shown in Figure 5.4, where it was assumed there were five unit cell sizes: 0.5, 0.65, 0.8, 0.95, and 1.1. The radius of the
Figure 5.3: Diagram of hypothetical unit cell that describes the spacing between CNTs in a CNT forest, where \( r \) is the radius of solid material, including the initial CNT (\( r_i \)), and \( s \) is the size of the unit cell. This model assumes the entire unit cell can be filled and that all sizes of unit cells experience the same film growth rate.

Material was assumed to not exceed \( \sqrt{2} \). The average of all the porosities of the unit cells yields the “porosity sum” curve in Figure 5.4 which shows a sigmoid-like behavior and it is expected that the experimental porosity will behave similarly.

\[
\varphi = 1 - \frac{A_c}{s^2} \quad (5.7)
\]

\[
A_c = \begin{cases} 
\frac{\pi}{4} r^2 & r < s \\
\frac{\pi}{4} r^2 - \left( r^2 \arccos \left( \frac{s}{r} \right) - sr \sin \left( \arccos \left( \frac{s}{r} \right) \right) \right) & r > s \ 	ext{and} \ r < s\sqrt{2} \\
\frac{s^2}{2} & r \geq s\sqrt{2}
\end{cases} \quad (5.8)
\]

5.3.2 Total Porosity

For the carbon infiltrated carbon nanotube material it was predicted the porosity would be inhomogeneous, resulting in a centroid shift, and a more complex second moment of area correc-
Figure 5.4: Plot of porosity generated from simple square-packed unit cell porosity model. This model assumes a porous CNT forest consists of unit cells of various sizes and that all unit cells can be completely filled with material. The porosity in each unit cell size has an inflection point and by summing the equally weighted porosity across unit cell sizes the “porosity sum” curve emerges which shows a sigmoid like behavior.

Porosity as a function of carbon infiltration time, see Figure 5.6, is also plotted with Fit1, an arctangent function, a continuous function chosen to mimic the sigmoid behavior seen in Figure 5.4. The porosity of heavily infiltrated (greater than 210 min) CNT structures, in the range of 0.12-0.18, seem plausible values for completely infiltrated structures as they are bracketed by the porosities of uniform circles tightly packed in square ($1 - \frac{\pi}{4} = 0.21$) and hexagonal ($1 - \frac{\pi\sqrt{3}}{6} = 0.093$) arrays. However, VACNT array densities have been reported to range from

Porosity based on the porosity distribution. Figure 5.5 demonstrates a correlation between porosity and geometry, with taller samples exhibiting higher porosity. Note that the porosity for beams below a certain height threshold seem to remain constant. It is not clear from Figure 5.5 if porosity has any dependence on width. But when combined with the Young’s modulus versus width results, discussed below and shown in Figure 5.15, the data suggests that width is correlated with the porosity and Young’s modulus.
Figure 5.5: Porosity versus width is shown for samples less than 200 µm tall. Porosity versus height is shown for samples less than 80 µm wide. No data points overlap between the two graphs. All data depicted here is from samples infiltrated for 240 min.

$4 \times 10^9 \text{ cm}^{-2}$ to $1 \times 10^{13} \text{ cm}^{-2}$, with CNT diameters ranging from 1 nm to 40 nm [22, 62, 63]. Based on these values, the porosity of an as-grown CNT forest can range from 0.83 to 0.98, meaning a maximum porosity of 0.4 for a bare CNT forest, as measured in this study, does not match with published data. Figure 5.7 shows examples of porosity segmentation on samples with different carbon infiltration times where the pores are shown as a blue overlay on the original SEM image. It appears from these examples this method of porosity measurement fails for highly porous CI-CNT structures.

This failure is likely due to the difficulty in isolating the plane of particular CNTs from contrast alone when the depth difference of crossing CNTs is on the order tens of nanometers. This results in several planes of CNTs, or a single wavy CNT, being collapsed to a single plane for porosity determination, meaning the true, three-dimensional porosity of highly porous CNT structures is underestimated using this two-dimensional representation.

Using a Precisa balance HA 225SM-DR, $2.91 \times 10^{-2} \text{ cm}^3$ of highly infiltrated (240 min) CI-CNT beams were found to weigh $4.68 \times 10^{-2} \text{ g}$ for a density of $1.60(5) \text{ g/cm}^3$. Reported den-
Porosity versus carbon infiltration time appears to exhibit a sigmoid behavior. An arctangent function is fitted to the data, shown as Fit1. Assuming that porosity is underestimated for infiltration times below 240 min, and porosity at $t = 0$ is the porosity of a bare CNT forest, assumed here to be 0.95, Fit2 is proposed as a predictor of porosity. 5 µm square sections of the SEM images at each of the infiltration times tested are shown at the top of this figure. The blue overlay on the original image indicates regions identified as pores.

Densities of CVD carbon range from $1.7 \text{ g/cm}^3$ to $2.1 \text{ g/cm}^3$ [64], where the highest densities came from deliberate deposition parameter changes. The average porosity for CI-CNT material infiltrated for 240 min is 0.15 via pore segmentation of the SEM images. Comparing the measured density to the reported density of carbon materials the porosity of 240 min CI-CNTs falls between 0.06 to 0.24 depending on the true density of the CVD carbon. Taking the average porosity via pore segmentation as accurate would indicate a CVD carbon density of $1.88 \text{ g/cm}^3$. While not proof the extracted porosities at high infiltration times are accurate, the density measurements indicate that these values fall within the expected range.
Figure 5.7: Shown here are 5 µm x 5 µm tiles cropped from the center of SEM images acquired for samples with different carbon infiltration times: (a) 10 min, (b) 150 min, (c) 240 min, (d) 360 min. Regions identified as pores are overlaid with blue. It appears the porosity of highly porous structures (i.e., 10 min infiltration) is underestimated due to difficulties in differentiating the depth of overlapping CNTs.

If one assumes the porosity of highly infiltrated structures is accurate and defines the porosity of a bare CNT forest to fall within the range of published data, 0.95 is taken here, it is possible
to generate a speculative function of porosity versus time, shown as Fit2 in Figure 5.6. The arctangent function used for fitting is given as equation 5.9, where \( t \) is time, and \( c_1, c_2, c_3, \) and \( c_4 \) are fitting parameters. The coefficients corresponding to fits Fit1 and Fit2 are given in Table 5.1.

\[
E = c_1 \arctan\left( c_2 \left( t - c_3 \right) \right) + c_4 \tag{5.9}
\]

Table 5.1: Fitting coefficients for arctangent equation 5.9.

<table>
<thead>
<tr>
<th>Fit</th>
<th>( c_1 )</th>
<th>( c_2 )</th>
<th>( c_3 )</th>
<th>( c_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fit1</td>
<td>-0.29</td>
<td>3.5e-2</td>
<td>1.3e+2</td>
<td>5.55e-1</td>
</tr>
<tr>
<td>Fit2</td>
<td>-1.08e-1</td>
<td>1.72e-2</td>
<td>1.08e-2</td>
<td>2.79e-1</td>
</tr>
</tbody>
</table>

5.3.3 Porosity Profiles

To check the assumptions of porosity distribution depicted in Figure 5.1, line profiles of the porosity were taken across the binarized image. Eleven profiles were taken in the both x and y directions, evenly distributed across the height or width respectively. Every profile used a 20 µm wide band centered on the profile location (except for extreme edges where the band butted against the edge but still included a 20 µm wide region) and the porosity was averaged every 2.5 µm. Samples representing the baseline case in this study, see Figure 5.8, the tallest, see Figure 5.9, and widest, see Figure 5.10 were examined and each of these samples were infiltrated for 240 min. Additional, a sample similar in geometry to the baseline, but with 120 min of infiltrated was analyzed and presented in Figure 5.11. These four figures together represent the porosity profile of the baseline and some of the extremes in height, width, and time, and in each case the same general shape emerges.

There is a strong, nearly linear, trend of porosity increasing from top to bottom (1.0 to 0.0 in \( y' \)) and the trend seems to hold regardless of whether the data is taken at the edge or in the center of the sample. This is supported by the \( x' \) direction profiles as they show a near constant porosity across the width of the sample. The porosity in the \( x' \) direction does appear to have more variation
Figure 5.8: Visualization of the porosity ($\varphi$) taken as a line profile across different points of the sample cross-section. $x'$ and $y'$ represent the normalized axes of the sample cross-section. $x'$ direction profiles, shown in blue, are acquired at the locations of the blue lines overlaid on the SEM image thumbnail on the left. Each point was averaged over a 20 $\mu$m x 2.5 $\mu$m region, where 20 $\mu$m was a band bounding the profile line, and 2.5 $\mu$m was the step size in the profile direction. Sample details: 240 min of carbon infiltration, 208.5 $\mu$m tall, and 61.7 $\mu$m wide.

in the bottom portion of the structure where higher porosity dominates, but is to be expected as part of sampling a relatively small area in a high porosity region. There also appears to be a slight drop-off in porosity at the sides of the sample ($x' = 0.0$ and $x' = 1.0$) in the lower half of profiles ($y' < 0.6$). An interesting exception to this is the 120 min infiltrated sample which, despite much higher total porosity, has fairly smooth, near constant $x'$ direction profiles.
Clearly the predicted porosity distribution of Figure 5.1 is not an accurate picture of the porosity in these CI-CNT structures and the strong dependence on the height with near constant porosity across the width is a surprising result. If one considers that gas flowing horizontally through the CNT forest experiences less resistance and thus carbon deposition is not source limited,
Figure 5.10: Visualization of the porosity ($\phi$) taken as a line profile across different points of the sample cross-section. $x'$ and $y'$ represent the normalized axes of the sample cross-section. $x'$ direction profiles, shown in blue, are acquired at the locations of the blue lines overlaid on the SEM image thumbnail on the left. Each point was averaged over a 20 $\mu$m x 2.5 $\mu$m region, where 20 $\mu$m was a band bounding the profile line, and 2.5 $\mu$m was the step size in the profile direction. Sample details: 240 min of carbon infiltration, 151.8 $\mu$m tall, and 372.3 $\mu$m wide.
Figure 5.11: Visualization of the porosity ($\phi$) taken as a line profile across different points of the sample cross-section. $x'$ and $y'$ represent the normalized axes of the sample cross-section. $x'$ direction profiles, shown in blue, are acquired at the locations of the blue lines overlaid on the SEM image thumbnail on the left. Each point was averaged over a 20 $\mu$m x 2.5 $\mu$m region, where 20 $\mu$m was a band bounding the profile line, and 2.5 $\mu$m was the step size in the profile direction. Sample details: 120 min of carbon infiltration, 205.6 $\mu$m tall, and 63.3 $\mu$m wide.

It might explain the lack of a horizontal variation. However, in this scenario, the carbon structures, regardless of height, should show no vertical trend with porosity because the lateral diffusion of gases would dominate the deposition at a rate higher than that coming from the upper surface.

The author’s proposed explanation is that there is a temperature gradient from the base to the tip of the CNT forest, where the CNT tip is at a lower temperature. CNTs have excellent thermal conductance and a forest of CNT would have a high surface area. Assuming the process
tube, substrate, and CNT forest are all at steady state temperature, but that gases entering the system have not yet reached steady state, the CNT forest could be imagined as a heat fin, where the cooler process gases are conducting the heat away from the CNT forest. If the deposition of carbon is mass transport limited, as depositions in high-aspect-ratio porous structures might be, then a lower temperature can result in a higher deposition rate. This hypothesis does have weaknesses as typically higher temperatures yield higher film growth rates and it is unknown if the CNT forest actually has a temperature gradient during carbon infiltration. It could be that defectivity in the outer wall of the CNTs evolve during growth and CNTs with more defects are more favorable to deposition. This topic deserves more attention, and the shape of the porosity distribution should be confirmed on other CI-CNT structures produced with different reactors and process conditions.

5.3.4 Centroid

Looking at the centroid shift confirms some of what was seen in the porosity profiles. Shown in Figure 5.12 is the ratio of the calculated centroid (\(\bar{x}'\) and \(\bar{y}'\)) to the expected position in a rectangular cross section (\(\bar{x}\) and \(\bar{y}\)). Interestingly, \(\bar{x}'\) shows no dependence with \(\bar{y}'\) remaining around 1.0 for all measurements, indicating that any non-uniform mass distribution in the structure is symmetric about the y-plane. \(\bar{y}'\), on the other hand, shows a correlation with porosity, width, and height, but the total shift is small, up to 6% of the original centroid, or, in other words, a shift of up to 3% of the height. This again supports the findings from the porosity profiles, but generalizes it to all the samples measured.

\[
I_x = \frac{bh^3}{12} \tag{5.10}
\]

\[
I_{xc} = \frac{bh^3}{12} + Ad^2 \tag{5.11}
\]

\[
= \frac{bh^3}{12} + bh(h\bar{y}')^2 \tag{5.12}
\]

\[
= \frac{bh^3}{12} + bh^3 \left( \frac{h\bar{y}'}{2\bar{y}} \right)^2 \tag{5.13}
\]
Figure 5.12: Depiction of the centroid shift as a function of porosity, time, width, and height. Centroid shift is given as the ratio of the porosity extracted centroid to the expected center a rectangular cross section.

\[
\frac{I_{xc} - I_x}{I_x} = \frac{bh^3}{12^2} + \frac{bh^3}{4} \left( \frac{\bar{y}'}{\bar{y}} \right)^2 - \frac{bh^3}{12^2} \tag{5.14}
\]

\[
= \frac{bh^3}{4} \left( \frac{\bar{y}'}{\bar{y}} \right)^2 \quad \tag{5.15}
\]

\[
= 3 \left( \frac{\bar{y}'}{\bar{y}} \right)^2 \quad \tag{5.16}
\]
5.3.5 Second moment of area

Equation 5.16 shows the increase in \( I \) of a solid rectangular cross-section, using the parallel axis theorem, if the centroid is shifted by some percentage away from the geometric center. Given the maximum centroid shift of around 6\%, the upper bound of the second moment of area increase is 1.08\%. Instead, the ratio of the extracted second moment of area to its theoretical value \( (I'/I) \) exhibits a linear, one to one, relationship with porosity as shown in Figure 5.13. This is the relationship expected from a homogeneously porous structure, showing the total porosity of the structure, not the centroid shift, dominates the calculation of \( I' \). Despite not having a homogeneous mass distribution, it appears as though total porosity can still be used as a predictor of \( I' \) and, in theory, could be used to calculate the corrected modulus \( E_{corr} \).

5.3.6 Young’s Modulus

Results from 62.5 µm wide beams that were produced in CVD1 are shown in Figure 5.14, where Young’s modulus is plotted versus time. From the data the Young’s modulus appears to approach upper and lower limits, with a steep transition in the middle. This data was fit using an arctangent function, see equation 5.9, to demonstrate its sigmoid nature. Based on this fit the predicted Young’s modulus of the structure with no infiltration would be 0.74 GPa, which is in the range of modulus measured for CNT forests [65]. The upper limit of Young’s modulus, as \( t \to \infty \), is estimated as 27.05 GPa. Samples were produced with infiltration times less than 90 min, but the structures could not be removed from the substrate without fracturing the beams. Similarly, samples with infiltration times ranging from 10 min to 240 min were produced using CVD2 but only beams that were infiltrated for 110 min or longer could be removed and tested, see results in Figure 5.15.

The Young’s modulus data shown in Figure 5.15 might be exhibiting the same sigmoid behavior as Figure 5.14, but lacking more data at the upper and lower ends, it can’t be confirmed. However, it is clear wider beams exhibit a lower overall modulus, and thus a lower overall porosity at all infiltration times.
Figure 5.13: Depiction of the ratio of $I'/I$ as a function of porosity, time, width, and height.

Applying the theory that porosity could be used to extract the true modulus of the material without including pores, equation 5.6 was used to predict $E_{corr}$ from the data shown in Figure 5.14. Arctangent function 5.9, using Fit1 and Fit2 was applied as the porosity function to calculate $I_{corr}$. Applying these corrects yields the results given in Figure 5.16, where Fit1 does a poor job yielding a uniform extracted modulus, while Fit2 seems to bring most data in alignment with an average $E_{corr}$ of 30.2 GPa. This correction is based on assumptions as to the nature of porosity versus time, both at the limiting cases and in the overall shape. However, this does indicate some merit to the theory of determining the true modulus of the deposited carbon through an understanding of the
Figure 5.14: Depiction of Young’s modulus as a function of time for CVD1 produced samples. All samples depicted were grown to the same approximate height and had the same width.

porosity in the structure. For the moment, this correction is only valid for 62.5 µm beams produced in this reactor system because it calculates porosity as a function of time. Generalizing porosity as a function of height, width, and other deposition parameters could enable broader predictive power of the true Young’s modulus.

5.4 Methodology

5.4.1 Catalyst preparation

The catalyst film stack was comprised of a reactively sputtered iron thin film (10 nm) on 30 nm of sputtered aluminum oxide supported by 500 nm of thermal silicon oxide on 150 mm single crystal silicon substrates. The alumina and iron films were lithographically patterned via liftoff processes and diced into 13.26 mm x 14.86 mm chips with a diamond saw system. All catalyst preparation was performed externally at a commercial MEMS foundry.
Figure 5.15: Depiction of Young’s modulus as a function of time for CVD2 produced samples of different widths. All samples depicted were grown to the same approximate height.

5.4.2 CNT growth and Carbon Infiltration

Vertically aligned CNTs were grown and infiltrated with carbon in a custom, automated CVD system (CVD Equipment Carbon 150+) designed by the author. The system was designed to be capable of atmospheric pressure CVD processes using hydrocarbon precursors for substrates as large as 150 mm. The CVD system used a rectangular cross-section process tube in atmospheric mode with the samples positioned at the center of the process tube and in the middle of heated region (three zone heater) of the furnace. Temperature was controlled via thermocouples inside the
Figure 5.16: Plot of Young’s modulus (GPa) versus infiltration time (min), showing the original data and two corrected data sets. The goal of correction is to isolate the true Young’s modulus of the material without including the porosity. Shown in red is the corrected modulus using Fit1, which was fit directly to the porosity measurements. Show in green is the corrected modulus using Fit2, a theoretical arctangent fit where the porosity of the highly infiltrated samples is assumed correct and the porosity of a bare CNT forest is chosen to fall within a range given by literature. The theoretical Fit2 brings much of the data into alignment and indicates the true Young’s modulus of the CVD carbon is around 30.2 GPa.

furnace, just below the quartz tray that supported the samples. CNT growth and carbon infiltration follow the general process outlined in earlier chapters and previously published work [9–11, 27] where ethylene is used as the hydrocarbon precursor and hydrogen is used to inhibit or modify the rate of carbon deposition [66, 67]. The commercial nature of the process used by the TAG Heuer Institute prevents sharing the specific gas flows and ratios, but the general process is outlined below and shown in Figure 5.17.

Prepared chips are placed into the furnace and the temperature was ramped under inert gases to the growth temperature. At growth temperature (T₁) hydrogen is introduced for a specified time to allow the iron catalyst to form. Immediately after catalyst formation, ethylene is added and CNT growth continues until the desired height is achieved. In this study three growth times were used to produce samples of different heights: 10 min, 29 min, and 60 min. After growth, the
system was purged of reactants with an inert atmosphere before changing the temperature. The temperature was ramped to the higher infiltration temperature where ethylene and hydrogen were reintroduced (at different flow rates and ratios than for CNT growth) to begin carbon infiltration. The carbon infiltration times explored in this study were: 10 min, 30 min, 60 min, 90 min, 120 min, 150 min, 180 min, 210 min, 240 min, and 360 min. All samples in this study were produced using the same gas flow rates, gas ratios, temperatures, and temperature ramp rates. The only process conditions that varied were the CNT growth time and the carbon infiltration time and each of these were adjusted while holding all other process parameters constant.

Figure 5.17: Diagram and description of the CNT growth and carbon infiltration process in an atmospheric thermal CVD furnace. (A) Ramp temperature under inert gas flow until growth temperature $T_1$ is reached. (B) Catalyst formation under hydrogen atmosphere. (C) CNT growth for specified time at temperature $T_1$ with ethylene precursor and hydrogen. (D) Inert gas replaces flammables to purge and settle the system. (E) Ramp furnace under inert gas until carbon infiltration temperature $T_2$. (F) Ethylene and hydrogen are reintroduced for carbon infiltration at temperature $T_2$ for specified time. (G) Inert gas replaces flammables to purge and settle the system. (H) Heaters are turned off and the clamshell furnace is opened to cool the system. Samples are unloaded at temperatures below 200 °C.

5.4.3 Mechanical testing

Mechanical responses of the beam geometries were measured by three-point bending on an Instron 3342 tensile tester with a 10 N load cell (Instron 2519-10N). A custom fixture with a
fixed gap of 3 mm ($L_{gap}$ in Figure 5.18) and a probe tip diameter of 0.2 mm was used for all tests. Machined, vertical walls on each side of the test fixture align the beam sample perpendicular to the gap. Figure 5.18 shows the test fixture and its relevant dimensions. Mechanical tests were displacement controlled with a rate of 1.2 mm/min until sample failure.

Figure 5.18: Custom three point bending test fixture fitted onto an Instron table top tensile tester. P is the applied force, t is the thickness of the sample in the direction the load is applied, and $L_{gap}$ is the gap between the base supports of the fixture. This system uses a 10 N load cell and all tests were displacement controlled at a rate of 1200 μm/min.

The carbon-carbon material of interest is not expected to exhibit any plasticity based on previous work [27] and the nature of it’s components. However, some of the force displacement curves do show some non-linear behaviors as seen in the example profile given in Figure 5.19. It was suspected that this steady decrease in slope was the beam sliding along its base supports and increasing the engaged length of the beam, reducing the apparent stiffness of the system. To
confirm this theory, a finite element analysis model was built in ANSYS Workbench where a purely elastic material is assumed. The similarity between the data and ANSYS simulation shows that the non-linearity in the experimental force-displacement profile is likely due to changing boundary conditions over the course of the test. The stiffness of the any given structure is taken from the linear region of the force-displacement profile.

Figure 5.19: Comparison of measured the force-displacement profile of a rectangular carbon infiltrated carbon nanotube beam that that of an ANSYS simulation of the same beam. This particular beam was 3 mm, 62.5 µm wide, grown to 239 µm tall and was tested such that the CNTs were perpendicular to the direction the force was applied. The ANSYS simulation assumed purely elastic properties in the material, a 5 µm radius at the sample support, and no friction.

Due to the small dimensions of the samples used (widths from 62.5 µm to 200 µm and heights less than 400 µm) it was possible for beams to be tested in the wrong orientation. For this reason, the modulus was calculated using both Ix and Iy for every sample, though the intended orientation was always initially assumed to be correct. For samples that exhibited a modulus outside the normal distribution of a sample type, the alternate modulus, assuming it was actually tested in the wrong orientation, was checked. When this correction resulted in the sample rejoining
the grouping, it was accepted. If the difference was not large enough to be certain of the orientation, or if either value was an outlier, the original orientation was taken for calculations. All assumptions about the orientation of each sample were recorded.

5.4.4 Sample cross-sectioning

The carbon infiltrated carbon nanotube structures in this study exhibit a range of porosity and the methods for sample preparation were adapted based on the sample though the first step was to expose a cross-section of the material. Initially, for all specimens, samples were oriented and glued (cyanoacrylate) to a glass slide while being embedded in Struers ConduFast conductive resin (acryl with iron filler) using a Struers CitoPress 15 at 150°C and 250 bar for 3.5 min. The samples with a high degree of porosity (infiltration time less than 2 hr) were much more fragile and susceptible to damage during the resin embedding process. These samples were additionally covered in a small amount of the same glue prior to the resin as protection against the extreme pressure. It was found that the glue was actually impregnating highly porous samples (infiltration time less than 240 min) as shown in Figure 5.20, though it is not known whether this occurred while the glue was applied or during the high temperature, high pressure resin embedding process. These samples could not be used for porosity analysis, though the nearly linear diffusion profile of the glue into the side of the carbon supports the porosity profile data in that the porosity in these structures appears linearly from top to bottom.

Figure 5.20: Sample with 150 min of carbon infiltration and a variety of widths ranging from 20 µm to 400 µm that was first coated in glue prior to embedding in resin. The glue seeped into the porous structure either when the glue was applied or during the high temperature, high pressure resin embedding process. No glue contaminated samples were used for porosity calculations.
Due to glue contamination issues, samples were either held in place with carbon tape for resin embedding or the resin was skipped entirely and samples were ion cut with a Gatan PECS II system. In ion cutting, the sample was masked with a flat edge metal blade for a defined cutting surface. Specimens were mechanically polished with four steps of increasingly finer grained polishing pads using a Presi MECHATEC 250 at 150 rpm with force applied by hand. The samples were rinsed in an ultrasonic water bath between each polishing step. In each case, the final step was low energy (200 eV) argon ion surface polishing for 1 hour using a GATAN PECS II system, followed by 7 nm of chromium. The chromium was used to electrically samples to the embedded resin and to reduce edge effects and charging. Even samples that weren’t embedded in resin were coated in chromium to keep the surface consistent. It is not believed that 7 nm of material can fill enough pores of the sort found in a carbon infiltrated CNT forest to measurably impact the apparent porosity of the structure. The sample preparation methods described were chosen over focused ion beam (FIB) preparation primarily due the strong curtaining effect present when milling porous structures, though cost and time to FIB large structures was also a consideration. Curtaining effects occur when a portion of the material masks the material below during ion milling, causing a non-flat cross-section surface that looks like a hanging curtain, an example is given in Figure 5.21.

5.4.5 Electron microscopy

The electron micrographs were all acquired using a ThermoFisher Helios G4™ FIB-SEM in field-free mode at 2 keV and 0.4 nA with the directional back scatter (DBS) detector. The backscatter detector gave a better contrast between the sample and pores. All samples were imaged at a resolution of 6.51 nm px$^{-1}$, based on a study described below, to give a good compromise between signal-to-noise ratio and the image acquisition/processing time. The cross-section of a given sample was too large for a single image at the desired resolution; therefore multiple scans were acquired and stitched using ThermoFisher Scientific’s Maps 2™ software. The resulting stitched images ranged from 0.2 GB to 2.8 GB and required special special care for processing.
Figure 5.21: Example of curtaining effect when trying to perform a complete cross-section of a carbon infiltration CNT structure using only a focused ion beam. The upper portion of the sample is cleanly cut, but defects accumulate towards the bottom.

5.4.6 Image Preparation

The purpose of the SEM images was to provide cross-section data that allows for analysis of the pores. Particle or pore analysis typically involves a binary image, which involves thresholding the grayscale image. Stitched include some of the surrounding area which adds materials and contrast that make proper thresholding more difficult. To that end, the image needed to be cropped to the region of interest (ROI), and that ROI should be orientated such that the top of the CNT forest was at the top of the image. Each image needed to be rotated to the correct orientation and cropped to the region of interest. OpenCV [68] is an open source tool for computer vision and image processing that is used heavily in this work. Images were resized with a Python implementation of OpenCV to provide images that could be easily viewed and manipulated. These thumbnail versions were used to check the required image rotation and ROI (in terms of percentage of the image width or height). Initial rotation angles were estimated by converting the image to a binary image using Canny edge detection and applying Hough Line Transform to get lines aligned with
the features of interest. The angle of these line gave the initial rotation angle, which was manually
corrected, usually by some multiple of 90 degrees, to get the desired orientation. The rotated im-
ages kept a background that bounded the entire rotated image, thus avoiding cropping caused by
rotation. ROI lines were drawn on the rotated thumbnails to verify the region to be cropped. Once
the ROIs looked good, thumbnail images were cropped and the ROI margins were adjusted based
on the result. All rotation and ROI margins were saved and associated with each image in order
to apply these same transformations on the original images. All image transformations were batch
processed using a Python script.

One challenge in applying the transformations to the original images was that OpenCV
had a limit on the size of image it could rotate (about 300 MB). This could maybe have been
overcome, but required bypassing assertions established in OpenCV that could have had a negative
impact on the computer. Instead, all rotations found using the thumbnails were applied to each
image manually using GIMP (GNU Image Manipulation Program) [69], an open source, cross-
platform software. Rotations were be arbitrarily specified based on the previously recorded values,
and then the image canvas was fit to the rotated image before exporting the rotated image to a new
folder. This made the rotations possible, but the 32 GB ram computer used for this work peaked at
22 GB of ram used during rotation of 2.7 GB images with no other processes running. Care must
be taken in computer hardware choice to replicate this process flow. All of the image cropping on
the rotated images was handling by the Python script using ROI margins saved earlier. An example
of the rotation, ROI, and cropping is shown in Figure 5.22.

5.4.7 Image Processing

The goal of analyzing cross-section SEMs was to calculate the porosity ($\phi$), porosity
profile($\phi(x', y')$), centroid ($C$), and second moment of area ($I'_x$, $I'_y$) of a given sample and corre-
late those values to the process parameters and experimentally measured mechanical properties
and calculations of these parameters required a binary image. The most basic conversion of a
grayscale image to binary one is to pick a pixel intensity level (between 0 and 255) above which
all pixels are set to 255, and below which all pixels are set to zero. The histogram of an image
describes the distribution of pixel intensities in the image. If all intensities are close to each other,
it is difficult to segment the image where desired without losing important information or gaining unwanted features. A histogram can be equalized to spread the intensity information across the whole range of 0-255, which in turn helps with thresholding. On an image with saturated pixels, like one with poor lighting, it is hard to gain information by global histogram equalization. Adaptive histogram equalization and adaptive thresholding techniques the same processes but only consider a single region, or block, of the image at a time. This avoids the problem or highly saturated or extremely dark regions from overwhelming the intensity equalization. Similarly, adaptive thresholding can segment images with less sensitivity to the global image.

Since the SEM images were a result of many individual acquisitions, it was possible that the histogram in each tile could vary. To that end, all cropped images were processed and binarized per the workflow shown in Figure 5.23 using a python script to automatically to batch convert all images to binary. Original SEM images, in .tif format, were imported into the system and immediately converted to grayscale. SEM images are essentially grayscale already, so this step collapsed the RGB channels to a single intensity channel. The histograms of the images were
then equalized using the OpenCV implementation of CLAHE (contrast limited adaptive histogram equalization), using a clip limit of 5.0 and tile grid size of (15,15), which enhanced the surface contrast between features, see (B) in Figure 5.23. The image was then binarized using the OpenCV implementation of Otsu’s adaptive thresholding, (D) after a gaussian blur with a (7,7) pixel kernel, (C). Binary image (D) had many captured many small pixel groups and the resulting pores, depicted in white, appeared larger than reality. A single erosion step, (E), with a (3,3) pixel kernel removed many of the speckles and better matched the apparent porosity as shown in the overlay in (F). The sample used to demo this method in Figure 5.23 was infiltrated for 120 min. Examples of pore segmentation of samples with different levels of carbon infiltration are shown in Figure 5.6.
5.4.8 Image Analysis

With the binary image it is possible to calculate geometrical properties, i.e. porosity, centroid, and second moment of area. The calculation of porosity, shown in equation 5.17, is simply the area of pores \( A_{\text{pores}} \) divided by the total area \( A_{\text{tot}} \). In an image, this is the number of white pixels divided by the total number of pixels in the image, where the white pixels have been associated with pores. To get a profile of the porosity in the x or y direction requires the same porosity calculation on slices of the image and associating those porosities with an x or y position.

\[
\varepsilon = \frac{A_{\text{pores}}}{A_{\text{tot}}} \quad (5.17)
\]

To capture the true mechanical properties of the material it is necessary to capture the true geometry of the system. The centroid and second moment of area can be calculated from the binary images described above. The centroid \((\bar{x}, \bar{y})\) is calculated using equations 5.21 and 5.22, where the subscript \(i\) indicates a specific pixel in the image, \(x_i\) and \(y_i\) are the positions of that pixel. \(A_i\) represents the area of a given pixel which is a constant and square in any given image, where \(b\) is the edge length of the pixel. \(N\) is the total number of pixels in the image and \(\varepsilon_i\) is binary value indicating whether the pixel contributes or not.

\[
A_{ix} = A_{iy} = A_i = b^2 \quad (5.18)
\]

\[
\bar{x} = \frac{\sum \varepsilon_i x_i A_i}{\sum A_i} \quad (5.19)
\]

\[
\bar{x} = \frac{A_i}{NA_i} \sum \varepsilon_i x_i \quad (5.20)
\]

\[
\bar{x} = \frac{1}{N} \sum \varepsilon_i x_i \quad (5.21)
\]

\[
\bar{y} = \frac{1}{N} \sum \varepsilon_i y_i \quad (5.22)
\]

The second moment of area can be calculated by using the parallel axis theorem for each pixel as shown in equation 5.24 where \(I_i\) is the inertia of each square pixels, and \(d_{ix}\) is the difference between the pixel center and the centroid. Substituting for \(I_i, A_i,\) and \(d_{ix}\) gives equations eqs. (5.25)
and (5.26). As it happens, there are built-in functions in OpenCV that calculate these parameters. The OpenCV module “Moments” provides all of these calculation and was used to improve calculation speed.

\[ I_i = I_{ix} = I_{iy} = \frac{b^4}{12} \]  
\[ I_x = \sum \xi_i (I_i + A_i d_{ix}^2) \]  
\[ I_x = \sum \xi_i \left( \frac{b^4}{12} + b^2 (x_i - \bar{x})^2 \right) \]  
\[ I_y = \sum \xi_i \left( \frac{b^4}{12} + b^2 (y_i - \bar{x})^2 \right) \]

5.4.9 Image Analysis Robustness

To process the images using the given workflow, four parameters have to be set: CLAHE clip limit, CLAHE tile size, blur kernel size, and erode kernel size. The base parameters used in this work were 5.0, (15,15), (7,7), and (3,3). As a simple check that the results are robust, the porosity was calculated using different parameters. Each parameter was varied independently and the following levels were used: CLAHE clip limit (1, 2, 3, 4, 5), CLAHE tile size ((7,7), (15,15), (19,19)), blur kernel size ((3,3), (7,7), (9,9), (15,15)), and erode kernel size ((3,3), (5,5), (9,9)). As expected, the erode kernel size had a significant impact on the results when using a large kernel, causing porosity values to drop. This is a parameter to be careful with, though it is still believed that an erosion step with a small kernel is best to match the visible pores. The results from all other parameter variations are summarized in Table 5.2 for images with different levels of carbon infiltration. The results here show that the porosity exhibits a maximum standard deviation of 0.03 when including all variations on CLAHE clip limit, CLAHE tile size, and blur kernel size. Unfortunately, this analysis does not allow for a quantitative determination of which level of carbon infiltration the pore segmentation begins to underestimate porosity. This will have to be a point of development in future work.
Table 5.2: Robustness analysis results from variation in three parameters: CLAHE clip limit, CLAHE tile size, and blur kernel size. Base parameters were 5.0, (15,15), and (7,7). The mean and standard deviation are taken from all calculations using different parameters. 20 µm x 20 µm tiles, taken from the center of images with varying degrees of infiltration, were used for parameter testing.

<table>
<thead>
<tr>
<th>Infiltration Time (min)</th>
<th>Base Parameter Porosity</th>
<th>Mean Porosity</th>
<th>Porosity σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.395</td>
<td>0.391</td>
<td>0.012</td>
</tr>
<tr>
<td>120</td>
<td>0.311</td>
<td>0.298</td>
<td>0.030</td>
</tr>
<tr>
<td>150</td>
<td>0.235</td>
<td>0.220</td>
<td>0.028</td>
</tr>
<tr>
<td>180</td>
<td>0.206</td>
<td>0.197</td>
<td>0.019</td>
</tr>
<tr>
<td>210</td>
<td>0.097</td>
<td>0.095</td>
<td>0.011</td>
</tr>
<tr>
<td>240</td>
<td>0.117</td>
<td>0.105</td>
<td>0.021</td>
</tr>
<tr>
<td>360</td>
<td>0.132</td>
<td>0.114</td>
<td>0.027</td>
</tr>
</tbody>
</table>

5.4.10 Image Resolution Determination

The goal of the study was to look at the effects of time, height, and width on the porosity of the sample. To have confidence in the results of the study it was first necessary to qualify the impact of the electron micrograph resolution on analysis. The same carbon infiltrated carbon nanotube composite sample was imaged at nine different resolutions from 6.51 nmpx$^{-1}$ to 81.4 nmpx$^{-1}$. It was expected at low resolution pores could not be differentiated and that above a certain resolution no new pore would be found. The total porosity, and the porosity near the top, middle, and bottom, was measured for each image. The resolution results are shown in Figure 5.24 and indicate that between 26.4 nmpx$^{-1}$ and 6.51 nmpx$^{-1}$ the measured porosity stabilizes. 6.51 nmpx$^{-1}$ was chosen as the resolution for this study as a the lowest resolution to represent the true porosity. All images used for quantification were at this resolution unless otherwise explicitly stated.

5.5 Conclusions

This work has demonstrated a method to automate the extraction of porosity from SEM images of CI-CNT cross-sections. The extracted porosity profiles indicate almost no porosity gradient across the width, but a nearly linear porosity trend from the bottom to the top of the structure, 0.2 to 0.05 for 240 min of carbon infiltration. This contradicts the expected porosity distribution, at least for the CI-CNT materials produced with this process at the TAG Heuer Institute. Despite the apparent centroid shift (up to 6 %), the true second moment of area dominated instead by the
Figure 5.24: Comparison of measured porosity and the resolution at which the image was acquired. Thresholding and binarization was performed with the same settings for each image. In porosity images, as shown in this figure, white pixels represent pores. Between 26.4 nm/px$^{-1}$ and 6.51 nm/px$^{-1}$ the measured porosity stabilizes. 6.51 nm/px$^{-1}$ was chosen as the resolution for this study as a the lowest resolution to represent the true porosity.

total porosity of the structure. Showing the true second moment of area can be predicted from total porosity alone. Using this hypothesis a method was proposed to extract the true Young’s modulus of the material, shown to be $\approx 30$ GPa for the process used. A more subtle outcome has been the evidence of CI-CNT structures with a large range of effective Young’s modulus possible (5 GPa to 26 GPa. With a modulus twice that reported in previous studies and with a wide range of tunability, this further expands this material’s potential application.
CHAPTER 6. CONCLUSION

6.1 Review

The aim of this research was to advance the capabilities and understanding of CNT-M techniques, namely microfabrication processes where CNTs play a structural role in the fabrication of the material or device. Key to that advancement is the development of strategies for producing more complex, three-dimensionally formed CNT templates and a better understanding of the final material these processes yield. This work explored both of these branches of progress, yielding novel strategies for template production and unique insight into the nature of carbon infiltrated CNTs.

Two forms of three dimensional, multilayer VACNT structures were developed and demonstrated. The first a patterned, stacked CNT forest that was possible through the use of sprayed CNTs which acted as a porous membrane on top of the base catalyst. This sprayed CNT layer served to couple the VACNT growth from the initial stages, resulting in a smooth, low roughness (44 nm) upper VACNT surface capable of supporting patterned thin films. With a minor amount of CVD carbon reinforcement, this mostly porous CNT structure was used to demonstrate the growth of a second, patterned VACNT forest. An extension of this technique was demonstrated in which the underlying growth catalyst was patterned and grown as initially coupled VACNTs (ICCNTs) that supported a sprayed CNT film spanning 2 µm gaps between array features as shown in Figure 6.1.

The second method for three dimensional structures was developed for and demonstrated using a CNT-based microneedle array for nanoinjection into thousands of cells simultaneously. Arrays of 5 µm, circular CNT pillars were plasma etched and densified using capillary forming to generate a needle-like structure. To improve the robustness of the needle structure, new catalyst was deposited between the CNT needles and new CNTs were grown from both the new and orig-
inal catalyst to create a continuous CNT forest beneath the needle array. The final structure was lightly infiltrated with carbon to link the CNT needles to base CNT forest and to link the base CNT forest to the substrate. This process resulted in the first CNT-M carbon needles robust enough for use in nanoinjection.

Figure 6.1: Examples of complex 3D structures produced with newly developed CNT-M techniques. (a) Multilayer, patterned VACNT forest. (b) Patterned ICCNT forest with smooth, solid upper surface. (c) CNT forest anchored, CNT-M lance array. (d) Hollow silica cavity via scarification CNTs.
From the development of a novel thermal barrier, the incredible tunability of CNT-M materials was demonstrated in a MEMS compatible layer with a thermal conductivity that can be tuned from $2.5 \times 10^{-2}$ W m$^{-1}$ K to 10 W m$^{-1}$ K. This material also provided a prime example of how CNTs can be used sacrificially in the structural construction of a material, but that the remnants of the CNT template or its base component may have to be considered in the final properties.

Finally, the Young’s modulus of carbon infiltrated CNTs were compared to their porosity distribution. A novel process for automatic pore identification was developed and implemented to yield the first look at the true porosity and geometric properties of CI-CNT structures. This study overturned the assumptions held regarding the distribution of carbon infiltration, showing instead that there is little to no gradient in the porosity from the sidewalls of the CNT forest inward as shown in Figure 6.2. Combined with insight into how infiltration time can affect the effective mechanical properties it was possible to develop an estimate of the true Young’s modulus of the CVD carbon.

6.2 Contributions

This work has resulted in the invention of two methods for producing patterned multilayer VACNT structures: regrowth from the original catalyst with new growth in parallel, and growth of an initially coupled CNT layer on which additional VACNTs can be patterned and grown. ICCNTs open a path to use CNTs as base layers to support any material or device. A biomedical device for DNA injection into cells using a multilayer CNTs from regrowth has been developed and tested. A low thermal conductivity porous silica layer, compatible with additional microfabrication has been developed and tested, and demonstrated a thermal conductivity with a high degree of tunability. It was shown that plasma deposition of silicon oxide penetrates poorly into CNT forests from any direction, but that this can be advantageous to produce hollow cavities. A method was developed to analyze SEM images of cross-sectioned CI-CNT materials to isolate pores within the structure. This work implemented the developed pore segmentation to provide the first measurements of porosity on a CI-CNT material, and from this the first calculations of centroid and second moment of area. The porosity measurements have disproven the previous held hypothesis of porosity distribution in CI-CNTs. Instead showing a linear gradient from top to bottom and a near constant
porosity across the width. A CI-CNT material was produced having a modulus ranging from 5 GPa to 26 GPa, with the upper limit being nearly twice that of previously reported work.

Figure 6.2: Example of porosity profile obtained with developed pore identification. Shows unexpected porosity distribution.
REFERENCES


[69] The GIMP Development Team Gimp.

CHAPTER 7. APPENDIX A: DESCRIPTION OF DATA PROVIDED AND LINK TO DATASET

Rather than include a lengthy appendix with scripts and data tables, all publically publishable data has been saved as a dataset on Mendeley Data [70]. This data can be found at http://dx.doi.org/10.17632/wzmfrp4x2b.1.

• Chapter 2 AFM data: 100 µm x 100 µm and 2 µm x 2 µm scan areas.

• Chapter 4 Thermal barrier data: Thermal conductivity measurements and analysis code, Raman Spectra, Compression Test Data.

• Chapter 5 Porosity data: 20 µm x 20 µm and 5 µm x 5 µm raw SEM demo images along with processed versions of the images that show pore segmentation. Also included are the python scripts used to binarize images and run porosity, centroid, and second moment of area calculations.

• Miscellaneous Useful Code: Various python scripts and latex snippets that were useful during the course of this work.

• BibTex bibliography is included.

• List of useful software is included.