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Patterned and Infiltrated Vertically Aligned Carbon Nanotube

Ultra-Black Materials

Kevin Laughlin

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

Patterned and Infiltrated Vertically Aligned Carbon Nanotube Ultra-Black Materials

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Doctor of Philosophy

Ultra-black materials reflect less than 1% of incident light, and are used in a wide variety of applications from low signal detector systems, to jewelry. The darkest ultra-black materials are made with vertically aligned carbon nanotubes (VACNTs). One downside to these VACNT based ultra-black material, is they are extremely fragile, and the types of surfaces they can be grown on is limited. Here I created a strengthened ultra-black material that can withstand light handling and drying from water exposure, and can be transferred to other substrates while remaining ultra-black. I also present theoretical models with supporting data on how to make the current darkest films even darker. I was able to create a material that had a 0.009% reflectance, making it the new darkest material.

Using VACNTs as a scaffold, I created high aspect-ratio patterned VACNT structures that were encompassed by a carbon encapsulation layer. I was able to expose weaknesses in the encapsulation layer by depositing a thin layer of silicon on the VACNTs inside the carbon encapsulation. Inserting lithium into the silicon caused the silicon to expand, resulting in stress on the encapsulation layer. This strain from the silicon stressed the encapsulation layer of the different geometries, exposing weak points.

Using VACNTs as a template, I created high aspect ratio 3D structures made from copper using Galvanic displacement and electroplating.

Keywords: microfabrication, carbon, carbon nanotubes, CNT, VACNT, ultra-black, electrodes, lithium ion, electroplating, encapsulation, CVD, PVD
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# TABLE OF CONTENTS

Patterned and Infiltrated Vertically Aligned Carbon Nanotube ........................................ i

ABSTRACT ................................................................................................................................ ii

ACKNOWLEDGEMENTS ........................................................................................................ iii

TABLE OF CONTENTS ........................................................................................................ iv

LIST OF FIGURES ................................................................................................................ vii

Chapter 1: Introduction to Carbon Nanotube Templated Microfabrication ......................... 1

  1.1 Carbon Nanotube Templated Microfabrication .............................................................. 1

  1.2 Microfabrication Process and CNT-M .......................................................................... 3

    1.2.1 Photolithography .................................................................................................... 3

    1.2.2 Thin Film Deposition ............................................................................................. 5

    1.2.3 Thermal Chemical Vapor Deposition ...................................................................... 7

    1.2.4 Etching .................................................................................................................. 9

    1.2.5 Microscopy .......................................................................................................... 11

    1.2.6 Additional Characterization .................................................................................. 12

  1.3 Contents of this Work ................................................................................................... 12

Chapter 2: Mechanically Robust Ultra-Black Materials ...................................................... 14

  2.1 Introduction .................................................................................................................. 14

  2.2 Methods ...................................................................................................................... 17
References..................................................................................................................................... 46

APPENDIX................................................................................................................................... 50

Appendix 1: Fabrication of Microscale Encapsulated Silicon Coated VACNT Electrodes....... 50

Appendix 1.1 Encapsulation Fabrication .................................................................................. 50

Appendix 1.2 Mechanically stressing the encapsulation layer ................................................. 54

Appendix 1.3 Cross-Hatch Encapsulated ................................................................................. 57

Appendix 1.4 Micropillar Encapsulation .................................................................................. 57

Appendix 1.5 Strengthened Micropillar Encapsulation ............................................................ 59

Appendix 1.6 Conclusion.......................................................................................................... 60

Appendix 2: Fabrication of High Aspect Ratio Copper Mesh...................................................... 62

Appendix 2.1 Introduction ........................................................................................................ 62

Appendix 2.2 Fabrication .......................................................................................................... 63

Appendix 2.3 Galvanic Displacement ...................................................................................... 64

Appendix 2.4 Electroplating ..................................................................................................... 68

Appendix 2.5 Conclusion.......................................................................................................... 74
LIST OF FIGURES

Figure 1.1 CNT-M of the BYU Cougar logo................................................................. 1
Figure 1.2 High aspect ratio VACNT structure............................................................. 2
Figure 1.3 Photolithography process .......................................................................... 4
Figure 1.4 Schematic of the thermal evaporation process............................................. 6
Figure 1.5 Thermal Chemical Vapor Deposition Chamber .......................................... 7
Figure 1.6 VACNT growth process diagram ................................................................. 9
Figure 1.7 Depiction of Wet and Dry Etching .............................................................. 10

Figure 2.1 Diagram of the reflection and refraction of light at the interface between air and VACNT Forests........................................................................................................... 15
Figure 2.2 Fabrication diagram ................................................................................... 16
Figure 2.3 VACNT nanotube diameter vs. infiltration time .......................................... 19
Figure 2.4 Mechanical robustness of strengthened VACNTs ....................................... 21
Figure 2.5 Reflectance measurements ....................................................................... 23
Figure 2.6 Transferability ......................................................................................... 24

Figure 3.1 Illustration of reflection and refraction at an air/VACNT interface ............ 31
Figure 3.2 A 2D representation of refraction and reflection inside the VACNT void gap... 35
Figure 3.3 Carbon volume fraction and impact on reflectance .................................... 39
Figure 3.4 Representative SEM micrographs and reflectance data for patterned VACNTs ... 40
Figure 3.5 Reflectance data for patterned VACNTs with varying void gaps ............... 42
A1.1 Fabrication Diagram ................................................................. 51
A1.2 Etch Back Process ................................................................. 52
A1.3 Copper deposition holder .................................................... 54
A1.4 Half-Cell Assembly ............................................................... 55
A1.5 Half-cell battery charging and discharging .......................... 56
A1.6 Cross hatch encapsulation .................................................... 57
A1.7 Micropillar Encapsulation ..................................................... 58
A1.8 Strengthened Micropillar Encapsulation .............................. 59

A2.1 Mesh VACNT structure .......................................................... 62
A2.2 Fabrication diagram of the copper mesh ............................... 64
A2.3 Galvanic displacement deposition ....................................... 65
A2.4 Galvanic deposition ............................................................... 66
A2.5 Ammonium fluoride galvanic displacement .......................... 67
A2.6 Electroplating diagram ......................................................... 68
A2.7 Electroplating Circuit Diagram ............................................. 70
A2.8 Electroplating 8A/cm³ ........................................................... 72
A2.9 Electroplating 4 A/cm³ .......................................................... 73
A2.10 Successful copper deposition .............................................. 74
Chapter 1: Introduction to Carbon Nanotube Templated Microfabrication

1.1 Carbon Nanotube Templated Microfabrication

Carbon nanotubes (CNTs) were first discovered in 1991, and have since become a prominent area of research. Carbon nanotubes are long, thin tubes of rolled sp² bonded carbon. If CNTs are grown under specific conditions, they can grow perpendicularly to the growth substrate and are vertically aligned, as shown in figure 1.1. High electrical conductivity, high surface area, and high thermal conductivity are a few characteristics that make as-grown Vertically Aligned Carbon Nanotubes (VACNTs) compelling for research applications.

Carbon Nanotube Templated Microfabrication (CNT-M) is a process that we use to create patterned structures out of VACNTs for a variety of uses which include: cantilevers for mass sensors, high aspect ratio magnetic microdevices, MEMs, scaffolding for lithium ion batteries, media for chemical separations, and many other applications. Figure 1.1 shows that with CNT-M VACNTs can be patterned to be any shape.

![Image of CNT-M BYU Cougar logo](image_taken_by_Taylor_Wood)

*Figure 1.1 CNT-M of the BYU Cougar logo. SEM image of a CNT-M patterned BYU logo, (image taken by Taylor Wood), with a magnified view of the vertically aligned carbon nanotubes on the right.*
One important feature of CNT-M devices is they have high aspect ratio in height compared to nanotube width and also high aspect ratio height compared to feature size width, as shown in figure 1.2. On the nanoscale, the carbon nanotube diameters are only a few nanometers wide compared to the growth height which can be up to a few centimeters in length[14]. The VACNT forest can also be micro-patterned with feature sizes down to about a micron[15], and are grown to a height of 15-1500 μm tall, resulting in an extremely high aspect ratio of up to 1500.

![High aspect ratio VACNT structure](image)

*Figure 1.2 High aspect ratio VACNT structure. On the left is the VACNT structure with a feature size of ~1 μm and a height of ~1000 μm, giving an aspect ratio of 1000:1. The inset is the width of a single carbon nanotube with a diameter of about 10 nm.*

The carbon nanotubes which make up CNT-M structures also have a high surface area per weight, which can be used as a framework to deposit thin films such as carbon, silicon, oxides, metals, etc. Added thin films can alter the characteristics of the VACNTs, including chemical properties, electrical conductivity, higher strength and stiffness, and so forth.
Since the nanotubes are made of carbon, they are able to withstand high temperatures (above 1000 °C) in inert environments. This allows for carbon nanotubes to be processed at high temperature, as in the high-temperature deposition of thin-films. The sp² bonded carbon has high electrical conductivity along the direction of the VACNT growth making CNTs a good candidate for use as interconnects, nanowires, and vias, and helps with electrodeposition uniformity across the full height of the VACNT forest.

We use microfabrication processes to create CNT-M structures. Though microfabrication was first used to create integrated circuits, it has now become a ubiquitous technique for creating a wide variety of small devices including MEMs, solar cells, microfluidics, sensors, metamaterials, solar cells, and much more. There are many techniques used in microfabrication that I have applied to fabrication of carbon nanotube and have grouped them into the following categories: patterning, additive, subtractive, micro-forming, and characterization. Additive processes add material to the substrate through deposition, growth, or spin-on techniques, while subtractive processes remove material through wet or dry etching. Material characterization is critical in microfabrication process performance and revealing issues that may occur during and after fabrication.

1.2 Microfabrication Process and CNT-M

1.2.1 Photolithography

Contact photolithography is a foundational technique used in fabricating CNT-M structures which we used to reproducibly pattern features down to the single micron scale. The main components of contact photolithography are: a short wavelength light source, a polymer layer (photoresist) that is sensitive to the high energy light, and a patterned lithography mask to transfer a desired pattern to the photoresist.
Photoresist is spun onto a clean silicon wafer to create a thin layer (figure 1.3B). We generally use a 2-3 μm thick photoresist for structures with feature sizes larger than 10 μm. For patterning CNTs with feature sizes less than 10 μm, we use a thinner 1-μm photoresist. For the lift-off processes we use for patterning our CNTs, we prefer to use thicker photoresist to improve lift-off yields.

The lithography mask is held in place and pressed against the wafer (figure 1.3C). If the smallest feature size is between 1-5 μm, vacuum contact is required. Vacuum contact means that a vacuum is applied between the lithography mask and the chuck holding the wafer, creating an even force across the mask and wafer to ensure good contact between lithography mask and wafer.

High energy light is then shined through the patterned areas of the lithography mask into the photoresist (figure 1.3D), chemically altering it (figure 1.3E). If the resist is a positive resist, light chemically alters with the exposed portions, making those areas soluble in a developer solution and will be removed as shown in figure 1.3F.

Figure 1.3 Photolithography process. A) Bare silicon wafer. B) Positive photoresist is spun onto the wafer. C) Lithography mask is placed over wafer. D) High energy light exposes resist in the masks pattern. E) Lithography mask is removed and the exposed pattern is soluble in developer. F) Exposed photoresist is dissolved away, exposing underlying wafer.
If the resist is a negative resist, the high energy light will cross-link the polymers, causing them to become less soluble. When the photoresist is developed, the exposed areas of the resist will remain, and the unexposed regions will be removed.

1.2.2 Thin Film Deposition

Thin films are used as the growth catalyst for CNT-M and are also deposited around the individual carbon nanotubes to create a composite. Thin films are deposited by using physical vapor deposition, chemical vapor deposition, and spin-on techniques. Each of these techniques has different uses and applications.

Two physical vapor thin film deposition techniques are used for CNT growth and processing: thermal evaporation and electron beam evaporation. Thin-film evaporation is an additive process that we use to deposit thin-films of iron, alumina, and copper. Deposition takes place in high vacuum, so the mean free path of the deposited material is longer than the distance from the source to the sample, which also keeps the impurity content in the deposited thin-film low. While achieving the highest vacuum improves purity, it requires additional time and effort. For our purposes, we found that a pressure of $10^{-5}$ torr is a good compromise between time, effort, and purity. As depicted in figure 1.4, material is placed in a crucible where the material is heated up and begins to evaporate. The vapor travels in a straight line, condenses onto every exposed surface, and leaves behind a thin film. The sample is exposed to the vapor until the target thickness is reached, as determined by an XTAL crystal monitor. The chamber is then vented with nitrogen until the chamber reaches atmospheric pressure and the sample is removed.
Thermal evaporation is used to deposit copper as a current collector and iron as the VACNT growth catalyst. For thermal evaporation, the desired material is placed in an alumina-coated tungsten crucible which doubles as a resistive filament. A current is run through the crucible to heat it up, and the crucible in turn heats up the deposition material. The deposition material must have a melting/boiling point below that of the crucible, which typically limits its use to metals.

Electron beam deposition is used to deposit alumina as a diffusion barrier in the CNT catalyst stack. Electron beam deposition uses a graphite (or other high temperature) crucible to hold the material to deposit. When under vacuum, a high-energy electron beam is caused to strike the material, heating it up directly, which produces a higher purity thin film. Since the crucible is not directly heated, electron beam deposition is able to deposit materials with much higher...
evaporation temperatures, such as silica and alumina. One downside to electron beam deposition systems is they are more difficult to work with and costlier to maintain.

1.2.3 Thermal Chemical Vapor Deposition

Thermal Chemical Vapor Deposition (CVD) is a process that allows for thin-film deposition on non-planar surfaces. A gaseous chemical precursor is heated, which decomposes on the surface of a substrate to deposit target material. Since the target material is in gaseous state, it is not limited to line-of-sight deposition but will deposit on any exposed surface within the chamber. We deposit thin-film silicon for batteries and grow VACNTs using CVD techniques.

![Thermal Chemical Vapor Deposition Chamber](image)

*Figure 1.5 Thermal Chemical Vapor Deposition Chamber. After the sample and boat are in place, the heater increases the temperature of the chamber. The chemical precursor is then injected into the chamber through the gas inlet tube where it decomposes and deposits the target material on the sample. The remaining gasses exit through the backend.*

To deposit silicon, a low-pressure chemical vapor deposition reactor (LPCVD) (figure 1.5) is used. The samples are placed on a quartz boat inside a 6-inch outer diameter quartz tube. The chamber pressure is reduced to 20 mtorr vacuum and purged with nitrogen to remove any oxygen from the system. The furnace is then heated up to 535 °C when a thin conformal coating is desired,
or 585 °C to fill a structure faster, but not completely. 70 sccm of silane is flown through the quartz tube until the targeted time is reached. We use time for determining thickness since we do not have a way to take in-situ thickness measurement in the furnace. To determine the amount of deposited silicon, we measure the weight of the CNTs before and after deposition, then calculate the thickness based on deposited weight and surface area of the carbon nanotubes.

To create the CNT-M structures, we start with a clean silicon wafer (figure 1.6A) and deposit a 50 nm layer of alumina (figure 1.6B). If the CNTs will be patterned, a positive photo resist is then spun onto the wafer and exposed with a lithography mask (figure 1.6C). A thin (1-8 nm) layer of iron is deposited onto the exposed alumina (figure 1.6D). The wafer is cleaved or diced to the desired size, and the residual photoresist is removed by immersing the sample in N-Methyl-2-pyrrolidone (NMP) (figure 1.6E), sonicating for 20 minutes, and then rinsing the sample with water for 30 seconds.

To grow the VANCs (figure 1.6F), a diced catalyst sample is placed on a quartz boat and inserted into a one-inch inner diameter quartz tube furnace[3, 16]. Argon is flown through the furnace tube for two minutes to remove any remaining oxygen from the tube, turn on 307 sccm (standard cubic centimeters per minute) of hydrogen, then we turn off the argon. The furnace is heated to 750 °C while flowing hydrogen then introduce 335 sccm of ethylene which is the carbon source for CNT growth. The CNTs grow about 50-100 microns per minute for the first few minutes, depending on the iron catalyst thickness. Ethylene is flown until the expected time for the target height is reached at which point both the ethylene and hydrogen are turned off, and an inert gas, argon, is turned on. We cool the furnace down to 200 °C before removing the sample.
For samples where nanocrystalline carbon infiltration is desired (figure 1.6G), immediately after the CNTs are finished growing the furnace temperature is ramped up to 900 °C and 335 sccm of ethylene is introduced. This coats the nanotubes with nanocrystalline carbon, and the more time the ethylene flows the thicker the nanotubes become.

1.2.4 Etching

Etching is a subtractive fabrication process that uses liquids or plasmas to remove material. Some common etchants used in this research are potassium hydroxide (KOH) to remove silicon and to release the VACNTs from the substrate, hydrofluoric acid (HF) to remove oxides and gently remove VACNTs from substrate, and oxygen (O₂) plasma to etch away carbon floor layer and the
top of a VACNT forest. If only part of the material is to be removed, a masking layer is required, as depicted in figure 1.7A. This layer is typically patterned with lithography, is more robust against the etchant than the underlying material and will transfer the desired pattern from the mask to the target material.

Wet etching uses liquids to etch away material and is driven by chemical reactions. One of the benefits of wet etching processes is that it can be very selective in what it removes. For example, KOH will etch silicon dioxide at a rate of about 8 nm/min, but will etch silicon at 1100 nm/min. This selectivity allows us to etch one material while leaving the other materials untouched. A disadvantage of wet etching is that it is usually isotropic, meaning it will etch the material in every direction equally, as illustrated in figure 1.5B.

Dry etching does not use liquids, but instead is a process that uses energized, ionized gasses that bombard the surface to remove the material. This process is much more directional than wet etching, but because it uses kinetic energy along with chemical reactions to remove material, it is usually much less selective. When
using a dry etching process, the masking layer thickness must be taken into account since the
masking layer is etched along with the target material as depicted in figure 1.5C.

1.2.5 Microscopy

It is important to track sample performance both during the fabrication process and after
the sample is complete. One way we follow the progress of our samples is with microscopy. Using
an optical microscope to image the sample is a nondestructive, quick, and easy way to obtain useful
information such as: lithography faults, the height of the VACNT forests, and the microscale
surface topography of a sample. The sample prep is minimal with usually no required preparation.
However, optical microscopes are limited by the wavelength of visible light and can only resolve
down to about a half a micron.

Sometimes, we work with structures or features that are on nanometer scales, and optical
microscopes are incapable of resolving these features sizes. For these cases, a Scanning Electron
Microscopes (SEM) is used to get detailed resolution. SEMs are able to image down to a few
nanometers using high energy electrons to scan a surface instead of visible light. The wavelengths
of the high energy electrons are in the picometer range.

To image a sample, SEMs raster scan a high energy electron beam across a surface. Low-
energy secondary electrons are knocked off by the electron beam and collected by a detector and
digitized to create a bitmap image of the surface. The number of secondary electrons determine
the gray scale amount for the pixel, and the beam moves to the next spot/pixel and repeats the
process. The topography and materials properties of the surface will result in varying secondary
electron fluxes that reach the detector. Higher dwell times for the electron beam result in a higher
signal to noise ratio and cleaner images but are slower to acquire.
SEMs are also used for elemental analysis using Energy Dispersive Spectroscopy (EDS). EDS is an analytical technique that uses the high energy electrons from the electron beam to knock out core electrons in an atom. The higher energy state electrons bound to that atom will fall into the lower energy state releasing a characteristic x-ray which is collected. This signal is used to determine the relative quantity of certain elements in a sample but is generally limited to elements that are heavier than lithium.

1.2.6 Additional Characterization

We use additional characterization techniques further detailed in later chapters. For strength measurements, a 3-point bending setup with a mini Instron is used to flex VACNT structures to their breaking point which I discuss further in chapter Two. Optical reflectivity measurements are obtained using a 633 nm wavelength laser, an integrating sphere, a photodiode, and a picoammeter. For further details, refer to chapters two and three.

1.3 Contents of this Work

In Chapter 2 we increased the mechanical strength and modulus of VACNT based ultra-black materials through infiltration of the VACNT structure with nanocrystalline carbon. The manuscript *Mechanically Robust Vertically Aligned Carbon Nanotube Composites for Applications in Ultralow Reflectance Optical Elements* has been published on May, 2022 in *ACS Applied Nano Materials*[17]. DOI: 10.1021/acsanm.2c00947

Chapter 3 is on creating the least reflective films using patterned VACNTs, with theory relating the carbon volume fraction and the reflectance of the VACNT forest. *Three Dimensional Ultra-
Black Materials from Patterned Vertically Aligned Carbon Nanotube Structures has been submitted for publication as a journal article in Nature Nanotechnology. Additional works using CNT-M to create non-ultra-black structures and devices have been included in the appendix as a way of keeping record of these applications.

Appendix 1 contains unpublished work on creating a carbon encapsulation layer surrounding coated carbon nanotubes. The carbon nanotubes were silicon-coated to help stress the encapsulation layer and were used as the anode in lithium ion batteries. I was also a coauthor on the paper, Carbon Monolith Scaffolding for High Volumetric Capacity Silicon Li-ion Battery Anodes.

Appendix 2 contains unpublished work on creating high aspect ratio copper structures using galvanic displacement and electroplating.
Chapter 2: Mechanically Robust Ultra-Black Materials

2.1 Introduction

Ultra-black materials reflect less than 1% of light, and have many uses including broadband absorbers, light to heat generators, stray light absorbers for low light systems, and even aesthetics such as jewelry and art. Currently, the darkest ultra-black material utilizes VACNTs, as they have an effective index of refraction close to air, and the carbon has a high absorption. While VACNT based materials are the darkest, other materials are still used, including black silicon[18-21] and nickel-phosphorous alloys[22], since they are fully compatible with standard CMOS processes.

In this work, I have focused on the understanding and improvement of VACNT based ultra-black materials. I have created a strengthened ultra-black VACNT structure that is capable of being handled, exposed to water, and transferred to other surfaces, while reflecting less than 0.1% light (633 nm wavelength).

Ultra-black materials can reflect less than 1% of incident light and can be used to reduce stray light in low signal detector systems (e.g. deep space images)[23-25] and as broadband absorbers[26-28]. Vertically aligned carbon nanotube (VACNT) forests[1] are currently the darkest man-made material[29-32] and have resulted in a reflectance down to ~0.01%[31] for red light. The low reflectance is caused by two factors: first, the extremely low carbon density in the VACNT forests[29, 33] (they are mostly air) resulting in an effective refractive index very close to the index of air, and second a high coefficient of optical absorption. Certainly this is a highly heterogeneous material but the spatial variations happen on a scale much smaller than the optical wavelength, resulting in an effective index of refraction (we will use “index of refraction” to refer to this effective index of refraction) that is dominated by the relative volume fraction of air to...
carbon\[34\]. The close index matching between air and the VACNT forest results in extremely low reflectance at the air/VACNT interface. Figure 2.1 illustrates reflection and refraction at an interface between air and the VACNT forests. The extremely low carbon density in the VACNT forest results in an index of refraction very close to that of air yielding an ultra-low reflection at the surface (figure 2.1B) for normal incidences.

![Figure 2.1 Diagram of the reflection and refraction of light at the interface between air and VACNT Forests. A) An interface between air (index of refraction $n_1$) and a material with higher index ($n_2$). Part of the incident beam (labeled I) will reflect at the interface (reflected beam, labeled R), while part of the light will refract (refracted beam, labeled T) into the higher-index material at an angle closer to normal to the interface (the dashed black line illustrates the original direction of the incident beam). B) Reflection off a nanotube forest (a very low density of nanotubes in air), which has an effective index of refraction much closer to $n_1$. C) Infiltrating the VACNT structure with nanocrystalline carbon significantly strengthens the VACNT forest but increases the carbon density and index of refraction. D) An O$_2$ plasma increases the surface topography, lowering the carbon density and index of refraction near the surface.](image)

High quality VACNTs are synthesized at high temperatures (approximately 750 °C), which limits growth substrates to high temperature metals and ceramics. The VACNTs also have a very low strength that makes them difficult to handle\[16\], limits their transferability, and prevents them from being used in some applications such as where contact with solids or liquids could occur.
These limitations greatly restrict the materials to which these ultra-black coatings can be applied. One approach that allows CNT coatings on a wider variety of surfaces has been to use CNT based sprays or composite films[27, 35] to coat the materials, but these coatings are significantly more reflective (0.2% reflectance) than VACNTs.

Here we have fabricated VACNT/carbon composite films with significantly higher strength than as-grown VACNTs, while maintaining low reflectance. The higher mechanical strength is achieved by infiltrating VACNT forests with nanocrystalline carbon (Figure 2.1C), but this infiltration increases the carbon volume and reflectance. Reflectance increase can be offset by roughening the top of the infiltrated VACNT forest by exposure to an oxygen plasma[36] (figure 2.1D). This lowers the carbon density near the top surface, reducing the index of refraction and thus the reflectance. Precise measurement of these low strength materials is challenging, however a dramatic increase in strength from as-grown (10±4 kPa) to infiltrated forests (500 ±100 kPa). While still a delicate material, these composites are robust enough to be exposed to water, handled, cut to a desired

**Figure 2.2 Fabrication diagram.** A) Start with a clean silicon wafer. B) Deposit 50 nm of alumina C) Deposit a thin layer of iron to act as the catalyst for carbon nanotube growth D) Grow the VACNT forest E) Infiltrate the VACNT forest with nanocrystalline carbon F) Etch back the tops of the VACNT forest to roughen it up.
shape, and transferred to other surfaces all while maintaining a reflectance of less than 0.1% at normal incidence.

### 2.2 Methods

#### 2.2.1 VACNT Forest Growth

Carbon nanotubes were grown and infiltrated as described in [9, 16], a diagram to illustrate this process is shown in figure 2.2. An alumina/iron catalyst bilayer was first deposited as follows. A 50 nm layer of alumina was deposited onto a 4-inch silicon wafer using an e-beam evaporator (as measured by quartz crystal thickness monitor). The 1-nm thin film of iron (as measured by quartz crystal thickness monitor) was then thermally evaporated onto the surface, and the wafer was diced into 7 mm square pieces. The catalyst coated squares were placed in a 1-inch inner diameter tube furnace which was then heated to 750 °C with flowing 307 sccm of hydrogen. Once the furnace reached 750 °C, 335 sccm of ethylene was introduced to grow the VACNTs. After the desired growth time, the ethylene was shut off, and the furnace was cooled for as-grown VACNTs or heated to infiltrate with carbon.

#### 2.2.2 VACNT Forest Infiltration

Infiltration of the VACNT forest with nanocrystalline carbon was performed to strengthen the forest as follows. Immediately after the ethylene was shut off following VACNT growth, the furnace was heated up to 900 °C while flowing 307 sccm of hydrogen. When 900 °C was reached 335 sccm of ethylene and 307 sccm of hydrogen was flowed for 2-5 minutes, depending on the desired infiltration. The tube furnace was then cooled down to 200 °C with flowing hydrogen.
The hydrogen was then shut off and the furnace was flushed with argon for 120 seconds and samples were removed.

Under visual observation the as-grown VACNT forest appear black to the naked eye but following infiltration they became a lighter grey color. The samples were then placed in a directional oxygen plasma for 1 minute to roughen the tops of the nanotubes. After oxygen plasma exposure the infiltrated VACNTs appear black.

2.2.3 Scanning Electron Microscope (SEM) characterization

Due to the size of the individual nanotubes of the VACNT forests, the use of a SEM is required to image the microstructure. Prior to imaging, samples were cleaved down the middle to make the interior of the VACNT forest visible. Samples were connected to aluminum SEM stubs with carbon tape, and placed in a Thermo Scientific Verios G4 UC SEM. SEM imaging was at 10keV and 0.1 nA in immersion mode. Three to six images at varying magnification were taken in both side view orientations for cross-sections (figure 2.3A-E) and top down (figure 2.3G-H) to show how the nanotube diameters change with infiltration time and etching. Each SEM image was taken towards the top of the forest where the nanotubes are thickest. To get a good sample of the nanotube diameter, between 150-200 diameter measurements were taken (using ImageJ software) for each of the infiltration conditions and the average was plotted in figure 2.3F.
Figure 2.3 VACNT nanotube diameter vs. infiltration time. SEM images of VACNTs scale bar is 200 nm for A-E, 1 um for G-H, and 200 nm for the inset of G-H. A) No infiltration B) 2-minute infiltration. C) 3-minute infiltration. D) 4-minute infiltration. E) 5-minute infiltration. F) Nanotube diameter vs. Infiltration time. The error bars come from the standard deviation of the measured samples. G) Top of infiltrated VACNT forest with higher magnification inset. H) Angled view of the top of etched infiltrated VACNT forest with higher magnification inset.
2.2.4 Modulus and Strength Characterization

To measure the ultimate strength and Young’s modulus of the VACNT forests, a 3-point bending setup[37] with a gap of 2.5 mm was used (figure 2.4A). The samples were carefully released from the substrate by applying a sideways force to the strengthened VACNT structure. Release is possible due to the low adhesion the infiltrated samples have to the silicon substrate. The released samples were then placed over a gap in a mini Instron machine as illustrated in figure 2.4A. A blade connected to the Instron load cell was brought down to the middle of the sample without contacting it. At this point the force and distance measurements were zeroed. Increasing force was then applied to the sample causing it to bend until the sample broke, and the force and displacement data was recorded. The initial force vs. displacement can be related to the Young’s modulus and the breaking force to the strength of the material[10]. We measured seven samples of each type of infiltration with widths and heights of 2-4 mm and 0.6-0.9 mm respectively.

To determine the capability of the strengthened VACNT structures to withstand the forces caused from immersing in water and drying, samples with different infiltration times were placed in a water bath filled with milli-Q water for 24 hours then taken out to dry in ambient conditions. Following drying, optical images were taken of the samples (figure 2.4B). If a sample did not crack or delaminate from the growth surface during the immersion and drying procedure, the samples reflectance was measured.
2.2.5 Optical Characterization

Optical reflectance was measured using an integrating sphere[22] (Thor Labs) with a PIN photodiode detector, and a helium-neon laser was used as the light source as shown in figure 2.5A-B. While a 633 nm laser was used for our measurements; prior work has demonstrated that VACNTs have a uniformly flat response over visible wavelengths[32, 38]. A small aperture was
used right before the light entered the integrating sphere to minimize stray light. The laser was
aimed through the apertures onto the back of the integrating sphere where there is a removable
port to either load a sample, a reflectance reference sample as seen in figure 2.5B, or let the light
pass through to a beam dump as seen in figure 2.5A.

Three types of measurements were taken, a ‘reference’, a ‘background’, and a ‘sample’. The ‘reference’ is a PTFE coated sample of known diffuse reflectance of 99% placed at the back port of the integrating sphere. The ‘background’ is taken with the back port of the integrating sphere removed, the light being allowed to travel through the integrating sphere into a beam dump. The ‘sample’ is the ultra-black specimens placed on the back port of the integrating sphere. To find the total reflectance of the sample, the ‘background’ signal was subtracted from both the ‘reference’ and ‘sample’ signals, and then the 'sample' scattering was divided by the ‘reference’ scattering, and then multiplied by the known references’ reflectance.

Because our ultra-black samples are significantly different in reflectance than the reference sample, we tested the linearity of our detector using the reference sample and neutral density filters to bring down the intensity of our light source in a known way. Thus, it was determined that the detector’s response is linear over the intensity range we are testing.
2.2.6 Transferred VACNT forest

After the ultra-black material has been strengthened (figure 2.6A), it is capable of being handled, and transferred from one substrate to another. To remove the VACNT’s from the growth substrate, double sided carbon tape was applied to the top of the VACNT forest (figure 2.6B) and...
the tape was used to peel the VACNT forest off of the substrate (figure 2.6C). The carbon tape was then used to affix the VACNT to another solid surface (figure 2.6D). It should be noted that during infiltration, the carbon creates a smooth coating on the growth substrate that we call the floor layer. Following transfer, the samples were placed in an O₂ plasma to remove the carbon floor layer as well as etch and roughen the exposed top of the forest (figure 2.6F).

**Figure 2.6 Transferability.** A-E) Fabrication diagram. A) Start with infiltrated sample. B) Place carbon tape on top of strengthened VACNT forest. C) Using the carbon tape, peel off the VACNT structure. Note the continuous carbon floor layer is now exposed on the bottom. D) Affix the carbon tape to a new substrate. E) Etch back the tops of the VACNT forest. F) Reflectance of the transferred strengthened VACNTs vs. non-transferred VACNTs. The error bars come from the standard deviation of the measured samples.

### 2.3 Results

To determine the impact of infiltration time on a single nanotube diameter, SEM measurements were taken of forests prepared with infiltration times of zero, three, four, and five minutes (figure 2.3A-2.3E). We see in figure 2.3F that the longer the VACNT forest is infiltrated, the larger the individual nanotube diameter becomes. The as-grown nanotubes start with a radius
of about 4.1 ±1.5 nm, and after 5 minutes of infiltration the nanotube radius became about 21.5 ±3 nm, where the uncertainties come from the standard deviations.

The impact of oxygen plasma on forest surface morphology was determined by SEM imaging before and after plasma exposure. Figure 2.3G shows an image of the top surface of an as-grown VACNT forest, showing that nanotube alignment is low at the top of the VACNT forest. Other images taken in cross section show that this low alignment segment only extends down from the top of the forest less than 0.5 microns. Figure 2.3H shows an angled view of the top surface after exposure to an oxygen plasma. We observe that the top of the forest is now rough with sharp peaks that come to a point of only few nanometers and the exposed nanotubes have high alignment.

The mechanical stiffness (Young’s modulus) and strength of the as-grown VACNT forests are very low, with an average of 60±20 kPa and 10±4 kPa respectively (figure 2.4C and 4D), the reported ranges are the standard deviation of the samples tested. These low numbers are consistent with damage observed even by light touching or contact with liquids. While there is significant variation in the measured values of strength and stiffness, they both dramatically increase with increasing infiltration time. After 4 minutes of infiltration the stiffness and strength have increased to roughly 500x and 50x that of as-grown VACNTs. The samples infiltrated for 4 minutes or more were sufficiently robust to allow for routine handling and could be immersed in liquids and dried without damage. There was no detected strength or stiffness difference between etched and non-etched samples.

Figure 2.4C-D shows that the Young’s Modulus and the ultimate strength of the VACNTs increase as the samples are infiltrated for more time. Each point graphed is the average of at least seven samples and the error bars are the standard deviation. Even though there is only a modest
change in measured strength or stiffness from 2 minutes to 4 minutes, there is a large improvement in how the VACNT forest survives the stresses from water exposure drying.

Figure 2.4B shows images of infiltrated samples that were exposed to water and dried. The samples that were infiltrated for 2 minutes broke into little clumps that were ~0.1-2 mm in size during the drying process. In contrast, after 3 minutes of infiltration the VACNT forest survives drying more or less intact. Nevertheless, there were some cracks that formed revealing the silicon substrate below. With 4 minutes or more of infiltration, the infiltrated VACNT forest was sufficiently strong to withstand drying stress. We do not show an image of non-infiltrated VACNTs after water exposure because there were no nanotubes remaining on the substrate after drying.

As seen in figure 2.5C, the reflectance of as-grown VACNT forests was about 0.06±0.01%. As the forests were infiltrated, their reflectance increases significantly, and after 5 minutes the reflectance has increased over 50 times to 3.3±0.3%. However, for all infiltrated samples represented in figure 2.5C, an O₂ plasma etch reduced the reflectance by approximately ~50x. This resulted in a final reflectance close to the pre-infiltration reflectance.

Figure 2.5D shows the reflectance of the infiltrated and etched VACNT forests when dried from water. The red box indicates infiltration conditions where the VACNT forest was not able to withstand the destructive forces of drying from water, so no data could be taken. The post drying reflectance for the 4-minute infiltration samples are 50% higher than before immersion, while the 5-minute infiltration samples post drying reflectance is only 17% higher than before immersion. These changes indicate that even in these stabilized samples there is a structural change due to water exposure and drying.
After the VACNT samples were transferred to another substrate and then etched (figure 2.6E), the reflectance was measured. Figure 2.6F shows that the transferred samples have less than half the reflectance of etched VACNT samples with the same infiltration time which were not transferred.

2.4 Discussion

The as-grown VACNTs are too weak to handle, even with care. This is due to each nanotube having a low density of contacts with its neighbors, and that these contacts are held together by weak van der Waals attractive forces. However, post infiltration the VACNTs are strong enough to be handled, though they are still somewhat fragile. When the forest is infiltrated with nanocrystalline carbon, neighboring nanotubes are locked together wherever they touch, creating a significantly stronger material. As more material is added the points of contact grow stronger, and other points are bonded that were close to touching before. However, as the VACNTs are infiltrated, the reflectance increases. Reflection increases with increasing infiltration times as shown in Figure 2.5C.

The top <0.5 μm of the as-grown VACNTs are randomly oriented as seen in figure 2.3G, resulting in a higher carbon fraction and thus a higher index of refraction. By removing that top layer with an oxygen plasma, the VACNTs are roughened, and show the higher CNT alignment characteristic of the forest below the as grown tops. In addition, the structures end in bundled points (figure 2.3H). The lower carbon density which results from etching is expected to lower the surface’s index of refraction which would lower reflectance, as was observed. As shown in figure 2.5C this lowered index of refraction significantly reduces the amount of reflected light, bringing the reflectance close to its value prior to infiltration.
During transfer, the sample is flipped top to bottom, exposing the lower density nanotubes [39] to the O₂ plasma. The transferred VACNT structures, after etching, have an even lower reflectance than non-transferred as shown in figure 2.6F. The measured low reflectance is consistent with the known lower density of carbon nanotubes at the bottom of the VACNT forest[39, 40]. The reason for the lower CNT density at the bottom is gradual inactivation of the iron catalyst nanoparticles during growth[41]. This lower density region at the bottom, right near the catalyst, could potentially be further reduced by adjusting VACNT growth parameters[3], resulting in an even lower reflectance.

2.5 Conclusion

By infiltrating VACNT structures with nanocrystalline carbon, we are able to increase VACNTs stiffness and strength from 60±20 kPa and 10±4 kPa to 7000±1000 kPa and 500±100 kPa respectively. These strengthened VACNTs are much more resistant to breaking during light handling and after water immersion and drying. We were also able to reduce the reflectance of these strengthened films to below 0.1% by etching the top layer of the VACNTs in an oxygen plasma. This results in an ultra-black material which could be useful for applications where as-grown VACNTs are impractical due to their low strength.

Since VACNTs can only be grown on high-temperature substrates, many structures such as plastics, carbon composites, or lower melting point metals, cannot have VACNT ultra-black coatings. Strengthening the VACNTs allows them to be handled, removed from their growth substrate, and later affixed to another surface. The transfer process flips the VACNT forest top to
bottom. This transfer followed by a brief oxygen plasma exposes lower density VACNTs (from late in the VACNT growth process), resulting in an even lower reflectance than before transfer. We believe these strengthened materials could significantly increase the diversity of applications where ultra-black VACNTs can be used.
Chapter 3: Patterned VACNT Based Ultra-black Materials

3.1 Introduction

Ultra-black materials reflect less than 1% of incident light[18, 42] and are of interest in applications including broadband absorption[26, 27, 43, 44], thermal detection[23], and low signal detection systems[24]. An ultra-black material relies on both its intrinsic material properties as well as the surface morphology of the film[20] to help reduce the amount of light that is reflected. Vertically aligned carbon nanotube (VACNT)[1] forests are currently the darkest man-made material and can have reflectance down to ~0.012%[31] with red light. The main reasons for this ultra-low reflectance come from two factors: First, a close index match between air and the VACNT forest [29] results in an extremely low reflectance at the air/VACNT interface. Second, carbon has a high optical absorption meaning most of the light that comes in contact with or enters the VACNT forest gets absorbed. While these VACNT films are currently the least reflective, there is an ever-present desire to further understand and improve on decreasing the reflectance.

In order to understand and improve ultra-black materials, an understanding of the interaction with light between two mediums is important. Figure 3.1A shows an interaction of light at the interface between air, with an index of refraction $n_1$, and a VACNT forest, with index of refraction $n_2$. Since $n_2$ is a higher index than $n_1$, some of the light will reflect out, and some of the light will refract towards the normal into the second material where it is absorbed.

When carbon volume fraction in the lower material is reduced, $n_2$ will become closer to $n_1$ [45]. Carbon nanotube forests are mostly air with ~1-10 % graphite (depending on growth conditions), so $n_2$ will closely match $n_1$, and the reflectance will be extremely low. Physical properties of carbon nanotube forests impact reflectance including nanotube alignment[46], diameter[3, 47], and density[7, 48], and these parameters can be adjusted through modification of
the CNT growth conditions. Although lowering carbon density will reduce reflectivity, there is a lower limit to the density that can be achieved in VACNT forest growth[3]. Below a critical nanotube growth density, the intertwining support of neighboring nanotubes required for stable vertically aligned growth does not provide sufficient mechanical support to enable forest growth. The carbon volume fraction at the top of the VACNT forest can also be lowered by exposing the as-grown forest to an oxygen plasma, resulting in lower reflectance[36]. Oxygen plasma treatment has also been shown to significantly reduce reflectance, to < 0.1%, for more mechanically robust ultra-black structures made from partially infiltrated VACNT Forests[17].

Here we report a study of the impact of voids on VACNT forest reflectance. We studied the impact of both subwavelength size voids which depend on nanotube forest growth conditions, and larger than wavelength voids formed by growing patterned VACNT forests. Subwavelength voids were varied by growing VACNTs with catalyst thickness ranging from 1-7nm resulting in

Figure 3.1 Illustration of reflection and refraction at an air/VACNT interface. A) Reflectance at an interface of air (index of refraction $n_1$) and carbon (index of refraction $n_2$). Part of the incident beam (labeled ‘I’) will reflect at the interface (reflected beam labeled ‘R’) and refract into the VACNTs (labeled ‘T’) at an angle closer to the normal of the interface. B) Reflectance at an air/VACNT interface with higher density, but thinner nanotubes. C) Reflectance at an air/VACNT interface, with light entering large void gaps from lithographically defining the iron growth catalyst and reflecting off the sidewalls. D) Schematic of VACNT hedges and open void areas. ‘A’ is the area of a unit cell, and $W$ is the width of the open void space.
differing nanotube densities and diameters, as illustrated in with figure 3.1A and 3.1B. We formed larger than wavelength voids by lithographically patterning the iron catalyst to create 1-100 micron openings in the VACNT forests as illustrated in figure 3.1C and D. These larger scale voids significantly reduce reflectance of the VACNTs. In this paper we also present a theory relating reflectance to patterned void space and good agreement is found between this theory and our experimental measurements. We used a high sensitivity laser and integrating sphere setup at 633 nm to measure the total reflectance (including both diffuse and specular reflectance). Patterned VACNT forests incorporating 4 μm voids showed a total reflectance of 0.009 %, about ~ 4 times lower than reflectance values previously reported in this wavelength range.

### 3.2 Theory

Creating large (compared to the wavelength of light) open gaps devoid of nanotubes by lithographic patterning of the nanotube catalyst, as illustrated in figures 3.1C and D, results in lower reflectance. We model the main impact of these voids to be the reduction of the VACNT forest top surface area, resulting in less light reflecting off the VACNT forest top surface. This top surface reflection \( R_{TS} \) is predicted using geometric optics to be the ratio of the top surface area \( A_{TS} \) to the total area \( A_{Total} \) multiplied by the reflectance of non-patterned top surface nanotubes \( R_{CNT} \).

\[
R_{TS} = R_{CNT} \frac{A_{TS}}{A_{Total}} \tag{5}
\]

For a square patterned lattice, as shown in figure 3.1D, \( A_{TS} \) is equal to the total area of a unit cell \( A_{Total} \) minus the square void gap with width \( W \). \( R_{TS} \) becomes:

\[
R_{TS} = R_{CNT} \frac{A_{Total} - W^2}{A_{Total}} \tag{6}
\]
In addition to the reflection off the top surface, the reflection off the substrate needs to be accounted for. At normal incidence, light that enters the gap is transmitted down through the gap ($T_{gap}$), reflected off the substrate ($R_{Sub}$), and then transmitted up through the gap to the top, where it contributes to the total reflectance. The total reflectance of the material will then be:

$$R_{Total} = R_{TS} + T_{gap}R_{Sub}T_{gap}$$  \hspace{1cm} (7)

As we will see below, the transmission through the void gap will be small for small void gaps but will increase with gap size.

Although the void gap width is larger than the wavelength of light, diffraction still plays a role as the light is transmitted through the void gap, especially for high-aspect ratio gaps. Using Fraunhofer diffraction from a square aperture\[49\] at the top of the patterned VACNT forest as a model, we estimate the light that will be transmitted through the void gap without reflecting off the sidewall.

$$I = I_0 \text{sinc} \left( \frac{\pi W x}{\lambda H} \right)^2 \text{sinc} \left( \frac{\pi W y}{\lambda H} \right)^2$$  \hspace{1cm} (8)

where $W$ is the void gap width, $\lambda$ is the wavelength of light, $H$ is the height of the VACNT structure, and $x$ and $y$ are the substrate plane. To get the percentage of light that will be transmitted through the void gap ($T_{gap}$) without reflection, we integrate equation (8) over the area in the void gap and normalize it by dividing by the intensity over the whole substrate plane.

$$T_{gap} = \frac{\int \int \text{sinc} \left( \frac{\pi W x}{\lambda H} \right)^2 \text{sinc} \left( \frac{\pi W y}{\lambda H} \right)^2 \text{d}x \text{d}y}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \text{sinc} \left( \frac{\pi W x}{\lambda H} \right)^2 \text{sinc} \left( \frac{\pi W y}{\lambda H} \right)^2 \text{d}x \text{d}y}$$  \hspace{1cm} (9)

However, as the light is transmitted down the void gap, some of the light will reflect off the VACNT sidewalls and contribute to the transmission. As illustrated in figure 3.2, some of the light will transmit down the gap without reflection (order ‘0’ with angle $\theta_0$), some will be reflected
once (order ‘1’ with angle \( \theta_1 \)), some will be reflected twice (order ‘2’ with angle \( \theta_2 \)), and so on (order ‘n’). To account for each reflection, we have a separate integral for each reflection order:

\[
T_{gap}(n) = R_{sw}^{n} \frac{\int \int \text{sinc} \left( \frac{\pi W x}{\lambda H} \right)^2 \text{sinc} \left( \frac{\pi W y}{\lambda H} \right)^2 \, dx \, dy}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \text{sinc} \left( \frac{\pi W x}{\lambda H} \right)^2 \text{sinc} \left( \frac{\pi W y}{\lambda H} \right)^2 \, dx \, dy}
\] (10)

Prior work has shown that top surface reflectance is dependent on angle but changes by no more than 2X between 0 and \( \sim 50^\circ \)[30]. In our model we do not incorporate the angle dependance of reflectance, the top surface reflectance is used only as an estimate of the side wall reflectance, \( R_{sw} \). We use a value of 0.06% for \( R_{sw} \) with 1 nm iron catalyst thickness samples which is based on top surface reflectance from non-patterned 1nm Fe samples at normal incidence that we report on in the results section. The bounds for each integration in the numerator will correspond to the limits of that reflection order. As depicted in figure 3.2, for n=0, the there is no light reflection on the VACNT sidewalls, and the limits of integration are \( x = -W/2 \) and \( W/2 \). For n=1, the limits of integration are for reflections off the right wall are \( x = W/2 \) and \( 3W/2 \), but there is also a reflection off the left wall of equal magnitude. To account for reflections off both walls, we will multiply the integral, or the right wall reflection, by 2. For n order one or higher, the integral bounds for the right wall reflection are \( (n-0.5)*W \) and \( (n+0.5)*W \). The resulting \( T_{gap} \) for each reflection is:

\[
T_{gap}(n) = R_{sw}^{n} \frac{2 \int_{-(n-0.5)W}^{(n+0.5)W} \int_{-(n-0.5)W}^{(n+0.5)W} \text{sinc} \left( \frac{\pi W x}{\lambda H} \right)^2 \text{sinc} \left( \frac{\pi W y}{\lambda H} \right)^2 \, dx \, dy}{2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \text{sinc} \left( \frac{\pi W x}{\lambda H} \right)^2 \text{sinc} \left( \frac{\pi W y}{\lambda H} \right)^2 \, dx \, dy}
\] (11)
Summing up all the terms then gives the response from the light diffracting through the VACNT structure:

$$T_{\text{gap}} = \frac{\int_{-0.5W}^{0.5W} \int_{-0.5W}^{0.5W} \text{sinc} \left( \frac{\pi Wx}{\lambda H} \right)^2 \text{sinc} \left( \frac{\pi Wy}{\lambda H} \right)^2 \, dx \, dy}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \text{sinc} \left( \frac{\pi Wx}{\lambda H} \right)^2 \text{sinc} \left( \frac{\pi Wy}{\lambda H} \right)^2 \, dx \, dy}$$

$$+ \sum_{n=1}^{\infty} R_{\text{sw}}^n \left( \frac{4 \int_{(n-0.5)W}^{(n+0.5)W} \int_{(n-0.5)W}^{(n+0.5)W} \text{sinc} \left( \frac{\pi Wx}{\lambda H} \right)^2 \text{sinc} \left( \frac{\pi Wy}{\lambda H} \right)^2 \, dx \, dy}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \text{sinc} \left( \frac{\pi Wx}{\lambda H} \right)^2 \text{sinc} \left( \frac{\pi Wy}{\lambda H} \right)^2 \, dx \, dy} \right)$$

Figure 3.2 A 2D representation of refraction and reflection inside the VACNT void gap. To more easily show the lateral distance for n reflections, the light lines continue through the VACNT to the substrate. The lateral distance that light will traverse through the VACNT structure without reflecting off the sidewalls is between x = (-W/2, W/2), with 0 being the center of the void gap. The lateral distance that light will traverse through the VACNT structure with a single reflection off the sidewalls is between x = (W/2, 3W/2). The lateral distance that light will traverse through the VACNT structure with two reflections off the sidewalls is between x = (3W/2, 5W/2).
Since each additional reflection contribution has significantly less light than the previous one. Using a $R_{sw}$ of 0.06 %, reflections above 5th order have a total contribution of less than 0.1 % of the total reflected light (less than 0.00001 % of incident light) and were truncated.

### 3.3 Methods

#### 3.3.1 VACNT Forest Growth

The VACNT growth process is described by[9, 16]. For patterned VACNT growth, catalyst patterns were formed on the surface of a 100 mm silicon wafer using a lift-off process as follows. First 50 nm of alumina was deposited as catalyst support using e-beam evaporation. Then photoresist (AZ Electronic Materials AZ3312) was spun onto the wafer and contact lithography was used to pattern the resist. Following lithography, a thin film of iron was deposited onto the wafer as the VACNT growth catalyst. The photoresist was then removed by sonicating the samples in NMP for 20 minutes and rinsed with water for 30s. For non-patterned forest growth, the catalyst deposition consisted of alumina deposition followed by iron deposition. All wafers were cleaved into 7 mm square pieces prior to VACNT growth.

The catalyst coated wafer pieces were placed in a 25 mm inner diameter tube furnace and heated to 750 ºC in ~ 6 minutes while flowing 307 sccm of hydrogen. Once 750 ºC was reached, the VACNTs were grown by adding 335 sccm of ethylene to the hydrogen flow. After 10 minutes, the VACNTs reached the desired height of ~600 μm, the ethylene was shut off, and the furnace was shut off to cool down. While cooling, at around 400 ºC, argon gas was introduced and then the hydrogen was shut off. After the furnace reached 200 ºC, argon was shut off and the samples were removed.
To roughen the tops of the VACNT forests, some samples were etched with an oxygen plasma using a parallel plate etcher (Technics Planer Etch II). A base pressure of 60 mtorr was established and then 100 sccm of oxygen gas was flowed. The etch process pressure was 300 mtorr, the etch power was 200 watts, and the etch duration was 1 minute.

3.3.2 SEM characterization

Since the carbon nanotube diameters are only a few nanometers, we used a high-resolution scanning electron microscope to get the diameter and an estimate of CNT density in the top surface region. Images are taken on a FEI Co VARIOS G4 at multiple magnifications with a beam current of 0.1 nA and an energy of 10 keV. Nanotube diameters, visible lengths, and areal densities are extracted from top surface images of the VACNT forests, using ImageJ software. The areal density is the number of tube visible in a given area, and CNT volume density is estimated using the areal density and a depth of field of 1 μm.

3.3.3 Reflectance characterization

Optical reflectance was measured using an integrating sphere setup[17, 22, 30]. Our setup contains an integrating sphere (ThorLabs IS200-4) with an 8-mW helium-neon laser (633 nm) as the light source, a PIN photodiode as the signal detector, and a picoammeter (Keithley 487) to measure the photodiode current.

To acquire the total reflectance of the VACNT forests, scattering measurements of a ‘reference’, ‘sample’, and ‘background’ were taken. The ‘reference’ signal was from a PTFE material (ThorLabs SM05CP2C) with a known reflectance of 99 %, the ‘sample’ signal was from the VACNT forests, and the ‘background’ was the background light signal which includes
scattered light from air and dust in the air. ‘Background’ was obtained by letting the laser pass through and exit the integrating sphere into a beam dump on the far side.

Since our VACNT forests are four orders of magnitude less reflective than the reference, we verified the linearity of our detector system over the range of optical intensity used by adjusting the laser intensity with a set of neutral density filters.

3.4 Results

To understand how iron catalyst thickness physically affects the carbon volume density on the top of the forest, we took SEM images of VACNTs grown using 1 nm, 4 nm, and 7 nm iron catalyst thicknesses. Figures 3.3A, 3.3B, and 3.3C show the tops of VACNT forests grown with these iron catalyst thickness. Diameters of nanotubes for these three iron catalyst thicknesses were measured to be 8.2±2 nm, 9.4±3 nm, and 12.5±6 nm (± range is the standard deviation). Figure 3.3D shows that as the iron catalyst gets thicker, the average nanotube diameter increases, with a much higher variation in the nanotube diameter for thicker iron layers. The graphed diameters are the average of 150-300 nanotube diameter measurements taken at the top of the VACNT forest for each growth condition.

Figure 3.3E contains a graph of the top surface visible areal density of nanotubes at the top of the forest and the estimated nanotube top surface length vs. iron catalyst thickness. The measured areal density is the number of visible nanotubes in a given area. The top surface visible nanotubes are the those within the SEM depth of field which was estimated to be ~1 μm. The ~1 μm was derived from examining SEM images with known vertical feature sizes to find the depth of field. The density of nanotubes from 1 nm, 4 nm, and 7 nm catalyst were measured to be 110±12, 83±9, and 70±8 CNT/μm³ respectively, the error ranges are the standard deviation.
The average length of nanotube segments observed in top surface SEM images was estimated using in-plane measurements of length of nanotubes on SEM micrographs taken with a horizontal field width of 4.14 μm and a working distance of 4.2 mm. More than 200 nanotubes were measured for each catalyst thickness, and for the 7 nm catalyst, measurements were taken from multiple images. Nanotube segments that extended outside the field of view were not included. As seen in figure 3.3E, thicker iron catalyst resulted in longer visible nanotube segments; these lengths were measured to be 66±10, 105±11, and 204±15 nm for 1 nm, 4 nm, and 7 nm iron thickness respectively; the error ranges are the calculated standard deviations. Figure 3.3F shows the reflectance measurements vs the iron catalyst thickness of non-patterned VACNTs.
Figure 3.4A is a SEM micrograph showing the top of a non-patterned VACNT forest. Figure 3.4B, 3.4C, and 3.4D are SEM micrographs for various top area surface fractions (TFAS) of the VACNT forests with patterned void gaps of 1 μm, 4 μm, and 100 μm respectively. Figure 3.4E contains reflectance vs TFAS data for 1 nm thick iron catalyst growths. Figure 3.4F contains the TFAS, reflectance, and standard deviation data used for the plot in figure 3.4E.

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<th>Reflectance</th>
<th>STD</th>
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<td>0.061%</td>
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<td>Yes</td>
<td>0.009%</td>
<td>0.002%</td>
</tr>
</tbody>
</table>

Figure 3.4 Representative SEM micrographs and reflectance data for patterned VACNT with various top surface area fractions (TSAF).  A) Top surface image of a non-patterned VACNT forest, TSAF = 1.  B) Top view of a VACNT forest with 1 μm void gap yielding a TSAF of 0.75.  C) Top view of a VACNT forest with 4 μm void gap yielding a TSAF of 0.4.  D) Top view of a VACNT forest with 100 μm void gap yielding a TSAF of 0.075.  E) Table of reflectance data for 1 nm iron catalyst VACNT samples with various TSAFs.  F) Reflectance vs TFAS plot. Both etched and non-etched data is included.

To determine the repeatability of the reflectance measurements, a single 0.4 TSAF sample was measured five times. Each time it was measured, the sample was mounted, measured, and then removed from the optical test setup. The repeated measurements on the sample yielded an
average ‘reference’ of $5.4 \times 10^{-5}$ A, an average ‘background’ of $1.4 \times 10^{-9}$ A, and an average ‘sample’ of $1.5 \times 10^{-8}$ A, with standard deviations of $5.0 \times 10^{-9}$ A, $7.2 \times 10^{-11}$ A, and $1.7 \times 10^{-10}$ A respectively. This resulted in an average reflectance of 0.0257 % with a standard deviation of 0.0002 %. This measurement uncertainty is roughly equal to the background measurement variation and is ~1/100 of the measured reflectance values.

Sample to sample variability was measured using three separately grown samples of our lowest reflectance geometry (TFAS of 0.4, plasma etched). The measured reflectances for the three samples were 0.0098 %, 0.010 %, and 0.0083 % yielding an average reflectance for this geometry of 0.0094 % and standard deviation of 0.001 %. This sample-to-sample variation is five times larger than the reflectance measurement repeatability on a given sample (described in the previous paragraph).

### 3.5 Discussion

Effective medium theories predict that as volume fraction of carbon decreases in a non-patterned VACNT forest, the effective permittivity (and reflection) decreases as well[32]. Thinner iron catalyst (over the range tested) resulted in a higher density of nanotubes, but the nanotube diameter and length at the top of the forest both decreased, resulting in an overall lower carbon volume fraction. As seen in figure 3.3F, as the carbon volume fraction was reduced, the reflectance was lowered in qualitative agreement with effective medium theory.
Figure 3.5A contains data for 1 nm iron catalyst with varying top surface areas including no pattern (100 % VACNT top surface area), 1 μm void gap pattern (75 % VACNT top surface area), 3 μm void gap pattern (55 % VACNT top surface area), 4 μm void gap pattern (40 % VACNT top surface area), and 100 μm void gap pattern (7 % VACNT top surface area). The etched samples (in the red box in figure 3.5A) are of non-patterned VACNT forests and 4 μm void gap patterns.

Figure 3.5B shows reflectance results for patterned VACNTs vs void gap size, grown with 1 nm iron catalyst. Predictions for patterned VACNT reflectance (equation 7) is also plotted for figure 3.5B. In the small void gaps (<10 μm) we appear to be limited by the top surface reflection, i.e., reflection drops with increasing void gap size. Once the void gap reaches ~10 μm, the $R_{Void}$ contribution ($T_{gap}R_{sub}T_{gap}$) becomes significant and starts to noticeably increase the total reflectance. For large void gap sizes (~100 μm), light will transmit through the VACNT structures with almost no loss ($T_{Void} \approx 1$), and since $R_{Void} = T_{Void}R_{sub}T_{Void}$, $R_{sub}$ can be estimated to be the
measured reflectance at large void gaps. The 100 μm void gap measurement was used to fit the value of $R_{Sub}$ to 0.35%.

Patterned samples with a 1 nm iron catalyst thickness and a 4 μm void gap, had a reflectance of only 0.02%. We further reduced the reflectivity of these samples by exposing them to 30 seconds of an oxygen plasma. This O$_2$ plasma etches the carbon on the top of the VACNTs, roughening up the surface and lowering the carbon volume fraction. This results in a reflectance of 0.009%, the lowest reflectance (diffuse + specular) reported to date.

These very low reported reflectance values invite a comment on measurement sensitivity and uncertainty. Our measurement repeatability shows a variation of only ~1/100 of the measured reflectance, giving us good confidence in the reproducibility of our measured reflectance values. The sample-to-sample variation in our lowest reflectance samples (TFAS of 0.4, plasma etched) was ~1/9 of the average reflectance; this sample-to-sample variation is not surprising due to commonly observed growth-to-growth sample variations in nanotube diameter and density. While these measurements were performed at only one wavelength, 633 nm, prior work has shown that VACNTs have a relatively flat optical response throughout the infrared and into the red but increase by about 2X at shorter visible wavelengths[50].

3.6 Conclusion

We grew VACNTs with differing nanotube diameters and densities by adjusting catalyst thicknesses from 1-7 nm. Over this range, the 1 nm iron catalyst resulted in the lowest carbon volume fraction and the lowest reflectance. Furthermore, we lithographically patterned the 1 nm catalyst to create open void gaps in the VACNT forests with widths of 1, 3, 4, and 100 microns. These larger than wavelength scale voids significantly reduced reflectance of the VACNTs,
particularly for the 1-4 micron openings. To understand the total reflectance from patterned VACNT forests, we developed a model incorporating top-surface reflection and void-space transmission, which was in good agreement with our measured data. The lowest observed total reflectance (diffuse + specular) was in 4 micron void patterned VACNT structures (40 % top surface area) treated with oxygen plasma which exhibited an average reflectance of 0.009 % ±0.0008%, lower than any total reflectance previously reported.
Chapter 4: Conclusion

I created a mechanically robust ultra-black material which can be handled and transferred from one substrate to another. The reflectance of this ultra-black material is less than 0.1%. To create darker materials, we can tune the end growth of the VACNT forest to have an ultra-low density of nanotubes. The process of inverting and transferring the sample to a new substrate allows the darkest part of the material, which is the bottom of the nanotube forest, to be utilized.

I also created and tested mathematical theory for the reflectance of a VACNT based ultra-black material using the surface area of the top growth and area of the growth catalyst. As of March 2022, I have created the darkest material known, with a proposed plan to create even darker materials.

In the future, I propose further reducing the reflectivity of a VACNT material by tuning the open area patterned catalyst and tuning the end of growth parameters to lower the CNT density at the bottom of the forest. I recommend including a second, non-patterned growth that would cover the substrate floor layer to reduce the reflectivity of the substrate and would allow for larger openings to be patterned.
References


APPENDIX

Appendix 1: Fabrication of Microscale Encapsulated Silicon Coated VACNT Electrodes

Appendix 1.1 Encapsulation Fabrication

The fabrication process for micro patterned encapsulation layers is outlined in figure A1.1. To fabricate the cells, we started with a polished silicon wafer (figure A1.1A). Using electron beam deposition (figure 1.4), we coated the wafer with 50 nm of alumina (figure A1.1B) to act as our VACNT growth catalyst diffusion barrier. We then patterned 1 cm² circles with either a cross hatch pattern or a paver stone pattern using UV lithography (figure A1.1C), and, using a thermal evaporation process, deposited 4 nm of iron for the VACNT growth catalyst (figure A1.1D). We used a lift-off process to remove the photoresist by sonicating the sample in a NMP bath for 20 minutes, then rinsed with water for 30 seconds. This transferred the pattern from photoresist to the iron catalyst (figure A1.1E).

To grow the VACNTs (figure A1.1F), we placed the sample in a tube furnace (figure 1.5) and flowed 307 sccm of hydrogen. The furnace was then heated to 750 °C and 335 sccm of ethylene was introduced to the hydrogen flow. We varied the height of the carbon nanotube forest by adjusting the time that the gases are flown across the sample, with the VACNTs having a growth rate of ~1 μm/s for the first five minutes of growth. After growth, we heated the furnace to 900 °C and flowed ethylene for 5 minutes, depositing a thin layer of nanocrystalline carbon uniformly over the carbon nanotubes (figure A1.1G). This additional carbon layer helps structurally lock the carbon nanotubes together, making the carbon scaffold more mechanically resilient to stresses from handling and liquid process steps. Once the VACNTs have been infiltrated with carbon, the ethylene was shut off, and the furnace was turned off to cool. When the furnace reached ~400 °C,
we introduced argon gas, and shut off the hydrogen gas. Once the furnace temperature dropped below 200 °C, we removed the sample and shut off the argon.

We then fully infiltrated the VACNT structures with silicon, as shown in figure 4.9H. This silicon is a sacrificial material used to enable the deposition of the encapsulation layer around the VACNTs. We placed the sample in a LPCVD tube furnace, and purged the system with nitrogen for 5 minutes. We lowered the pressure inside the furnace to 20 mtorr, and heated the tube furnace to 585 °C. We flowed 70 sccm of silane for 60 minutes to completely fill the structure with silicon. We then turned off the silane, purged the system with nitrogen, and allowed the furnace cool off to 100 °C before removing the sample.
As seen in figure A1.2A, the top surface of the silicon filled VACNT structure has rounded silicon bumps, with the VACNTs buried underneath. To physically connect the VACNT forest with the encapsulation layer, we removed the top of the silicon to expose the VACNT structure, as seen in figure 4.9I. To do this, we placed the sample in a reactive ion etching chamber, brought the chamber pressure down to 5 mtorr, and turned on CF$_4$ gas to increase the chamber pressure to 200 mtorr. We chose this etchant since it preferentially etches silicon over carbon, though some carbon will still be etched. We then turned on a plasma, with a power of 300 W power to etch the silicon. After 4 minutes of etching, we turned the plasma and CH4 gas off and increased the chamber pressure to atmospheric pressure before removing the sample. The top of the silicon filled VACNT structure is now pointed and rough, with the tips of the carbon nanotubes sticking out of the carbon, as seen in figure A1.2B

We next deposited the carbon encapsulation layer, which completely encloses the VACNT structure (figure A1.1J). We deposited the encapsulation layer using the same setup that we used for carbon infiltration (figure 1.5). We placed the sample in a tube furnace, flowed 307 sccm of hydrogen and heated the furnace up to 900 °C. We then introduced 335 sccm of ethylene to the
hydrogen for 30 minutes. This created a solid layer of nanocrystalline carbon that encases the entire sample and is approximately 250 nm thick.

To release the encapsulated sample from the substrate, we scratched a mark into the substrate around the sample to expose the substrate to be etched. We needed to etch around the sample because there is a uniform layer of carbon encapsulating the sample and substrate, and our etchant to release the sample from the substrate does not etch carbon. We then placed the sample in a HF bath for 3 hours to release from the substrate (figure A1.1K). We then rinsed the sample in two consecutive baths made of water mixed with sodium bicarbonate to neutralize the HF, then rinsed in purified water, then IPA, and finally removed to dry.

To remove the silicon from the sample, we placed the samples face down in an oxygen plasma to remove a thin carbon floor layer that was created during the carbon infiltration of the nanotubes, exposing the bulk silicon. We then placed the sample in a KOH bath at 70 °C for 3 hours to remove all of the silicon (figure A1.1L). At this point, the samples consist of the carbon encapsulation layer with the carbon nanotubes that can be used as a scaffold to fill the structure with whatever is needed.

We deposited ~20% by volume of silicon back into the structure (figure A1.1M) to mechanically stress the encapsulation layer. We then added the copper current collector to the bottom of the sample, sealing the VACNTs inside a carbon encapsulation on the top and sides, with a copper film on the bottom. We used a custom holder to clamp the sample in place during copper deposition as depicted in figure A1.3. The holder has 1 cm diameter circular depressions half a centimeter deep into a 1 cm thick metal plate, and 0.9 cm² holes drilled through the plate centered in the larger holes. This created a hole large enough to fit the sample inside while resting on a lip. The smaller opening allowed for direct line of sight from the deposition source to the
bottom of the CNT sample. We deposited a 500 nm thick copper current collector onto the back of the structure using a thermal PVD technique (figure A1.1N).

**Appendix 1.2 Mechanically stressing the encapsulation layer**

We mechanically stressed these encapsulations by adding silicon around the nanotubes, and then inserted lithium into the silicon, acting as a half-cell battery. We chose this configuration because when silicon is filled with lithium ions, there are over four lithium atoms for every one silicon, resulting in a 300% expansion. This expanded thin-film silicon will push outward onto the encapsulation layer, causing stress, and exposing potential weak points in the encapsulation.
To use sample as a half-cell battery, as seen in figure A1.4, we placed a spacer in a bottom cap of a CR2025 coin cell, followed by the encapsulated silicon coated carbon nanotube structures. We added a few drops of LiPF6 electrolyte onto the nanotube structure to wet the sample, followed by two 25 μm Celgard 2400 polypropylene separator layers, and a Li metal counter electrode disk that is 15.6 mm in diameter and 250 μm thick (MTI corp.). We filled the rest of the cell with electrolyte, and placed a spacer and a wave spring on top, ensuring electrical contact for both the top and bottom electrodes. The electrolyte used for these batteries was 1M LiPF6 in a 1:1 ratio of ethylene carbonate/diethyl carbonate electrolyte.

A1.4 Half-Cell Assembly. Battery is assembled in a glove box, and is put together in order from bottom to top. A spacer is placed in a CR2025 bottom cap, then the encapsulated sample. A few drops of electrolyte are added, then two separators to prevent shorting between the cathode and anode, then a lithium foil to act as the counter electrode and to supply lithium ions. A second spacer and a wave spring are added to ensure electrical contact is maintained, and finally the top cap is placed on top.
To fill the encapsulated silicon coated VACNT (the anode) with lithium, we applied 0.1 V across the cell. As illustrated on the left side of figure A1.5, lithium atoms on the cathode side are divided into electrons and lithium ions and the latter travels through the electrolyte and separator into the more energetically favorable anode. The concentration of positively charged ions pulls the negatively charged electrons towards the anode. The electrolyte has high resistance for the electrons, so they travel through the cathode current collector, into a power source, then through the anode current collector and recombine with the lithium ion inside the silicon.

To remove the lithium from the half-cell, we applied 1V across the cell, forcing electrons to the cathode through the power source. The lithium ions then extricate themselves from the silicon, travel through the electrolyte to recombine with electrons in the cathode, as shown on the right side of figure A1.5. This process of adding and removing lithium from the electrode is repeated 30 times, before disassembling and imaging the samples.

A1.5 Half-cell battery charging and discharging. A) As the battery discharges, lithium ions cross through the electrolyte to the anode, and the electrons travel through an external path to recombine with the lithium ions. B) To charge the battery, electrons are pulled from the anode and pushed to the cathode, and the lithium ions travel through the electrolyte to recombine with the electrons in the cathode.

To remove the lithium from the half-cell, we applied 1V across the cell, forcing electrons to the cathode through the power source. The lithium ions then extricate themselves from the silicon, travel through the electrolyte to recombine with electrons in the cathode, as shown on the right side of figure A1.5. This process of adding and removing lithium from the electrode is repeated 30 times, before disassembling and imaging the samples.
Appendix 1.3 Cross-Hatch Encapsulated

We designed the cross-hatch patterned electrodes to have 10 μm square holes spaced 10 μm apart repeated in both x and y directions, as shown in figure A1.6A. We implemented the micro-hole design to increase the surface area of the encapsulation. The design was also intended to stop large cracks from forming and propagating through the whole structure.

After stressing the encapsulation layer, we disassembled the cell and imaged it using a SEM, and figure A1.6B shows that the cross hatch encapsulated cell was not able to contain the stress that we applied to the encapsulation layer. The inset in figure A1.6B shows that there are large, broken-apart chunks of the electrode that were deformed from the strain of the silicon expansion, and the top encapsulation layer was completely removed.

Appendix 1.4 Micropillar Encapsulation
To better contain the stresses on the encapsulation layer, we decided to pattern the VACNTs into self-contained micropillars, as shown in figure A1.7A. We hypothesized that smaller features would better contain the stresses, and if the encapsulation layer fractured on one micropillar, it would not continue on to the aggregate cell.

Depositing copper on these micropillar encapsulations required a different approach due to the fragility of the samples. The cross-hatch patterned or non-patterned cells were rigid enough to maintain their shape while being lifted around the edges, but the micropillar patterned samples would bend and fall out of the copper deposition holder. To deposit the copper electrode backing, we applied a drop of super glue onto a wafer, and carefully lowered the sample top side down onto the super glue and left it to dry. After deposition, we removed the super glue by gently submerging the wafer into an acetone bath for 1 hour. We rinsed the sample in IPA, removed it to dry, and later assembled and cycled it.

After cycling the half-cells, the cells were deconstructed and imaged using a SEM. The sample revealed that the micropillars were completely delaminated and disconnected from the current collector, as shown in figure A1.7B. The pillars, though disconnected from each other,
still had an intact encapsulation layer (inset of figure A1.7B). We believe the pillar separation came from the expansion and contraction of the silicon pushing on the encapsulation layer and putting stress on the connection between the micropillars and the floor layer. The stress was enough to break the connection between the micropillars and the floor layer at the joint.

**Appendix 1.5 Strengthened Micropillar Encapsulation**

During fabrication, we found a webbing structure between the micropillars on a few of the micropillar patterned encapsulated samples (figure A1.8A). The webbing created multiple connections between the pillars, holding them in place. After cycling, we found that the webbing held the micropillars together during the expansion and contraction processes, even though the floor layer broke free at the base of the micropillars, as seen in figure A1.8B.

In attempting to recreate this, we noticed that the webbing looks to be as thick as the carbon layer. We went through each of the steps that could result in the webbing to appear and narrowed the possible process steps to the following: during iron lift-off in NMP before VACNT growth and
the removal of bulk silicon with KOH. We then investigated this narrowed list of possible processes.

For the lift-off process step, we took an iron coated wafer and spray coated it with CNTs. The goal was that the sprayed on CNTs would grow into the structure as the VACNTs grew, adding the webbing structure. We found that the CNT film stayed on the surface and did not penetrate into forest as we hoped.

We hypothesized that the bulk silicon removal step was the more likely cause for creating the webbing since previous carbon nanotubes dislodged during the bulk silicon removal step. We theorized that the carbon nanotubes from the previous sample were floating in the KOH bath with the strengthened micropillar sample, and the CNTs dispersed between the micropillars and adhered to the encapsulation walls. We tried to replicate this by scraping carbon nanotubes into a clean KOH bath, sonicating the solution, and submersing a sample during the bulk silicon removal step. We also tried scraping CNTs into the IPA solution that we used after the KOH process, in case the nanotubes were affixed during that step. Unfortunately, we did not see webbing on any of these samples.

Appendix 1.6 Conclusion

We created carbon encapsulations that encompasses patterned VACNTs. We stressed these encapsulations through coating the carbon nanotubes with silicon, and then inserting lithium into the silicon, causing the silicon to expand. We found that high stresses from the expanding silicon to the encapsulation fractured the cross-hatch encapsulation layer, but the smaller micropillar encapsulation remained intact. Even though the encapsulation layer did not break, the micropillars detached from the floor layer which was holding the pillars together. The strengthened
micropillars were able to remain intact during stressing, but we were unable to recreate the strengthened web feature.
Appendix 2: Fabrication of High Aspect Ratio Copper Mesh

Appendix 2.1 Introduction

Copper has high thermal and electrical conductivities, and is used in many electronics to conduct electricity including interconnects and vias for semiconductor manufacturing. Selectively depositing copper in tight spaces is complicated and is needed for integrated circuits, MEMs, microchannel chemical reactors, etc. PVD copper deposition is appropriate for deposition on a nearly flat substrate with no crevices or high aspect ratio structures. But if there are uneven or irregular surfaces or structures, such as high aspect ratio structures, overhangs, or channels, line of sight deposition methods will not uniformly coat all surfaces. For these more challenging applications, CVD or liquid deposition methods are required[51, 52].

Our goal was to create a high aspect ratio copper mesh with 1 μm wide sidewalls and 4 μm wide openings, as shown in figure A2.1. We chose to deposit copper on patterned VACNTs because they have high electrical conductivity, are easily patterned, have a high aspect ratio[16], and other metals have been successfully deposited onto them[8]. We fabricated these high aspect ratio copper structures by depositing copper using galvanic displacement and electroplating.
Appendix 2.2 Fabrication

To create this structure, we grew patterned VACNTs using methods discussed in chapter 1.4. We deposited 50 nm of alumina on a silicon wafer (figure A2.2B). Since the desired pattern has 1 μm feature sizes, we patterned the wafer using the less viscous AZ3312 photoresist (figure A2.2C). We then deposited 1 nm of iron as the VACNT growth catalyst (figure A2.2D), and removed the remaining photoresist by placing the sample in sonicated NMP for 20 minutes, then rinsing with water for 30s. Using this lift-off process transfers the lithography pattern to the iron (figure A2.2E).

We grew the samples in a 1-inch inner diameter tube furnace as follows. We placed the samples in the furnace and heated the furnace up to 750 °C while flowing 307 sccm of hydrogen. Once 750 °C was reached, we grew the VACNTs by adding 335 sccm of ethylene to the hydrogen flow. After one minute, the VACNTs reached the desired height of ~100 μm (figure A2.2F). We shut off the ethylene, and heated the furnace to 900 °C. At 900 °C, we introduced 335 sccm of ethylene to the hydrogen flow for three minutes to infiltrate the VACNTs with a thin layer of nanocrystalline carbon, mechanically strengthening the structures enough to be submerged in a liquid solution and handled without breaking them (figure A2.2G). After infiltration, we shut off the furnace to cool down. While cooling, at around 400 °C, we introduced argon gas and then shut off the hydrogen. After the furnace reached 200 °C, we removed the samples.

We filled the VACNT structure with silicon using LPCVD as discussed in chapter 1.3. We placed the strengthened VACNT mesh into the LPCVD tube furnace, brought the pressure down to 20 mtorr, and heated it to 585 °C. We introduced 70 sccm of silane to deposit silicon into the VACNT mesh (figure A2.2H). After 90 minutes, we shut off the silane and cooled the tube
furnace down to 100 °C before opening it and removing the sample. With the high amount of silicon deposited, the stresses caused the samples to release from the substrate.

**Appendix 2.3 Galvanic Displacement**

We first created three dimensional copper structures using galvanic displacement[51, 53]. This is a highly selective process that does not require any pretreatment of the sample[54] or custom circuitry or equipment. Instead, this method uses a simple substitutional process where
copper ions automatically and selectively[55] replace silicon atoms [56]. The commonly reported chemical reaction for this process (adjusted for copper) is[57]:

\[
Cu^{2+}_{(aq)} + Si_{(s)} + 6F^{-}_{(aq)} = M_{(s)} + SiF_{2-}^{2}_{(aq)}
\] (4.1)

To prepare the galvanic displacement bath, we started with 67 mL of high purity H2O, then slowly added 0.188g of CuSO4 and 7.8 mL 48% HF[58], then stirred the mixture for one minute. We then placed the silicon infiltrated samples in the bath for galvanic for 12 hours to substitute the silicon for copper.

Figure A2.3A shows a 1 cm by 3 cm silicon infiltrated VACNT mesh before it was placed in the galvanic displacement bath, and figure 3.1B shows the same sample after being placed in the galvanic displacement solution for 5 minutes. The surface of the silicon filled VACNT mesh structure turned a copper color which suggests that the desired reaction has started to occur.

After deposition, we rinsed the sample in water and IPA then cleaved in half and imaged it under an optical microscope and a SEM to perform elemental analysis. As shown in figure A2.4A, copper dendrites formed on the top surface of the silicon filled VACNT mesh instead of
forming a smooth conformal film throughout the full structure. Figure A2.4B shows a SEM image of the same structure with an EDS line scan for elemental analysis with results displayed in figure A2.4C. The EDS line scan shows that copper deposited on the outside of the structure and almost none deposited inside the structure.

With this low amount of copper deposition inside the structure, we altered the galvanic displacement recipe using 62.5 mL NH₄F 40% as our silicon oxidizer, 25 mL microPore water, 0.22 g ascorbic acid (C₆H₈O₆) to increase copper adhesion, 37.5 mL Methanol (CH₃OH), and 0.175 g Potassium Sodium Tartrate (KNaC₄H₄O₆) to help lower the internal stresses and help with adhesion, and 0.313 g CuSO₄-5H₂O as the copper source[54].

A2.4 Galvanic deposition – Images from left to right are: optical image of sample with copper dendrites on the outside. SEM image showing elemental analysis scan. Elemental analysis showing no copper on the inside of the VACNT structure.
We created new samples, filled them with silicon, and submerged them in the altered galvanic displacement bath overnight. We removed the samples, rinsed them in water and IPA, and broke off a piece to inspect the interior for copper.

The SEM image in figure A2.5A shows there are solid deposits at the base inside the mesh structure. The EDS line scan in figure A2.5B shows that these solid deposits are copper, and about 10-15 microns into the structure, there is still solid silicon with no significant amount of copper deposition. We attribute this to the solid copper deposits sealing off the copper ions from penetrating deeper inside the mesh structure.

*A2.5 Ammonium fluoride galvanic displacement. A) SEM image of a cleaved sample after copper deposition. The arrow represents where the EDS line scan was taken. B) EDS line scan data.*
Appendix 2.4 Electroplating

Electroplating is a more controlled approach[51] where the deposition rate is regulated by an external circuit. As depicted in figure A2.6, a power source pulls electrons from a copper electrode, causing the copper electrode to become positively charged, and releases Cu$^{2+}$ ions into the electroplating bath. The electrons are pushed to the electrode holding the sample, drawing the copper ions toward it. The copper ions then deposit onto the sample where they recombine with the electrons. The amount of current forced through the electroplating bath will determine the deposition rate onto the sample.

Since electroplating does not use a substitution method like galvanic displacement, we did not need to deposit silicon on the carbon infiltrated VACNT mesh (figure A2.2H). Instead, after
growth and carbon infiltration (figure A2.2G), we placed the samples in a KOH bath heated to 70 °C for one hour to release the VACNT mesh from the substrate. We then rinsed the sample in water, IPA, then removed it to dry.

One of the downsides for electroplating is the necessary pretreatment of the sample. For the VACNT mesh structure, nucleation sites had to be created for the copper to deposit. To create nucleation sites, we functionalized the surface of the carbon nanotubes by placing a carbon infiltrated VACNT sample in an ozone generator for 60 minutes to break some exterior carbon-carbon bonds.

We then attached the treated VACNT mesh to a thinly cut copper foil for the cathode, and we used a copper foil for the anode to supply the copper ions, as shown in figure A2.6. To electrically isolate the copper foil holding the sample from electrodeposition, we wrapped insulated tape around the copper foil and cut out a hole the size of the sample. We used electrically conductive double sided carbon tape to affix the sample to the exposed copper foil.

To prepare the electrolyte solution, we started with 90.7 mL of H₂O, then slowly added 9.3 mL of H₂SO₄, and 6g of CuSO₄. We also included the additives 100 mg of PEG and 0.04 mL of HCl [59, 60] to slow the copper deposition near the top.

To control the current through the bath and the copper deposition rate, I created an electrical circuit, displayed in figure A2.7. We used a power supply to apply 5-20 volts across the circuit. Arduino pin D7 created a pulse width modulated signal, which was flattened to 2.5 V, using the resistor/capacitor pair. We connected the 2.5 V signal to the negative input of the op-amp as a reference voltage. Arduino pin D10 created a pulse that forced the op-amp output high/low depending on if the pulse was higher/lower than the 2.5 V reference voltage. When the op-amp output was high, the n-channel MOSFET turned on allowing current to flow through the bath,
depositing copper. We used a 100 Ω resistor to calculate the current through the bath. Current was pulsed “on” to allow copper deposition to occur to depletion, then “off” to allow the copper ions to diffuse into the mesh. This process was repeated for the deposition time.

To calculate how long we needed to electroplate to fill the structure with copper, we started with the relation \( \rho = \frac{m}{V} \). Substituting in \( m = \frac{t M_{\text{Cu}}}{N_a q/2} \) and solving for time, we get

\[
t = \frac{q \rho N_a V}{2 M_{\text{Cu}} I}
\]

where \( q \) is the charge of an electron, \( \rho \) is the density of copper, \( N_a \) is Avogadro's number, \( V \) is the volume to fill with copper, \( M_{\text{Cu}} \) is the molar mass of copper, and \( I \) is the current. Inserting all of the constants results in the simple relationship:

A2.7 Electroplating Circuit Diagram. An Arduino was used to create a pulse that would force an op-amp into the high and low states, which would turn on and off an n-channel MOSFET. This MOSFET would either block or allow current to flow through the bath, controlling the copper deposition. The 100 Ω resistor was used to measure the current.
\[ t = 6801 \times \frac{V}{I} \]

With this equation, we had an inverse relation with the current through the electrolyte and deposition time for a given volume. We had to balance the deposition rate with the current. If the current was too low, it would take unfeasibly long to fill the structure with copper. If the current was too high, copper ions would not have sufficient time to diffuse into the structure, and would accumulate on the top of the VACNT mesh, capping off the electrolyte from the inside.

The deposition rate for electroplating is typically measured as current per area since it is used to deposit thin-films. Unfortunately, VACNTs are 3D structures, and the surface area is constantly changing during deposition. Instead, we use current per volume to describe the deposition rate of copper into the sample.

We ran samples at 8 A/cm³ for 8 hours, with a 3 ms “on” pulse and a 27 ms “off” pulse[8]. After the deposition was complete, we moved the samples to acetone to release it from the electrode, rinsed them in IPA, and left them to dry. We broke the samples in half to expose the inside of the structure for imaging and EDS. Figure A2.8 is a SEM image with an accompanying EDS line scan of the internal mesh structure. Visually, there is a lighter region in the top ~20 microns of the mesh structure. The EDS line scan shows that the lighter region is where copper was deposited with very little copper in the remainder of the mesh.

With the copper only depositing within the top 30 μm of the VACNT mesh, that means the copper ions in the solution are depleting too fast for uniform deposition. To correct this, we needed to lower the deposition rate to allow the copper ions to diffuse further into the structure.
We increased the “off” time from 27 ms to 47 ms to allow for copper ions to penetrate further into the structure before depositing, and we lowered the deposition rate from 8 A/cm³ to 4 A/cm³, and ran for 15 hours so that about the same amount of copper would deposit on the structure as the previous run. After the deposition completed, we submerged the cathode in acetone to release the sample from the carbon tape, then rinsed the sample in IPA, dried it, and broke it in half to image the inside of the structure. A SEM image of the interior of the mesh structure (figure A2.9) shows a uniform color through the structure, indicating the deposition was uniform. The EDS line scan shows that there is significantly more copper through the whole structure than carbon, and confirms that the deposition is fairly uniform from top to bottom of the structure.

_A2.8 Electroplating 8A/cm³_. Cross section SEM image showing copper deposition in the top of the VACNT mesh. EDS line scan shows the copper deposited only in the top 30 μm.
Inspecting the top and bottom of the VACNT mesh show that the nanotubes are completely filled with copper (figure A2.10B). Even though the deposition rate was low enough and there was enough time for the copper ions to diffuse down into the mesh, the copper deposition did occur faster near the top of the structure. This higher deposition rate at the top created a thin film of copper that covered the entire structure, as seen in figure A2.10B. The top-down image seen in figure A2.10C shows the top surface copper film is porous, but is completely covering up the mesh structure.
Appendix 2.5 Conclusion

Galvanic displacement replaced the silicon at the surface of the mesh structure, however, subsequent copper ions would preferentially deposit on existing copper on the surface instead of penetrating deeper into the structure.

Electroplating is a more controlled process, allowing for the copper ions to reach the bottom of the mesh structure. With the additives to control the growth at the top of the structure, we were able to fill high-aspect-ratio VACNTs with copper without loss of structure. The copper film covering the top of the structure is only a few microns thick, and can be removed using standard microfabrication processes.

We have shown that VACNTs can be used as a high aspect ratio framework for copper deposition. We created a carbon mesh with 1 μm hedges and 4 μm square openings, and successfully deposited copper into the VACNT structure. Further work needs to be done to remove
the top film through etching, or tuning the deposition rate, time, and additives to prevent the cap from forming.