FABRICATION OF SUSPENDED GRAPHENE MEMBRANES GROWN BY CHEMICAL VAPOR DEPOSITION (CVD) USING CARBON NANOTUBES

by

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ABSTRACT

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Graphene is an exciting material that stands to have a large impact on the scientific community. Unfortunately, graphene cannot be fully utilized due to its small scale and time consuming production. Graphene grown by chemical vapor deposition solves these issues but comes with a cost of decreased mechanical and electrical properties due to defects. However, the exact properties of CVD graphene are not well quantified. In order to measure the qualities of CVD graphene it must be suspended. Carbon infiltrated carbon nanotube forests were fabricated with holes 2-20um in size. Imaging showed CVD graphene was suspended over up to 50 percent of the holes.

ACKNOWLEDGEMENTS

I am appreciative for the guidance provide by my advisors, Dr. Robert C. Davis and Dr. Richard R. Vanfleet. This thesis would not have been possible without the advice and explanations they provided. I would also like to thank Kyle Zufelt, Jonathan Abbot, Steven Liddiard, Anthony Pearson and Anthony Willey for the help that they provided. I am also grateful for research funding from Moxtek Inc. I would like to thank my parents for providing the possibility to take on this challenge. Finally, I would like to give special thanks to my wife Tyra and son Eli for their constant support and encouragement, without them none of this would be possible.

TABLE OF CONTENTS

LIST OF FIGURES

Chapter 1

Introduction

Graphene and Chemical Vapor Deposition

Graphene is a monolayer sheet of carbon one atom thick. This two dimensional material is tightly packed together in a honeycomb lattice. Graphene can be wrapped up into soccer ball like buckyballs, rolled up into nanotubes, or stacked to become graphite. Some familiar forms of graphite, multi-layer graphene, are charcoal or the material in pencils. [2] Graphene was first theorized in 1962 by Hanns-Peter Boehm. At the time graphene was considered to be a purely academic material. Even though know as a part of three-dimensional materials graphene was not presumed to exist on its own. Graphene was assumed to be unstable as a single sheet and would revert back to other forms such as nanotubes or buckyballs. It was first isolated by Geim and Novoselov in 2004, for which they won the noble prize. [11]

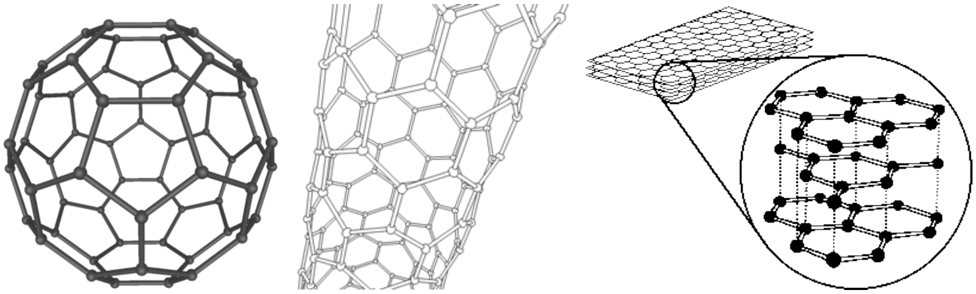

Figure 1.1 Left: Buckyball, Center: Carbon nanotube, Right: Graphite

Initially, graphene was isolated with mechanical exfoliation. This technique involved separating graphene sheets from bulk graphite using scotch tape. Scientists continually separated graphite until a single graphene sheet was produced. The sheet was then placed on a silicon wafer as a final substrate. This method was time consuming; additionally, the useable sample yield was very low, “a few monolayers per mm.”[3] This problem was exacerbated by the fact that the size of the sheets was less than 1000μm.[2][8] The time and effort required to produce such small amounts proved prohibitive. The challenges of the extremely low yield led researchers to investigate alternative methods of obtaining graphene. An alternative approach to obtaining graphene from mechanical exfoliation is the process of Chemical Vapor Deposition(CVD). CVD involves growing graphene.

I was part of a summer internship to Cornell University during the summer of 2010 working on graphene growth and characterization. I worked with Paul McEuen world famous research group and contributed to a publication in Nature on imaging grain boundaries in graphene grown by CVD. The growth process takes place in a standard furnace on a suitable substrate. Graphene growth has been demonstrated on various substrates such as ruthenium, iridium, and nickel. In this study a copper substrate was used due to its low cost and self-limiting growth capabilities. A chemical reaction occurs when a methane-hydrogen gas is passed over a copper surface. During this reaction graphene begins to grow when the carbon in the methane is removed by the copper catalyst. The individual carbon atoms combine in hexagonal arrays, forming a graphene sheet. The initial results have proved promising. Thus CVD solves the problems of scaling and size and the use of a copper substrate retains the low cost of production. However graphene grown by CVD has shown a decrease in mechanical and electrical properties.

This is due to the fact that defects develop on grain boundaries (See Figure 1.2).

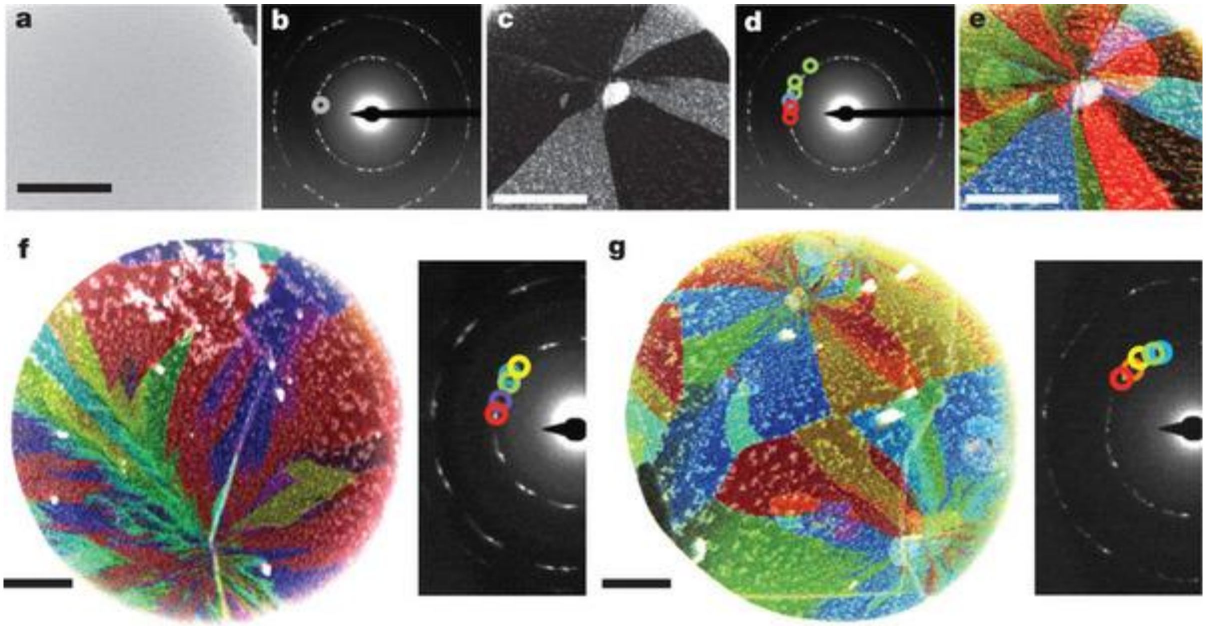

Figure 1.2 Grain Boundaries on Graphene [3] a-g: TEM images of grain boundaries, scale bars 500nm.

Graphene grown on copper has defects along copper grains as well as graphene grains. The low cost copper used in this study is polycrystalline and was manufactured by a rolling process. This process makes for many different copper grains across a single sample. The copper grain size is approximately 50um, so on a single sample there could be as many as 9,000 different grains. In addition, on a single copper grain there are many graphene grains. These graphene grains are approximately 0.5um, allowing for around 25,000 graphene grains on every copper grain.

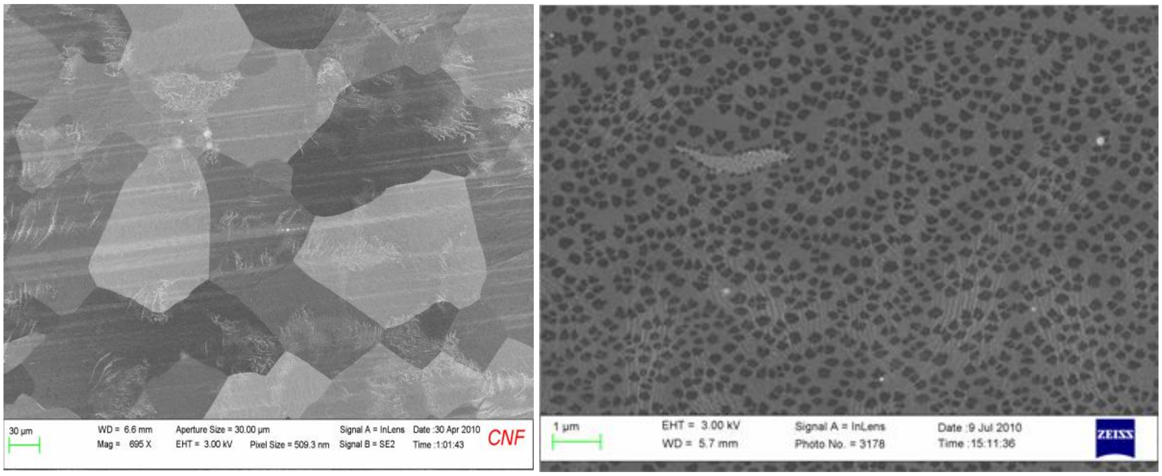

Figure 1.3 Left: SEM image of copper grain boundaries from a single copper foil, Right: SEM image of graphene grains on a single copper grain

Defects form every time a graphene grain meets another graphene grain. Additionally, there are defects formed across each of the copper grain boundaries. This study examines the strength properties of this graphene grown by chemical vapor deposition with significant amounts of defects.

Properties of Graphene

Graphene has been characterized and found to have many interesting and exploitable properties. Among these is the existence of a zero band gap making graphene a semi-metal, “the only known material in which the electronic band structure changes significantly via electric field effect”.[8] Graphene also exhibits the highest tensile strength of any known material; 200 times stronger than steel with a tensile strength of 130GPa(19,000,000psi). [1] Silicon is widely used in electronics because of its high mobility with <1400 $cm^2V^{-1}s^{-1}$. Experimental results have proven that at room temperature graphene’s electron mobility is extremely high, in excess of 15,000 $cm^2V^{-1}s^{-1}$. [7] The corresponding resistivity a graphene sheet would be 10^{-6}ohmcentimeters. This would make graphene less resistive than silver, the lowest resistivity of any material we know of at room temperature. [12] These properties make graphene an ideal substance to build smaller, faster and more powerful electronic devices. It will aid in producing next generation computers, cellular phones, and even microwave ovens. [2] Graphene's structure also makes it impermeable to gas, which is advantageous for scientific equipment and experiments. Until a sheet is grown that is completely free from defects, these exciting capabilities cannot be fully harnessed.

Carbon Nanotube Properties

Carbon nanotubes are a sheet of graphene rolled up and bonded to itself. Nanotubes can have length-to-diameter ratios of up to 132,000,000:1, significantly larger than any other material.[13] The catalytic vapor phase deposition of carbon was first reported in 1959 but were not formed this way until 1993.[14] Substrates are prepared for chemical vapor deposition with a thin layer of metal commonly nickel, cobalt or iron. During growth carbon nanotubes grow vertically upward from the substrate creating vertically aligned carbon nanotubes. The size of the nanotubes is determined by the length of growth and size of metal particles. The bending modulus of vertically aligned carbon nanotubes has been determined to be 0.91-1.24TPa and effective axial modulus to be 0.90-1.23TPa. [15] These forests have an areal density of 10 nanotubes per micron. [16] Infiltrating these nanotube forests with carbon makes these structures are extremely strong and good candidates for arbitrary substrates.

Scanning Electron Microscopy and Lithography

Scanning Electron Microscopes (SEMs) are used to image a wide variety of materials ranging from biological samples such as flies to nanotechnology such as circuits. An SEM generates images by scanning samples with an electron beam generated by a tungsten filament, field emission gun. These electrons are generated in a column of electro-magnetic lenses that focus the beam as it is sent down the column. The electrons interact with the sample and are emitted and captured by an electron detector. The amount of electrons that are released from the sample vary, which the computer interprets as varying levels of grey to produce an image a computer screen. [17]

Substances such as PMMA or ZEP react chemically when they are exposed to high intensity electron beams. Such substances are called “resist”. The electron beam from the SEM can be used to pattern these resists. A CAD program can be written that the can externally control the microscope to write specific patterns in resist like PMMA or ZEP. Once the resist is exposed it is placed in developer that removes the areas of resist that were exposed to the electron beam. In this process any desired pattern can be obtained down to the order of nanometers.

Graphene Transfer

This thesis theorizes a new process for transferring graphene to substrates. Graphene has been transferred to silicon substrates for some time now. [19] Ever since exfoliated graphene,

graphene has been placed on silicon for analysis and study. Silicon is a very robust and durable substrate but does not allow for every type of characterization, such as pressure testing. Researchers at Cornell patterned trenches in silicon that allowed for fabrication of graphene balloons but didn't have a hole completely through the silicon. Another approach at the University of Texas required creating a separate SiN_x membrane to be placed over holes etched in silicon. Additional membranes add more fabrication time and difficult alignment steps to an already challenging process.

Figure 1.4 Tapered edges of a silicon wafer having undergone an etching process. Also, an additional layer such as SiN makes fabrication and alignment considerably more difficult.

The difficulty with simply etching a hole completely through a silicon wafer arises from high aspect ratios. Etching all the way through a wafer results in tapered edges that weaken the silicon and make handling difficult. This thesis details a method of growing holes in carbon nanotubes that yields holes through the entire structure in a simple and easy process. This method is an improvement over existing methods and can be used for various applications.

Chapter 2

Methodology

Electron Beam Lithography

The first step in suspending graphene is making a structure to suspend over. To start, I took a 1-0-0 silicon wafer and broke it into 1.5cm rectangles. The wafer is then coated with alumina and iron on the surface. We used a thermal evaporator to obtain 30nm of alumina and 7nm of iron in preparation for carbon nanotube growth. (See figure 2.1)

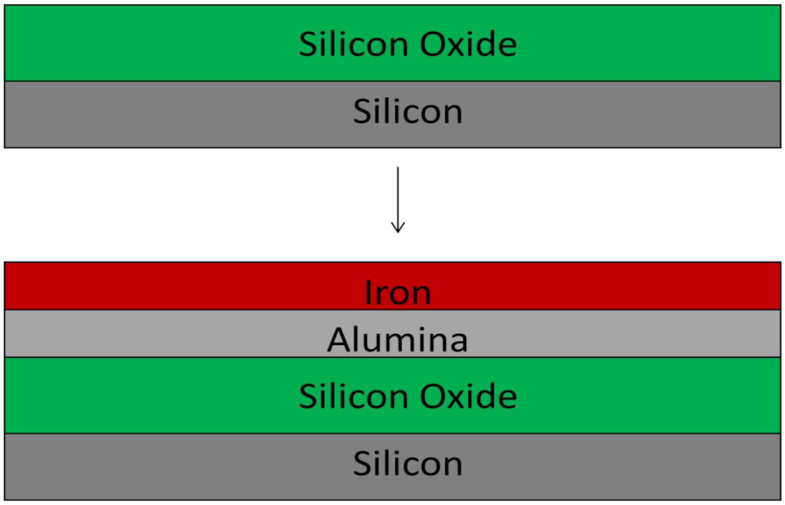

Figure 2.1 30nm of Alumina and 7nm of iron are deposited on a silicon wafer

The next step is electron beam lithography. We used a positive resist, ZEP 520A, to pattern the various sizes of holes. The resist was spun on at 5600 rpm for 90 seconds yielding a layer approximately 500nm thick. The resist was then baked at 170 degrees Celsius for 60 seconds. The electron beam lithography was performed on an environmental scanning electron microscope (ESEM). Nine arrays of circles were patterned. Each larger array consisted of nine smaller arrays of nine circles all the same size. The sizes of circles ranged from ten microns to one micron. (See Figure 2.2)

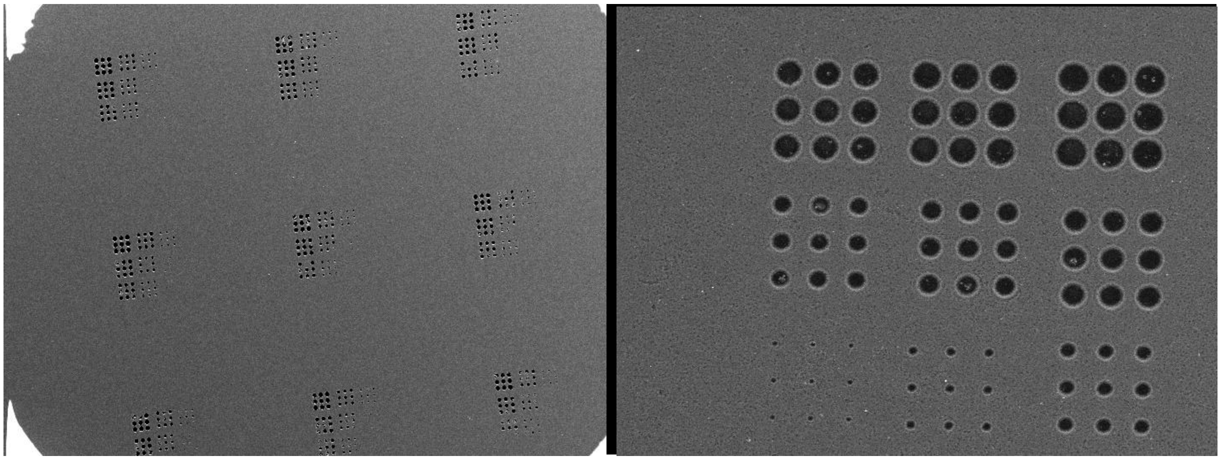

Figure 2.2 Left: SEM image of nine large arrays, Right: Nine arrays of nine circles ranging form 1-10 um

An accelerating voltage of 30kV and spot size five were used with a line dose of 1.0 nC/cm. The resist was developed in ZED-N50 for 60 seconds and blown dry with nitrogen.

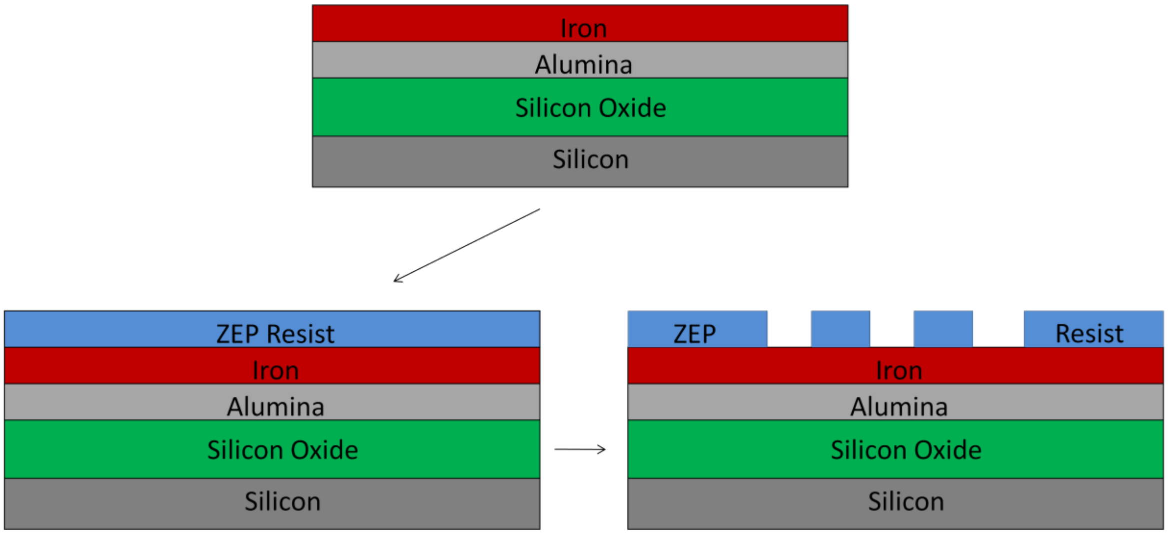

Figure 2.3 Left: ZEP Resist is spun on the iron layer, Right: The resist is patterned by electron beam lithography and developed away leaving a pattern in the resist

Etching

The iron was etched using dilute Hydrochloric acid HCl: H20 1:30 for 5 seconds and blown dry with nitrogen. The resist was then removed by sonicating the samples in 1165 for 20 minutes. With the electron beam lithography pattern transferred into the iron and the resist removed the samples are ready for carbon nanotube growth.

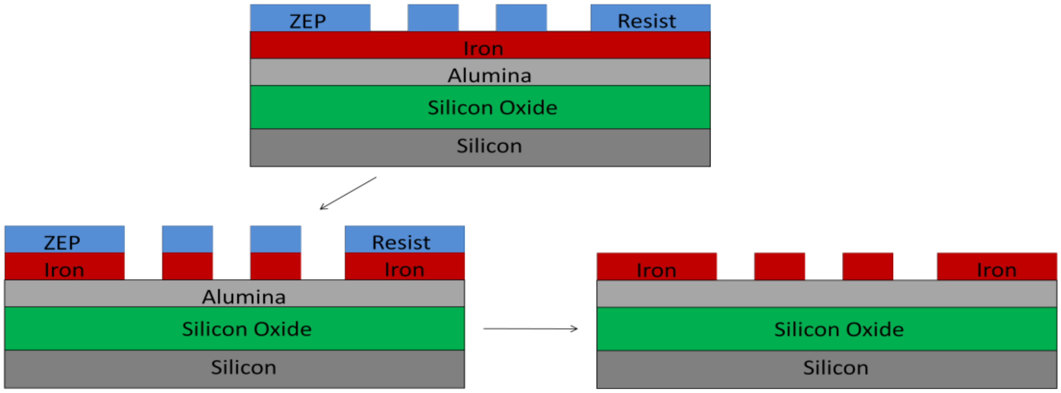

Figure 2.4 Left: Lithography pattern transferred to the iron by etching in HCl, Right: The resist is removed using 1165

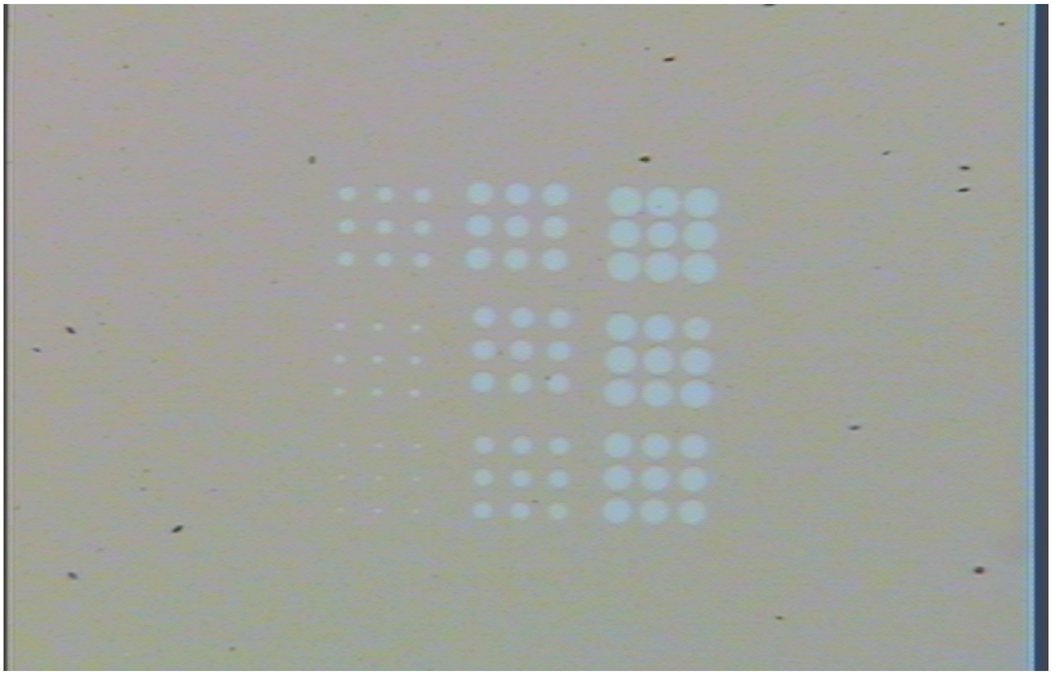

Figure 2.5 Light microscope image of lithography pattern transferred to the iron layer

CNT growth and release

The carbon nanotubes were grown in a one inch tube furnace. The samples were heated to 750 degrees Celsius while flowing 200 sccm hydrogen. Growth took place at 750^0C for 20 min while flowing 200 sccm hydrogen and 200 sccm methane. After 20 minutes the hydrogen and methane were turned off and 150 sccm argon was flown while ramping up the temperature to 900^0C. We infiltrated the carbon nanotube forest at 900^0C for 30 minutes while flowing 150 sccm argon and 200 sccm methane. The argon was chosen instead of hydrogen so that the carbon nanotube forest would release from the underlying substrate. After infiltration the samples were allowed to cool down slowly to around 750^0C over 15 minutes for maximum forest strength; after which the furnace was opened for rapid cooling. When the furnace was under 250^0C the samples were removed and the carbon nanotube forests were separated from the remaining sample. The carbon nanotube forest was then sonicated in water for 20 minutes to remove the carbon floor layer from infiltration. To clean the furnace we heated it 950^0C while flowing air for 20 minutes.

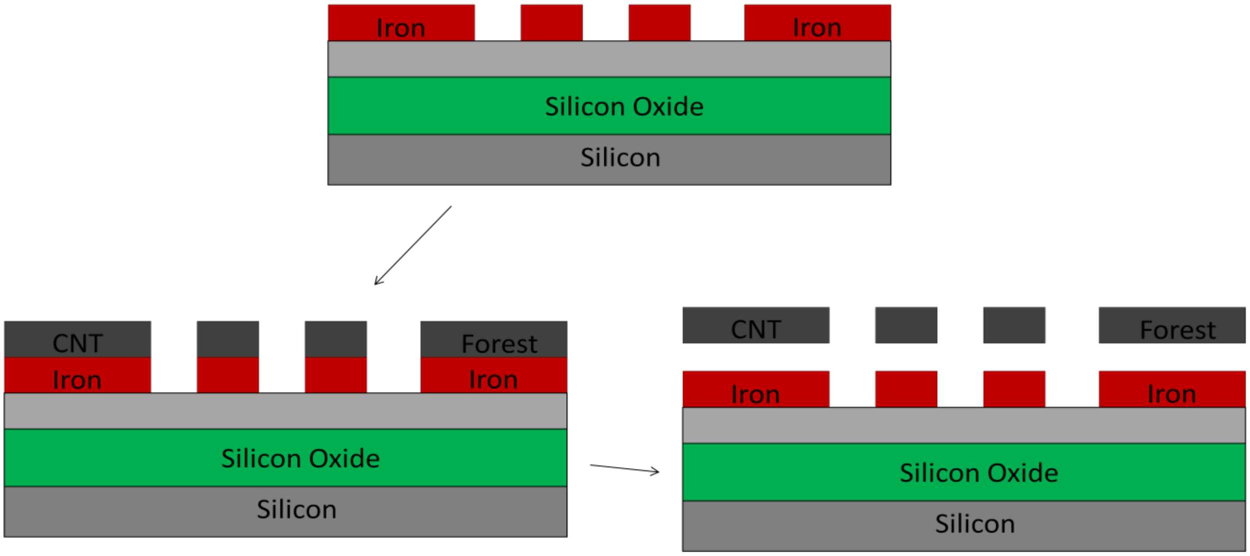

Figure 2.6 Left: A carbon nanotube forest is grown on the iron catalyst, Right: The CNT forest is released from the sample during infiltration

Graphene growth

Once the infiltrated carbon nanotube forest with holes is complete it is time to prepare the graphene to be placed on top of it.

The graphene was prepared using .025mm copper foils from Alfa Aesar as the catalyst. The copper foils were cut into squares with a side length of 1.5 cm. On the bottom right edge of the foils we cut a small triangle to help indicate top orientation. The foils were then placed between two glass slides to flatten the foils. The flatness of the foils is extremely important. Crumpled or bent foils can lead to cracked graphene and poor transfers.

After removing the foils from the glass slides they are treated with a series of cleaning dips: Acetone (10 Sec), Water, Acetic Acid (10 Minutes), Water, Acetone (10 Sec), IPA (10 Sec). The foils are then gently blown dry using a low flow nitrogen gun to remove the remaining IPA. Three to five foils were placed on quartz slides and put in a one inch furnace for chemical vapor deposition (CVD).

The furnace system was pumped down by a roughing pump for five minutes to reach a baseline pressure. After baseline pressure was achieved we would flow 150 sccm hydrogen while heating the furnace to 950^0C. The hydrogen is imperative while heating to avoid oxidation of the foils. The foils were annealed at 950^0C for 10 minutes. After the anneal 580 sccm methane was flown for 13 minutes. During this time a full mono-layer of graphene is grown in a self-limiting process. After growth the furnace was opened and allowed to cool past 200^0C. The methane and hydrogen were then replaced by 150 sccm argon. The argon was allowed to flow for two minutes before turning off the vacuum pump. Once the argon had re-pressurized the tube the samples were removed and placed in a non-stick tray.

In order to characterize the graphene it must first be transferred to a desired substrate. This method involved a thin support membrane for transfer. Care must be taken to keep track of which side of the graphene covered foil you are working with using the notch put in the foil before growth. In an effort to decrease crumpling the foils were stuck to three inch wafers using double sided tape for the spinning process. 3% Anisole-PMMA was spun on the graphene at 4000RPM for 60 sec, yielding approximately 500nm. No bake was necessary. An oxygen plasma was used to remove the graphene from the back side of the foil. The foils were then placed face up in a sodium persulfate copper-etch solution, .5g sodium persulfate 60mL water, for approximately eight hours. PMMA is hydrophilic so the foil will float on the acid surface. The free-floating PMMA membrane was transferred from the copper-etch solution using a glass slide into DI water. The membrane should float on the surface of the water with the PMMA side up and graphene side down. Keep the membrane flat to avoid cracking. The membrane was transferred into fresh DI water six times. Finally the membrane was scooped out with the desired substrate and allowed to dry for 24 hours. The PMMA was soaked in 1165 for 45 minutes for removal.

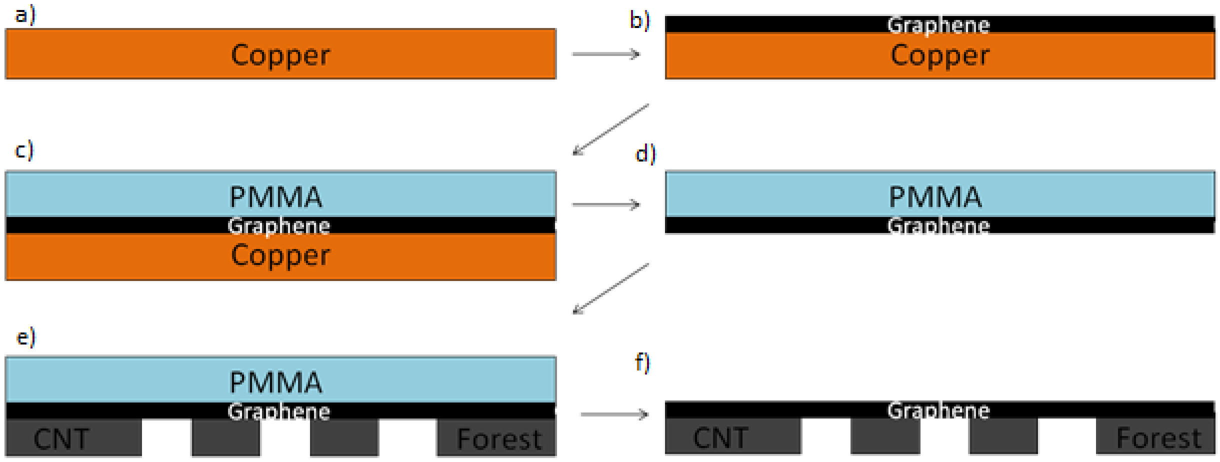

Figure 2.7 a) The copper foil is treated and prepped for graphene growth, b) graphene is grown by chemical vapor deposition, c) PMMA is spun on the graphene and copper foil, d) The copper foil is etched away using Sodium Persulfate, e) The PMMA/graphene membrane is transferred to the carbon nanotube support, f) The PMMA is removed with 1165 leaving a graphene suspended over holes in the carbon nanotube forest

Chapter 3

Results and Discussion

Carbon Nanotube Forests

The results of the carbon nanotube forests depended on several variables. If the lithography was not done well enough the holes would not be the right size or bleed into each other creating a large open area over which the graphene would not be able to be suspended. The etching process had to be done for a short enough time in order to ensure that the lithography pattern transferred to the iron and didn’t etch all the iron or resist away. Having the holes bleed together created opening too large to suspend a graphene sheet and rendered the sample useless.

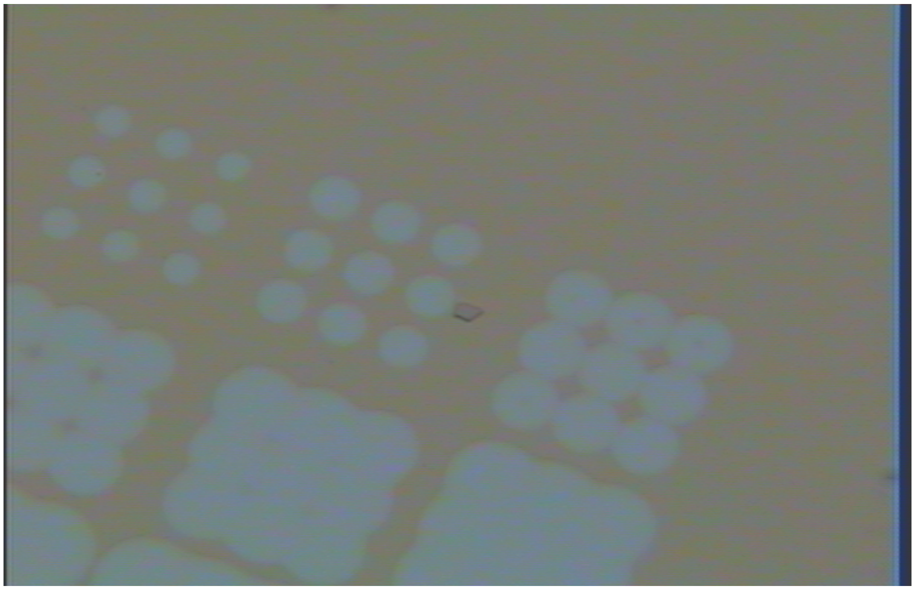

Figure 3.1 Light Microscope Image of etched iron. The holes bled into each due to the length of the etch, rendering the sample useless.

The forests had to be sonicated after release in order to ensure the floor layer was gone and the holes were in fact all the way through the forest. If the floor layer was kept intact then none of the advantages of this method could utilized.

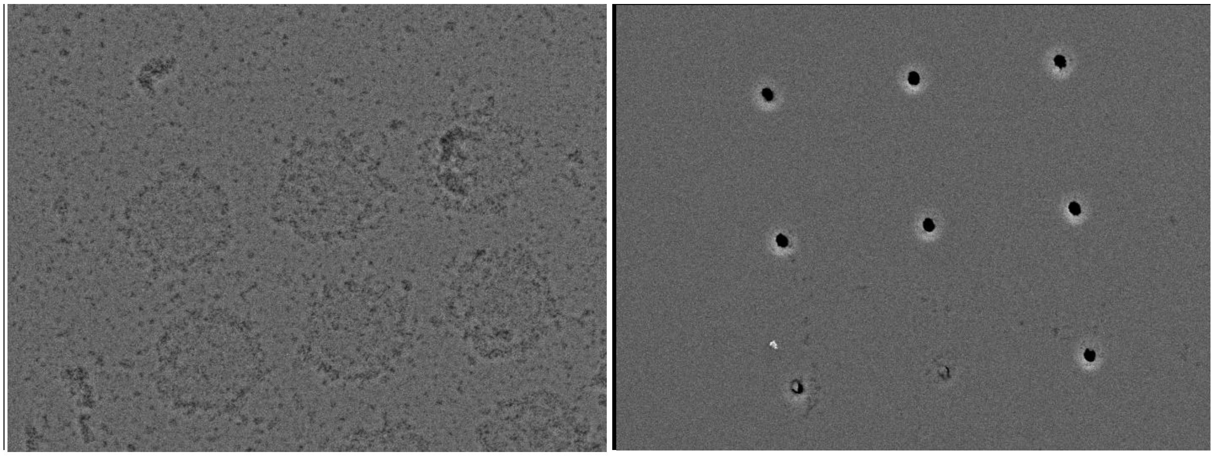

Figure 3.2 Left: SEM image of carbon nanotube forest after release and before sonication. The holes are covered in a carbon floor layer. Right: SEM image of carbon nanotube forest after sonication. Carbon floor layer has been removed and holes extend through the whole sample.

Flowing argon while infiltrating allowed for the forests to release on their own and not crack into pieces on release. The holes in the forests theorized to be 1-10um ended up to be approximately twice as big resulting in 2-20um holes.

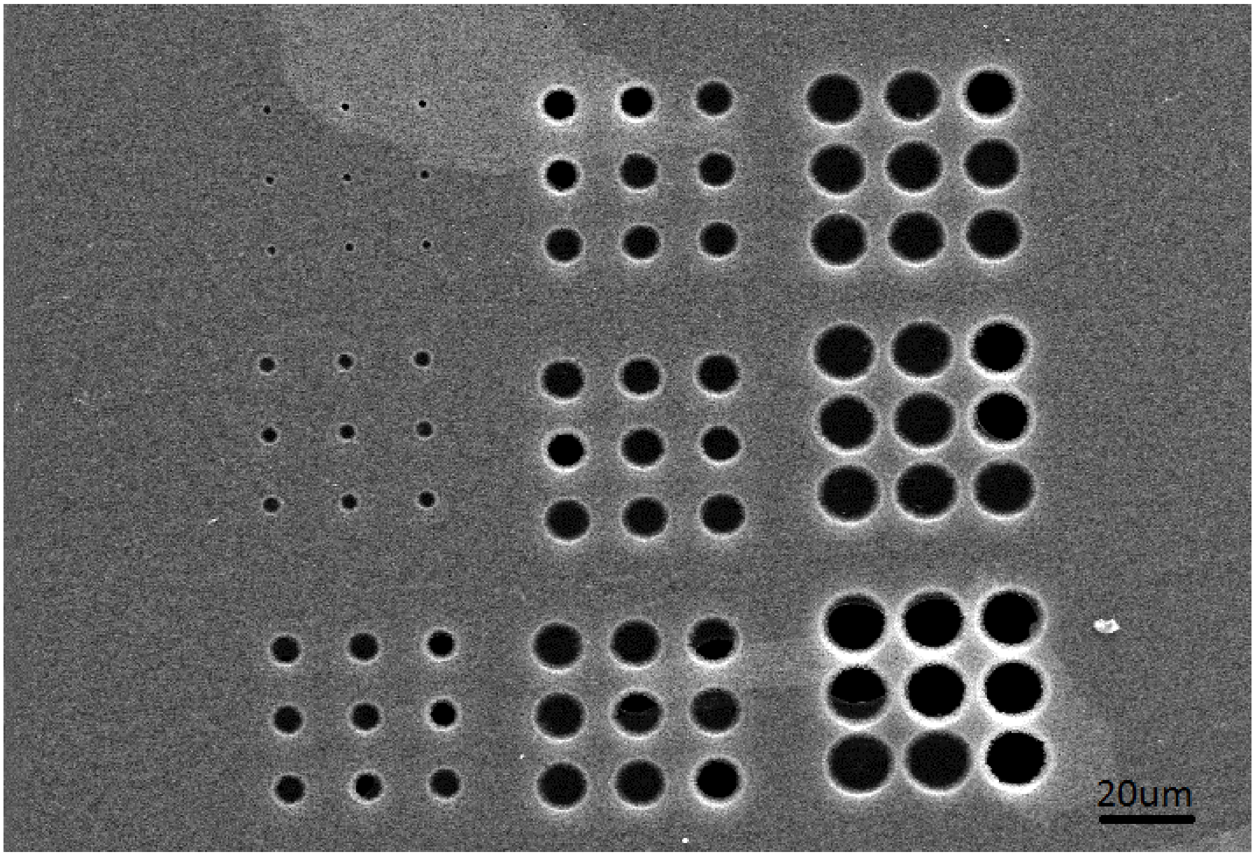

Figure 3.3 SEM image of holes in a carbon nanotube forest. The holes range in size from 2-20um.

Graphene Suspension

The graphene had to be handled very delicately to ensure successful transfers to the carbon nanotube forest supports. Being as graphene is only a single atom thick it is very easy broken or torn. Using a clean glass slide with containers mostly full of DI water was integral in the transfer from copper etchant to nanotube forest support. Unfortunately the majority of the holes did not have graphene suspended over them. Drying the membranes with a critical point dryer might have resulted in a higher percentage of suspended graphene membranes. The size of hole appeared to have no correlation to the chance of successful transfer.

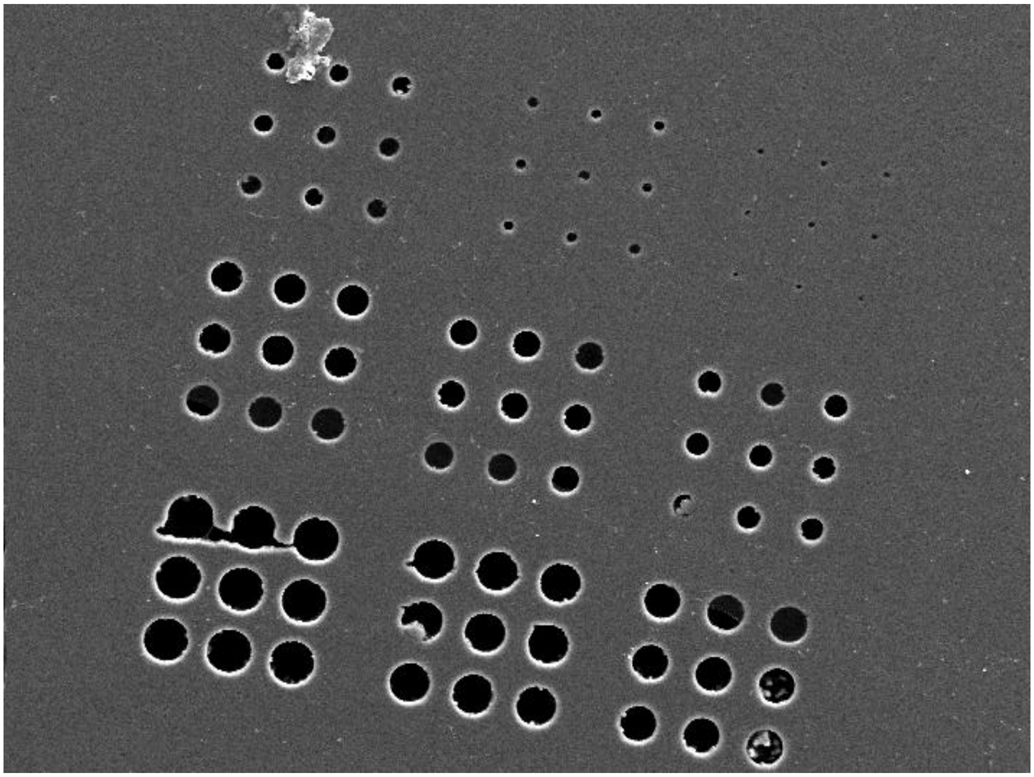

Figure 3.4 SEM image of successful graphene transfer. Only 11 of the 81 holes were successfully covered with graphene.

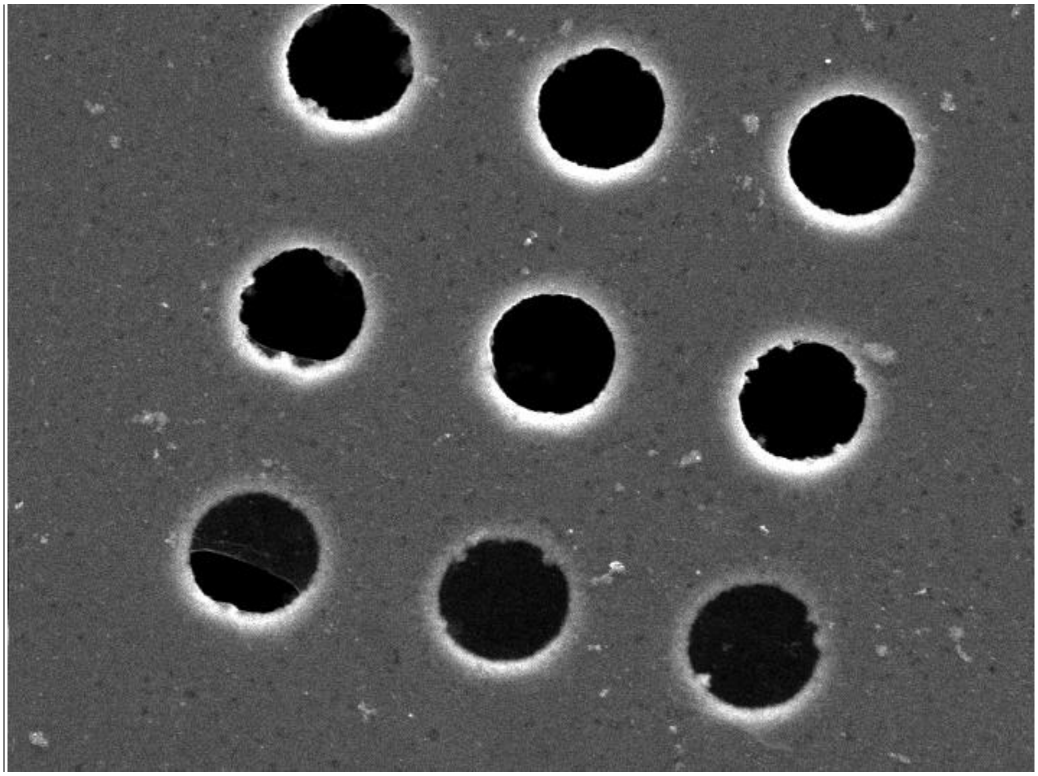

Figure 3.5 SEM image of an array from figure 3.4. Only three of the nine holes were covered with one being only partially covered.

However, I found that if the forests were plasma cleaned that the number of holes that were covered with graphene significantly increased. The transfer process proved to not cover the entire sample in graphene but the locations that were covered showed almost 100 percent success of having suspended graphene over the holes.

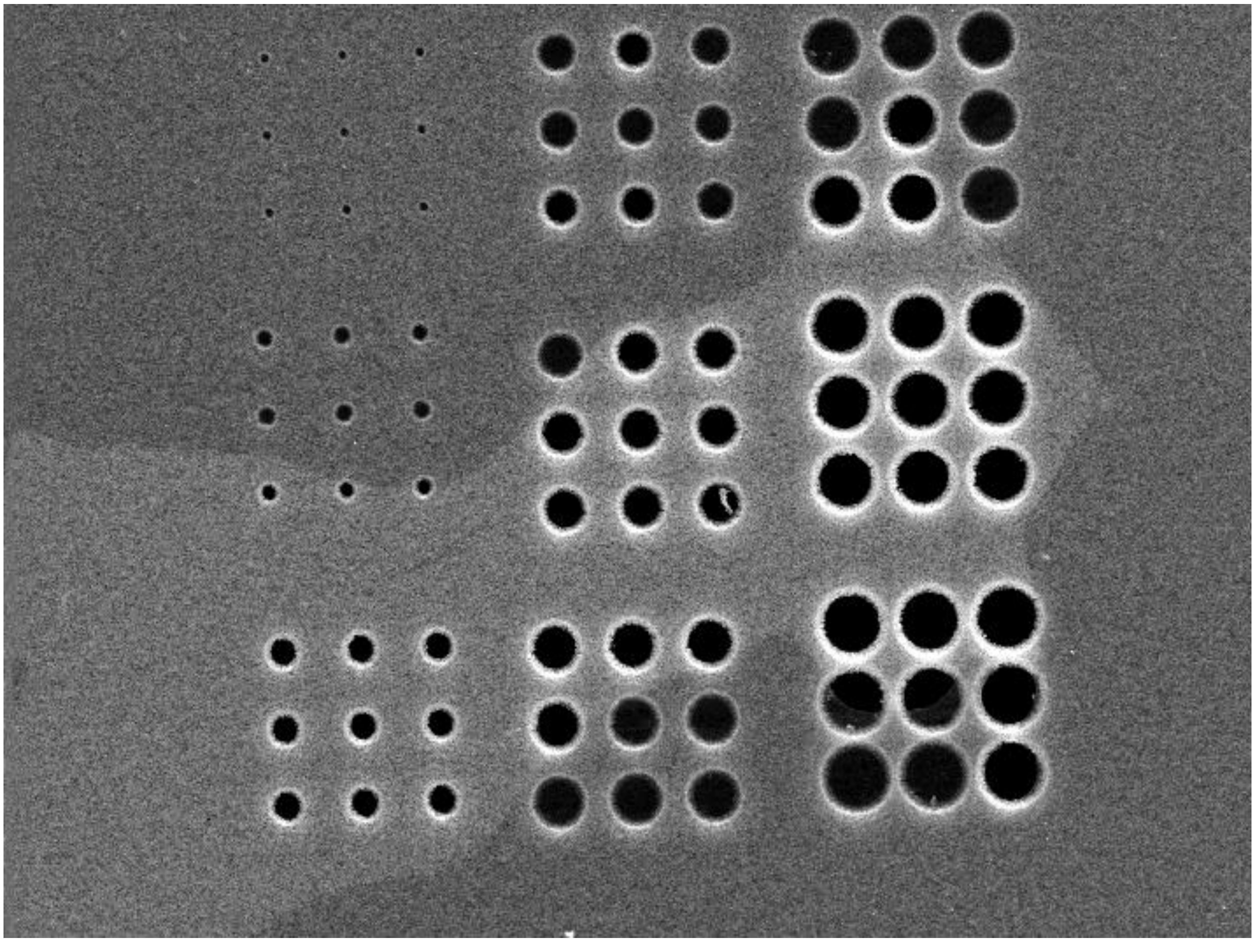

Figure 3.6 SEM image of plasma cleaned sample. Darker contrast areas indicate successful graphene transfer. In lighter areas no graphene was on the surface.

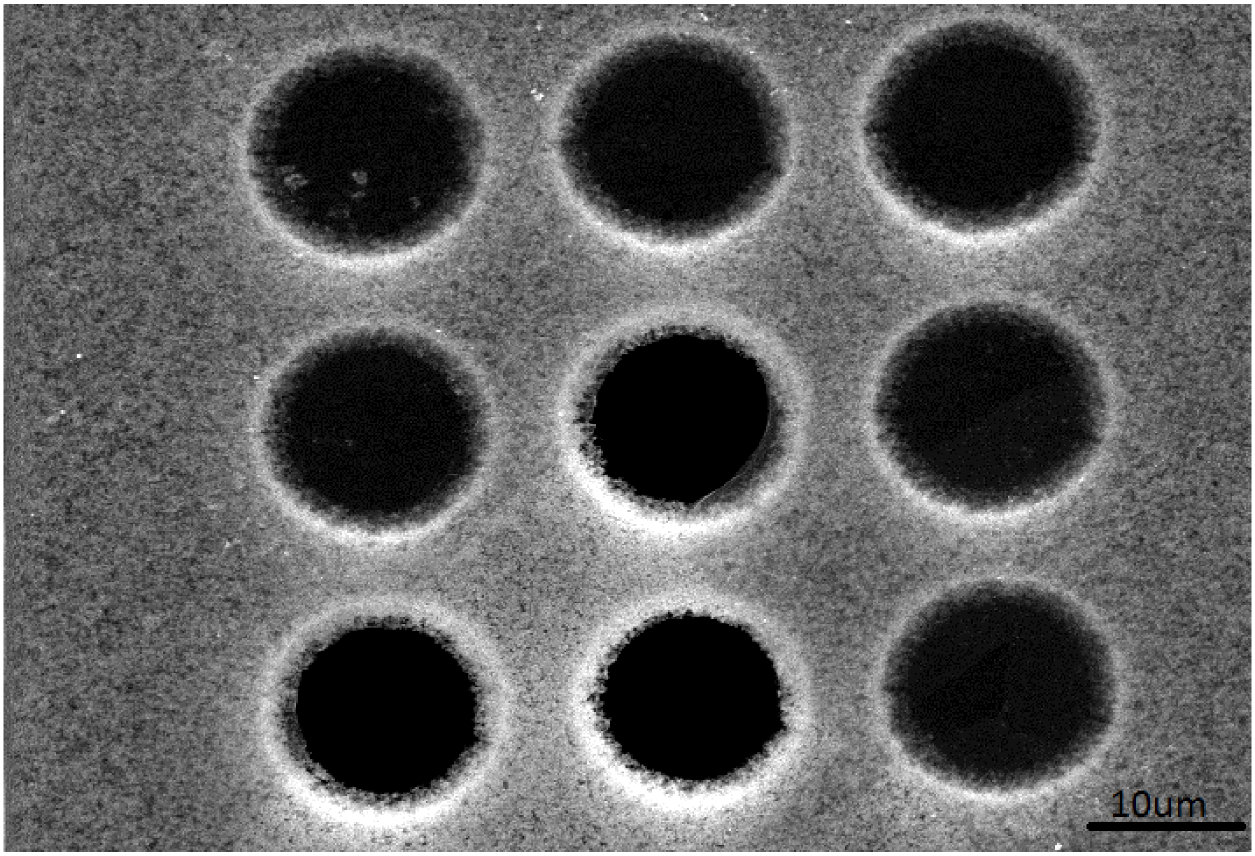

Figure 3.7 SEM image of graphene suspended over 10um holes in a carbon nanotube forest. The center and two lower left holes are not covered with graphene while the remaining six are. The copper grain structure can be easily observed in the lower right graphene membrane.

As can be seen in the above image, the copper grain structure can be seen in the suspended graphene. This shows that all the resist was indeed removed and that there is only the single graphene layer suspended over the hole. The grain structure can be seen due to different crystal orientations in the copper substrate during growth resulting in different orientations in the graphene. These different orientations of graphene have varied electrical properties and therefore interact differently with the electron beam and show contrast in the image.

Chapter 4

Conclusions and Future Directions

In this study I fabricated a new technique for transferring thin graphene membranes. Carbon nanotube forests were used as a substrate for transferring and suspending graphene. Electron beam lithography was used to pattern the catalyst for nanotube growth. The carbon nanotubes were grown and infiltrated with carbon to make them strong and durable. The graphene was grown by chemical vapor deposition and transferred using a sacrificial polymer layer. The result was a new way to suspend graphene that was strong and able to have opening through an entire sample. Characterization was performed using optical and scanning electron microscopes.

Graphene was successfully transferred to this new substrate and suspended over holes ranging from 2-20um. The amount of holes that were covered was less than anticipated with coverage of around 14 percent. Samples that were plasma treated had a higher coverage percentage, approximately 50 percent.

These results show that this technique is a viable way to suspend graphene membranes. This technique allows for new studies of CVD graphene that have been heretofore unable to be performed. Pressure testing of CVD graphene is one such option that is available using this technique that could add important information about the qualities of these large-scale graphene membranes.

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