**Title**
The Effect of Fluid Mechanics on Graphene Growths by Chemical Vapor Deposition

**Permalink**
https://escholarship.org/uc/item/9tk3h20w

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**Publication Date**
2013

Peer reviewed|Thesis/dissertation

UNIVERSITY OF CALIFORNIA
RIVERSIDE

The Effect of Fluid Mechanics on Graphene Growths by
Chemical Vapor Deposition

A Thesis submitted in partial satisfaction
of the requirements for the degree of

Master of Science

in

Mechanical Engineering

by

Jeffrey Michael Bell

June 2013

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## **<u>Acknowledgements</u>**

Isaac Ruiz, Wei Wang, Hammad Hosseinibay, Aaron Georg, Mihri ozkan, Cengiz Ozkan and to all those in lab who helped me complete my experiments and helped guide me on my research path.

ABSTRACT OF THE THESIS


The Effect of Fluid Mechanics on Graphene Growths by Chemical Vapor Deposition
Filing Their Thesis


by

Jeffrey Michael Bell

Master of Science, Graduate Program in Mechanical Engineering
University of California, Riverside, June 2013
Dr. Mihri Ozkan, Chairperson

## Abstract

Graphene's unique mechanical, electrical, and thermal properties have made it a very attractive material desired for use in future technologies.  Over the recent years, there have been many breakthroughs in research on graphene. Recently, the focus of the latest research has shifted towards scaling graphene production for commercial use by industry.  The most promising method for scaling graphene growth for industry usage is chemical vapor deposition (CVD).  CVD is a low cost, economic and scalable method for producing graphene.  However, consistently producing high quality graphene quickly on a large scale has eluded researchers. Here we detail a method for reducing growth time required to produce high quality, large area graphene by adjusting the fluid mechanics of the CVD

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## 1: Introduction

Scalable, controllable, cost effective, and economical methods of growing large-area graphene are a prerequisite for industry's adoption of graphene for commercial usage. Graphene's unprecedented potential application in the fields of solar, photonics, photo-dectors, sensing, and optoelectronics has generated a tremendous amount of momentum to push graphene into large scale production. Currently the most promising method for large-area growth of graphene to be applied by industry is chemical vapor deposition (CVD) with its variant of transition metals. The most attractive transition metal currently is copper (Cu), with its low carbon solubility and ease of transfer to arbitrary substrates; it is an ideal metal for commercial application. Graphene grown by CVD on transition metals has been thoroughly researched along with the method of how graphene is grown by CVD. Detailed in papers so far, graphene grown by CVD is a result of nucleation of active carbon species formed by decomposition of precursors on a metal catalyst surface (1). CVD is not a new method of growing graphene, but here we demonstrate a method that alters the fluid mechanics of the system in such a manner to help enhance growth times of graphene.

In context, adjusting the fluid mechanics of a CVD system is relatively new in the field of graphene growth. Research until now has focused on adjusting the gas ratio, temperature, pressure, prepping methods, metals, and gases (methane, acetylene, etc). Here we convert the turbulent air flow in the CVD system to a more laminar flow through use of an addition to the system. The addition is a 1 inch thick circular aluminum plate that has been machined to contain a honey comb cluster of small holes in the center. The aluminum plate is placed in the system and the honey comb cluster of holes in the center smooths out the airflow coming from

1

the inlet producing a more laminar flow.  A secondary result of the plate's introduction is a small

partition to the left of the plate that acts as a turbulent mixing chamber.  Gases that are not able

to pass through the small holes become turbulent which result in a high rate of mixing.  As a

result, the mixing creates a more homogenous gas mixture than was previously the case, which

then flows into the CVD furnace.   Shown here, altering the fluid mechanics of the chemical

vapor deposition system can greatly alter growth times and results.  Graphene grown by this

method tends to have a smaller grain size but growth times decrease by an astonishing amount.

The work presented here will be useful in pushing graphene closer to becoming more scalable

for industry use.   There is further work to be done on perfecting this method, but it shows much

promise.

### 2: Background

Graphene is a substance composed of pure carbon, with atoms arranged in a hexagonal

pattern similar to that of graphite, but in a one atom thick sheet.
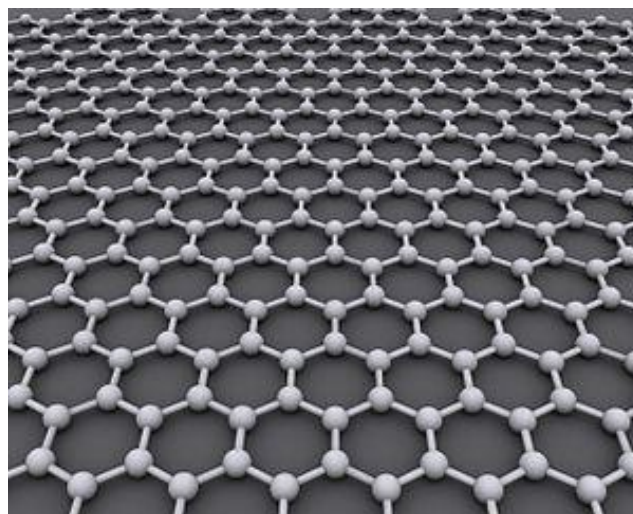


Figure 1: 3D image of 2-D carbon nano structure
or graphene.

Graphene was first isolated in 2004 by physicists at the University of Manchester through exfoliation.  From the exfoliated flakes of graphene, the physicists at the University of Manchester were able to bring to light graphene's unique properties.  Exfoliation is a mechanical process of using an adhesive tape to continually split graphite crystals into increasingly thinner pieces.  The method is illustrated below.
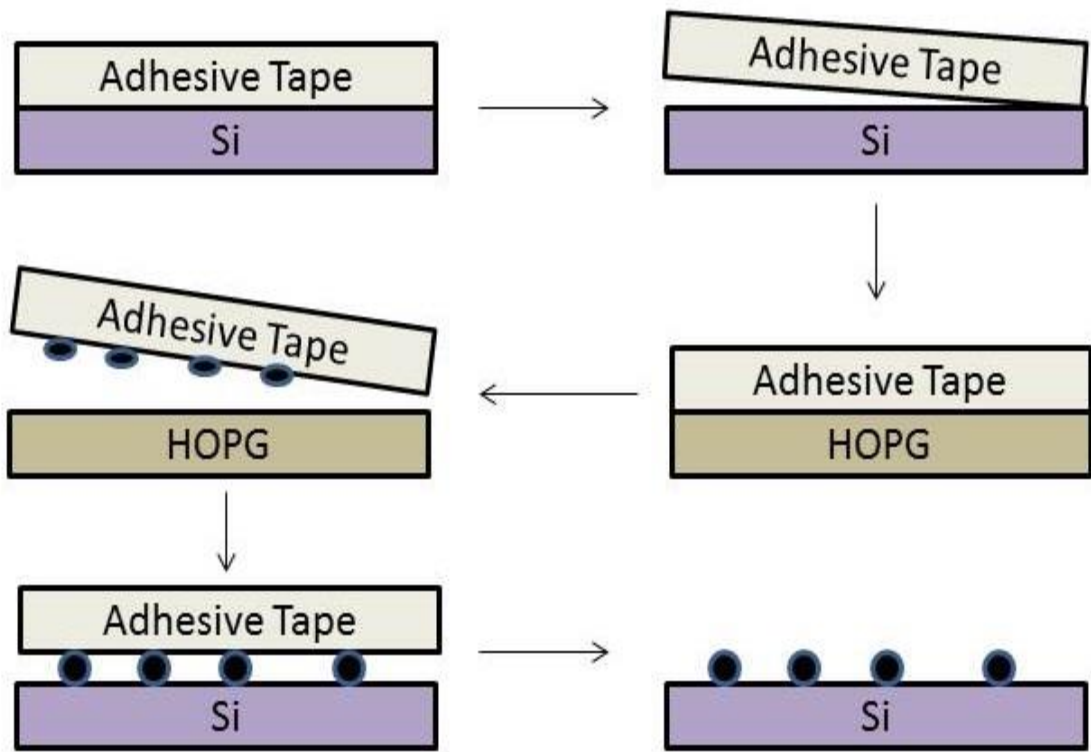
Figure 2:  illustration of the exfoliation process.  Adhesive tape is placed on silicon, then peeled off and placed on highly ordered pyrolytic graphite (HOPG).  When the tape is peeled off the highly ordered pyrolytic graphite, optically transparent flakes of grahene follow.  The adhesive tape is placed onto an insulating substrate of silicon.  The adhesive tape is than dissolved by using acetone.  What remains is a thin film of

Graphene obtained by mechanical exfoliation gives some of the best measured electrical properties.  The great electrical properties witnessed through mechanical exfoliation

results from the large crystal sizes that are able to be achieved from this method.  Although

large crystal sizes are achieved by this method, mechanical exfoliation encounters difficulties

when it comes to achieving a consistent single layer of graphene.  Most graphene achieved

through mechanical exfoliation has multi-layer and bi-layer areas with uniformity of the film

never being guaranteed.  The explosion of interest in graphene resulting from its discovery

generated tremendous interest in discovering alternative growth methods for graphene.  A few

of these methods include: epitaxial growth on silicon carbide, graphite oxide reduction, pyrolysis

of sodium ethoxide, and chemical vapor deposition.  The current mainstream method of

synthesizing graphene is chemical vapor deposition or CVD.  (1)

## 2.1: CVD

Chemical vapor deposition is a technique used to create thin nano material films by

exposing substrates to one or more volatile precursors. A typical CVD system, illustrated below,

is composed of a gas delivery system, a reactor, and exhaust system.  During the CVD process,

gas flows through a mass flow controller, a device which precisely alters gas flow to a desired

rate, into a gas mixing unit.  The gas mixing unit is responsible for the mixing of the multiple

incoming gases before the reach the inlet of the reactor.  The reactor is where the chemical

reaction takes place.  Gases flow into the reactor from the gas mixing unit.  Once in the reactor

they are subjected to high temperatures resulting from two heating units that surround the

reactor's quartz tube.  The heating units help facilitate the chemical reaction taking place inside

of the reactor.   The reactor is where the deposition takes place as a result of a chemical

reaction between multiple gases.  As time progresses, by-products and un-used gases need to

be pumped out of the system.  These un-wanted gases and by-products are removed by a gas

exhaust system consisting of a pump and pressure controller valve. These unwanted b-

products and gases then pass through a scrubber before they are vented out a fume hood. In

addition to facilitating the exhausting of the by-products and gases from the reactor, a pressure

controller valve is hooked up between the reactor and pump. This pressure controller valve

ensures the system maintains a low pressure. Maintaining lower pressure in the CVD system

helps ensure reduce the defects on the grapheme film.
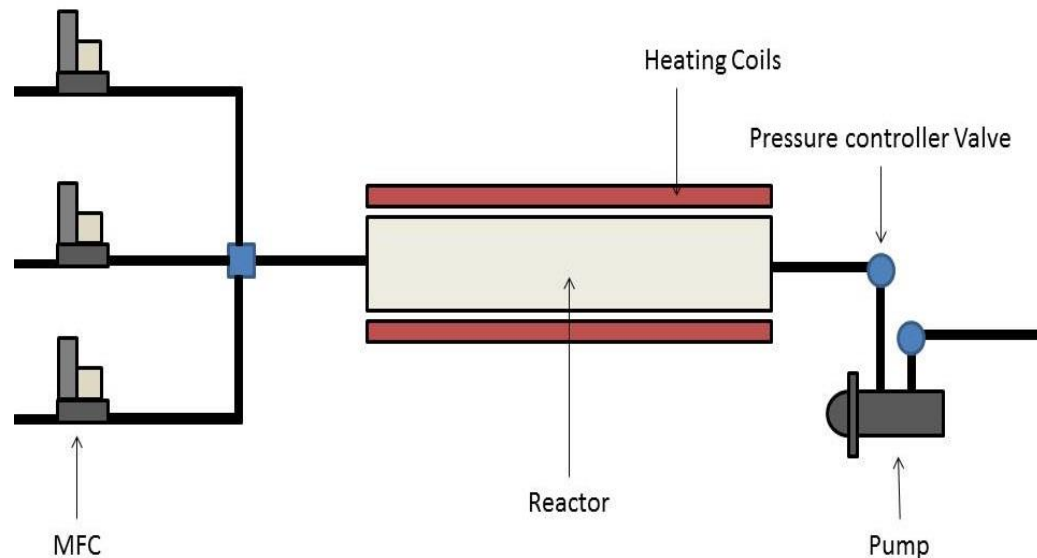


Figure 3: The schematic for a single zone tube furnace is shown above. Gas lines are connected to precision mass flow controllers that regulate the standard cubic centimeters per minute (sccm) of gas flow, gas is then fed into the system by a gas distribution unit. The actually chemical deposition takes place inside of the reactor. The exhaust is pumped out the end of the furnace by a gas exhaust system composed of a vacuum pump and pressure

The CVD setup is relatively easy, but to actually control the CVD process itself is far from

easy. With many variables such as time, heat, and gas ratio, CVD is a process that needs to be

conducted precisely and carefully in order to ensure consistent results. A successful chemical

vapor deposition process consists of diffusion dominating the surface of the substrate as a result

of reactants traveling though the reactor. The diffusion of the reactive species to or from the

substrate is complicated in that a non-uniform thickness is formed above the substrate as a

result of fluid mechanics.  The non-uniform boundary layer causes diffusion to occur in a non-

uniform fashion.  Another result of varying thickness in the boundary layer, diffusion will occur

slower at different points at on the substrate.  Diffusion is more likely to occur quicker at the

front of the substrate than the back of the substrate.  This is shown by Figure 4 that the

boundary layer is actually increasing from the front of the substrate to the back. (2)

Main Flow

Boundary Layer

Copper Substrate

Quartz Plate
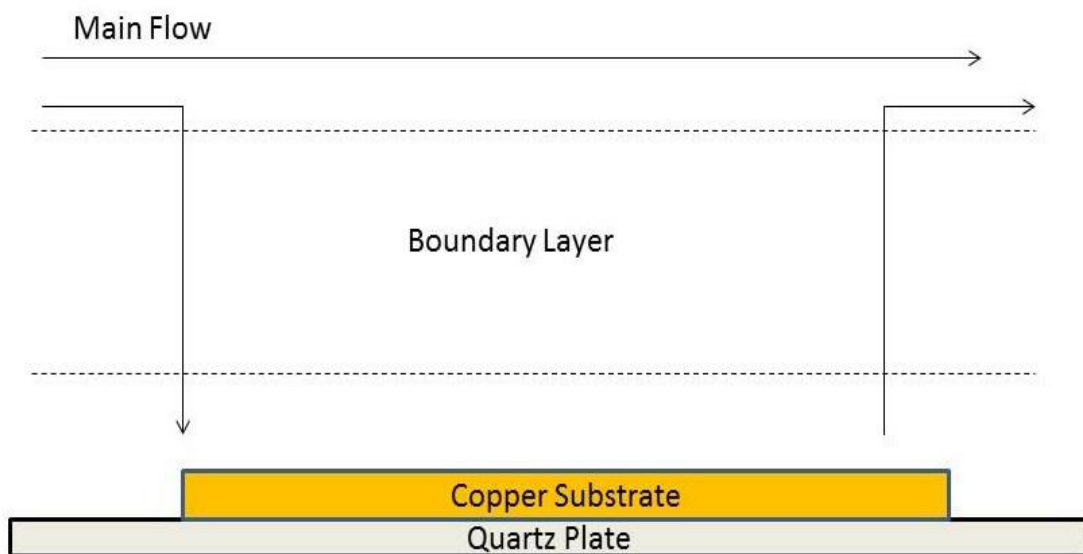
Figure 4:  The chemical deposition process taking place in CVD.  The main flow consists
of Hydrogen and Methane.  The Hydrogen gas acts as a carrier gas and etching gas.
Methane in the main flow cracks causing the carbon to pass through the boundary
layer.  The carbon that passes through the boundary layer deposits onto defects on the
surface of the copper substrate creating graphene domains.  (2)

A factor to consider too is the depletion of reactants as they travel through from one

end of the reactor to the other.  Due to the likelihood of the reaction occur at the front end of

the reactor and not near the end, it is beneficial to place the substrate in an area where you know the reaction is most likely to occur which would be closer to the middle front of the furnace.
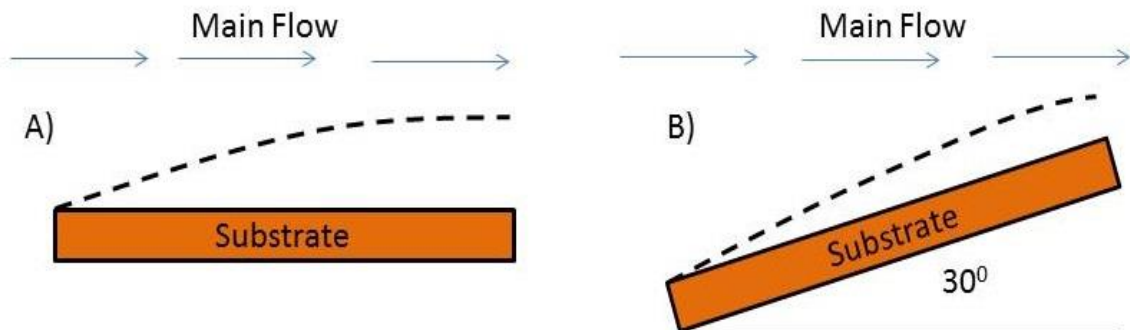


Figure 5: Example of a boundary layer over the surface of a substrate. A) Depicts the usual setup, a horizontal substrate with an increasing boundary layer generating over it. B) Depicts a angled substrate at $30^0$ which leads to a small boundary layer generated above the substrate. (2)

As depicted in figure 5, by adjusting the angle at which the substrate is positioned it is possible to decrease the thickness of the boundary layer. The decrease in the thickness of the boundary layer will increase the speed at which diffusion occurs. Although, this will not affect the randomness at which diffusion will occur along the substrate.

When it comes to graphene growths via chemical vapor deposition, catalysts play a huge role in the outcome of the growth. Catalysts are usually metals, which have finite carbon solubility and currently there are two predominant metals. The first is nickel which has non-negligible carbon solubility and the second is copper which has almost zero carbon solubility.

The first generation of graphene synthesis using CVD took place on nickel catalysts. Researchers already knew that nickel was a prominent catalyst in carbon nano tube growths and

discovered that by altering the partial pressure to a lower partial pressure, graphene could also be grown on nickel catalysts. The reason behind a low partial pressure is due to the fact that a higher pressure will lead to over deposition on nickel when only a thin or single layer film is desired. Although a very promising catalyst and easy to grown on, there are some issues with the use of nickel. Nickel significantly reduces the energy barrier to form graphene, but at the same time it is also promotes the deposition rate which leads to a combination of multi-layer and bilayer thick films. The second generation of graphene synthesis using CVD has focused mostly on copper catalysts. This is because copper is not as efficient as nickel in lowering the energy, this makes single layer a lot easier to achieve although different gas ratios and recipes need fine tuning to achieve single layer consistently.

While nickel may have some problems when it comes to graphene growths, the second generation of graphene growths on copper has shown much promise. Copper has virtually zero carbon solubility and this applies to the copper catalyst even after being heated to $1000^{o}$C. As a result, the carbon dissolution-precipitation process is not sufficient enough to form a single layer of graphene. This suggests that carbon atoms form directly on the surface of the copper catalyst directly during growth. The benefit of this mechanism is there is an easier control over the layer deposition in CVD. A few things that pose a problem to copper is it's reactivity relative to nickel. Due to coppers lower reactivity, it requires a much lower base pressure in the system in order to synthesize graphene. Another problem witnessed when copper is used compared to nickel is the defects or errors that might occur as a result of the transfer process.

## 2.2: Transfer of Graphene

Transfer of graphene grown by the CVD process is as difficult as the actual growth method itself.  In order to obtain the desired flow of electrical current through the graphene device it is imperative to transfer the thin film of graphene from the catalyst onto an insulating substrate, such as silicon dioxide.  Graphene that is not removed from the catalyst will short itself out as a result of the conducting catalyst that they were grown on.  The most common method of transferring CVD grown graphene is the etching and scooping method.   The etching and scooping method involves spin coating the graphene on top of the catalyst with polym-ethyl-methacrylate (PMMA).  The PMMA, for a lack of better terms, holds the graphene together after the catalyst is etched away in a strong acid.  The graphene coated with PMMA is fished out of the beaker onto an insulting medium.  As a result of the fishing method, moisture gets trapped under the graphene coated PMMA, requiring that the sample dry for a period of time before the next step is taken.   Once the moisture is finally gone, acetone is used to remove the top layer of polymer on the graphene.  The end result is a thin film of graphene on top of the medium used to fish it out.  Although the most common method of transferring graphene, it is very time intensive and subject to a great degree of human error.  Although this is most widely used method, recent research has shown direct synthesis of graphene onto silicon dioxide may be a better alternative. (3)

Direct growth of graphene via chemical vapor deposition entails evaporating a conducting catalyst onto an insulting medium then etching away the catalyst.  Previous research on this resulted in a myriad of mixed results.  The acid would etch the conducting catalyst

creating a gap between the medium and the graphene.  As a result, the graphene would have to

be fished onto the insulating medium.
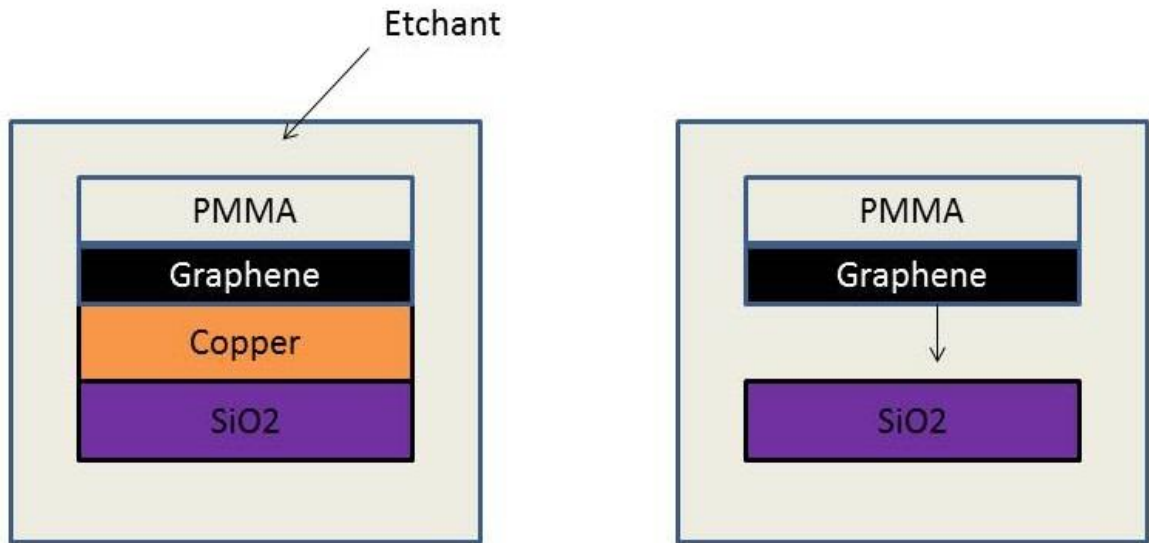


Figure 6:  Transfer method used in the direct growth of graphene by CVD.  Copper is evaporated onto silicon dioxide.  The sample is than put into a CVD furnace and graphene is synthesized on the evaporated copper.  Then a strong etchant is used to remove the copper catalyst.  Once the catalyst is removed, the graphene is fished out onto an insulating medium

graphene films would actually be present on the catalyst.  The presence of two films

complicated the transfer process where as hopes were to actually simplify it using the direct

growth method.  Recent research has explained this phenomenon showing that graphene will

actually synthesize on the top and bottom of the conducting catalyst.
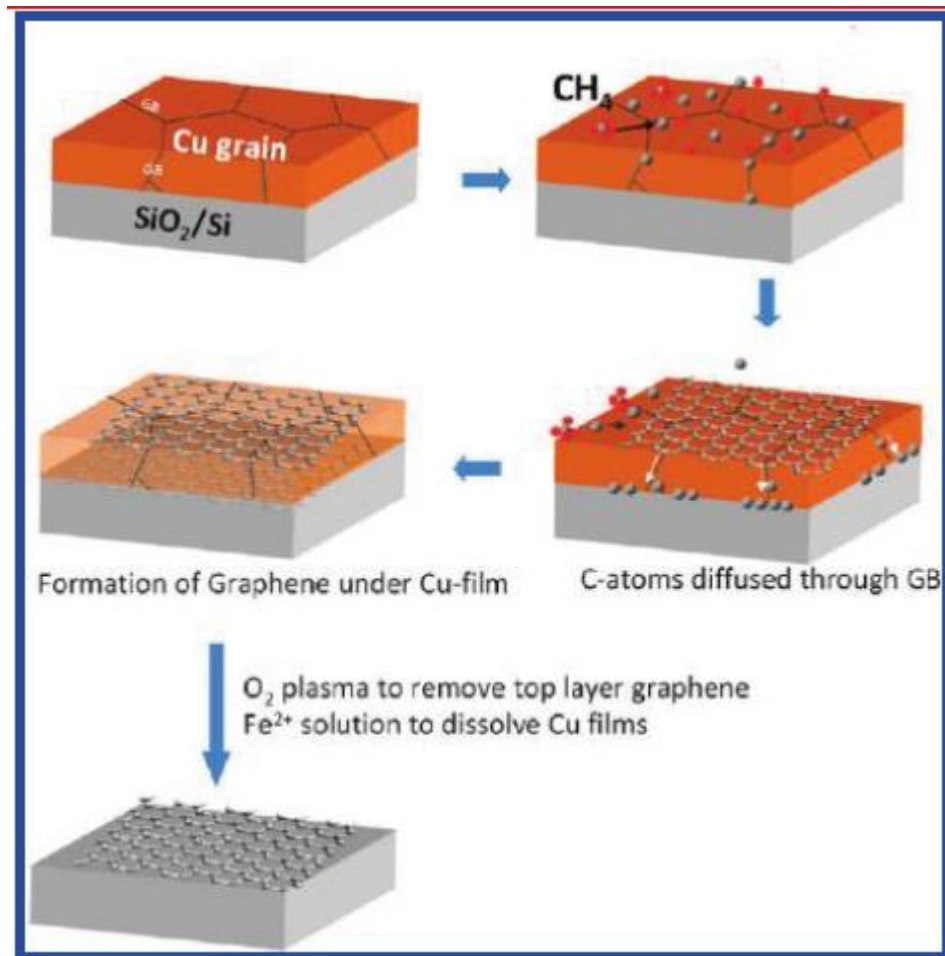
Figure 7: Illustration of graphene formation on the bottom side of evaporated copper. The substrate is thermally annealed creating grain boundaries. Carbon deposits on top of the evaporated copper, while some of the carbon diffuses through the grain boundaries. A layer of graphene will form on top of the evaporated copper. Even though a layer forms carbon will still diffuse through into the interface between the copper and insulating medium. (Ching-Yuan Su Nano Lett (2011) (2)

As depicted in figure 7, graphene synthesizes between the interface of the catalyst and insulating medium as a result of carbon diffusing through the grain boundaries. The top layer of graphene is easily removed using oxygen plasma then the catalyst is removed using a ferric chloride etchant. What remains is the thin film of graphene grown underneath the evaporated

copper.   Although this method was not used in this paper, it is a very promising method in

decreasing the time required to obtain a thin film of graphene on an insulating medium. (4)

**2.3: Raman**

Raman spectroscopy is a technique used to determine the morphological composition of

a material by observing the inelastic scattering of monochromatic light originating from a laser.

Radiation incident upon a molecule can undergo several types of scattering.
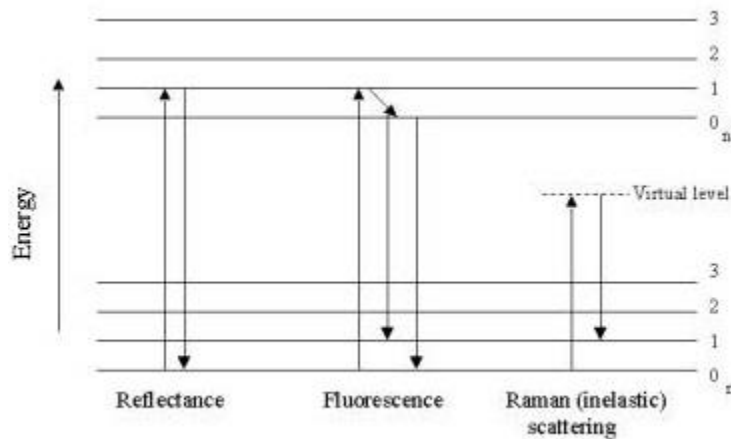


Figure 8: The illustration above depicts an energy level diagram showing the states involved in the Raman signal.

Elastic scattering occurs when the photon energy remains the same.  Inelastic scattering

occurs when the photon's energy strokes or anti strokes decreases and the resulting change in

energy is measure in vibrational motion.   Raman scattered light is dependent on the vibrational

modes of the molecule and is therefore different for every molecule, giving each molecule its

own unique fingerprint.   To understand Raman spectra for graphene it is necessary to

understand the Raman data received from performing a Raman analysis of the sample.

Illustrated in figure 9 below is a graph showing a Raman analysis and Raman mapping. (5)



Figure 9: Depiction of Raman and Raman mapping. 1) Raman mapping of graphene showing predominant single layer graphene with some multilayer regions. 2) Raman spectrum showing Raman's main features the D,G and G' peaks resulting from laser excitation.
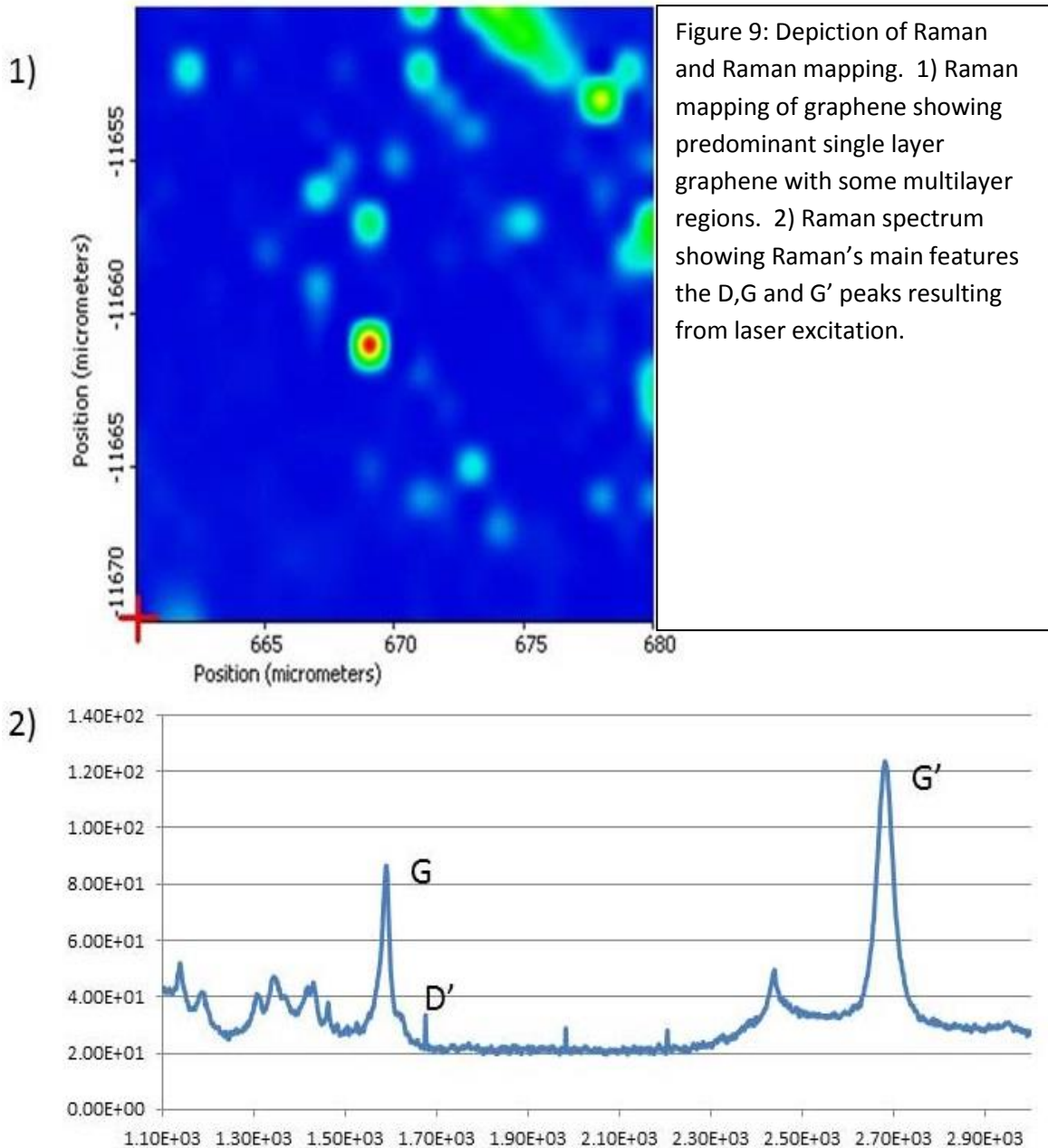
The most prominent features in Raman spectra analysis of monolayer graphene is the

ratio of the G' peak to the G peak. In order to determine if the graphene is monolayer or not,

the ratio of G'/G needs to be greater than 1. When the G' peak is approximately twice that of G

peak, some authors prefer to call it the 2D peak to indicate that the sample is monolayer. (5)

The presence of a D peak determines the presence of a significant number of defects in the

graphene.  The Raman mapping in figure 9 above gives a 20 by 20 micron area of the sample

showing the number of layers present.  Indicated by the predominant amount of blue regions

located on the map, it is possible to see that the graphene sample is predominantly single layer.

The presence of green and light blue indicates that there are some multi-layer regions present.

Due to the amount of time required to perform Raman mapping, this experiment will be using

Raman spectra analysis to show results of samples synthesized during chemical vapor

deposition.


## 2.4: Scanning Electron Microscope

A scanning electron microscope produces images of a surface's topology (SEM) by

scanning the surface with a focused beam of electrons.  The focused beam of electrons is

emitted from an electron gun fitted with a tungsten filament cathode.  Tungsten is used due to

its high melting temperature and its low vapor pressure compared to all other metals allowing it

to withstand the heat generated for electron emission.  The generated electron beam in SEM is

usually focused by one or two condenser lenses to a small nano-scale spot.  The beam passes

through coils or deflector plates in the column.  The final lens typically deflects the electron

beam causing the electron beam to scan in a raster fashion over a rectangular area of the

surface sample.   The interaction of the primary electron beam and the sample being scanned

causes the electrons to repeatedly lose energy by random scattering and absorption.  The

energy exchange between the electron beam and the sample results in the reflection of high-

energy electrons by elastic scattering, inelastic scattering, and electromagnetic radiation.  These

reflected electrons on the sample are detected by a series of sensors that use them to generate

a high resolution image depicting the surface of the sample.   With SEM it is possible to view

high magnification images of a sample at nano scale levels.   Illustrated below is the general
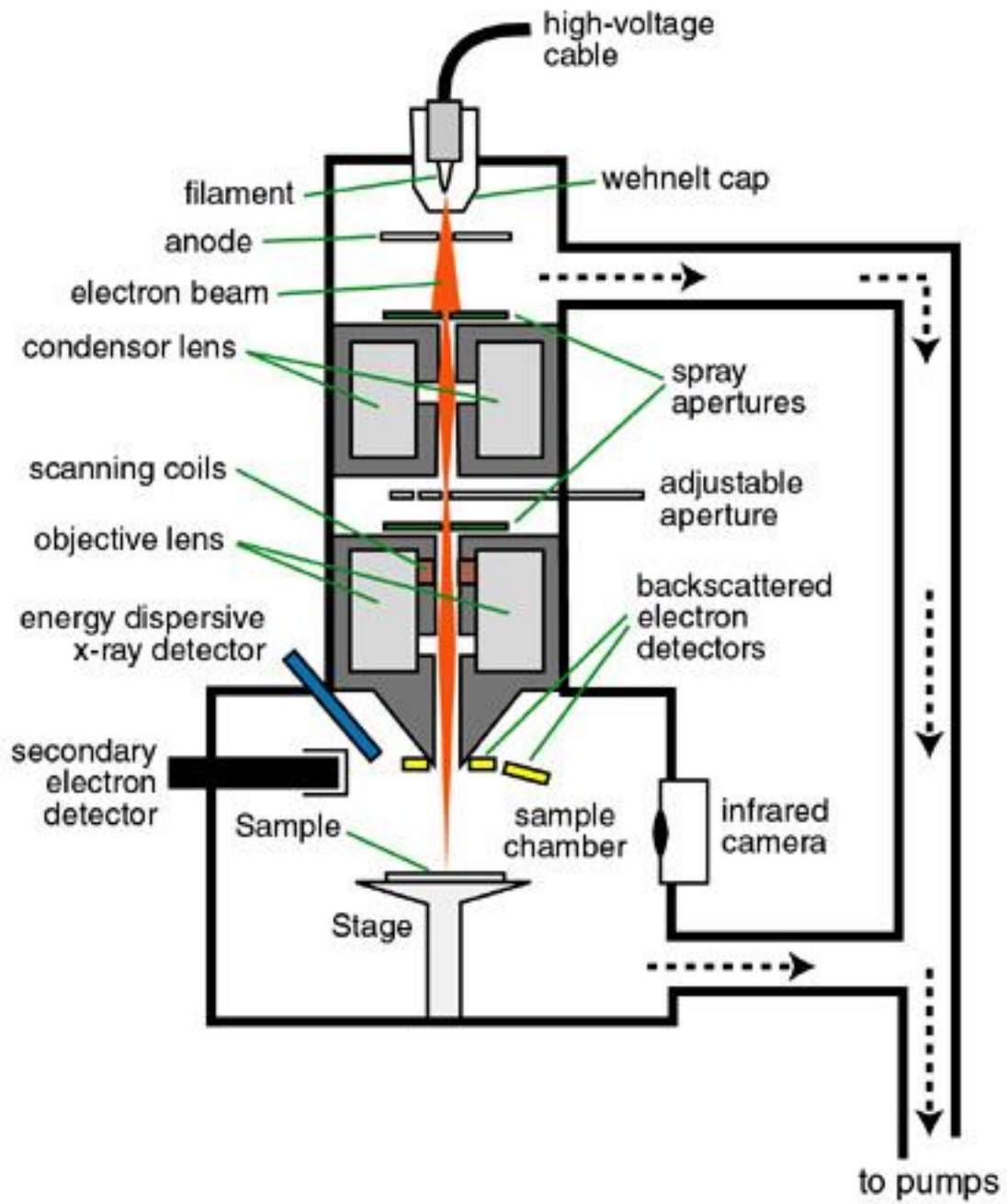
setup of a typically SEM.

Figure 10: The schematic of a typically scanning electron microscope

### 3: Details of Research

### 3.1.1: Methane

Methane is a hydrocarbon species typically used as a precursor for graphene growth, similar to acetylene and ethylene. Methane is one of the most commonly used precursors, as it is comparativey stable, has a low pyrolysis rate at high temperature, and has a simple atomic structure. Most other hydrocarbons tend to have a very high pyrolysis rate at high temperature resulting in large amounts of carbon deposition that isn't preferred for thin films of graphene.

### 3.1.2: Hydrogen

The growth of graphene strongly depends on hydrogen which has two roles when it comes to the synthesis of graphene. Hydrogen activates surface bound carbon that leads to monolayer growths and works as an etching agent that controls the number of layers of grapheme present during synthesis. During the growths noted in the experimental, a slow cooling time was preferred to allow hydrogen to etch away as many layers as possible to try and ensure single layer growths.

### 3.2: Catalyst

### 3.2.1: Copper

The catalyst used for the graphene growths during the experiments is a copper foil that is 99.9% CU due to its preferred properties. Copper is an excellent catalyst for making uniform large-area graphene films due to copper's low carbon solubility. In recent research, coppers impressively low carbon solubility has suggested that the copper catalyst is self-limiting.

### 3.3: Transfer Materials

### 3.3.1: PMMA

PMMA or polym-ethyl-methacrylate is a transparent thermoplastic synthetic polymer. PMMA has been used as a carrier material for transferring carbon nanotubes, mechanically exfoliated graphene flakes, and has been widely used to transfer CVD grown graphene to target substrates. (7)   Recent studies have shown that the addition of a second layer of PMMA exhibited enhanced performance of graphene's high optical transmittance and conductivity. (8)
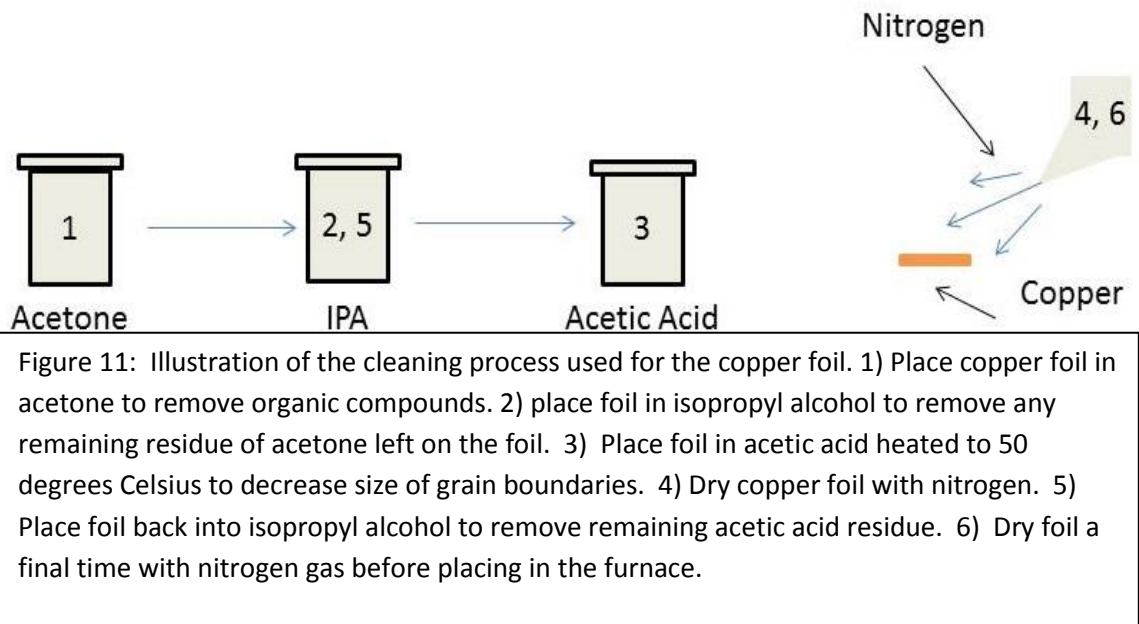
## 4: Experimental

The following details the steps and procedures taken in order to synthesize graphene in the lab from cleaning to transfer.  The metal catalyst used in the experiments was 99.9% pure copper foil.  Copper was chosen as the catalyst due to it preferable low carbon solubility which increases the ease of achieving single-layer uniformity during graphene synthesis.

## 4.1:  Cleaning

`        The copper foil is cut into 1 by 1 inch squares in order to ensure there is enough material during the transfer process to create as many samples as possible to be fished out. The one inch squares of copper foil are rinsed with acetone to dislodge any large particles on the surface of the foil.  The copper foil is then placed into a beaker containing a 70% acetone solution for 5 minutes.  Acetone is used as the first cleaning agent to make sure to remove any organic compounds and ionic salts that may be present on the copper foil prior to the growth. After 5 minutes in the acetone solution, the beaker is than sonicated to remove any remaining particles.   The copper foil is then removed from the beaker containing acetone and rinsed with isopropyl alcohol before being placed in a beaker with isopropyl alcohol.  The foil is rinsed in order to ensure that there is no contamination between the beakers containing acetone and isopropyl alcohol.  The copper foil is placed for 5 minutes in a beaker containing isopropyl

alcohol.  Isopropyl alcohol removes any residual residue of acetone that may have been left

behind as a result of using acetone to remove the organic compounds.    After 5 minutes inside

the isopropyl alcohol solution, the beaker is sonicated to ensure removal of any unwanted

residue.  The foil is then fished out and dried with a nitrogen gas.  Nitrogen gas is used because

it is a non-reactive gas, eliminating any concerns of a reaction taking place after being placed in

isopropyl alcohol.  The copper foil is then placed in a beaker that's been heated to 50 degrees

Celsius containing acetic acid for 5 minutes.  Acetic acid is used to reduce the grain size of the

grain boundaries in the copper foil.  Deep grain boundaries in the copper foil can lead to

problems during transfer and undesired wrinkles in the thin film of graphene.  After 5 minutes in

acetic acid at 50 degree Celsius, the copper foil is fished out, rinsed with isopropyl alcohol and

then placed once again in the beaker containing isopropyl alcohol.  Acetic acid is an organic

compound and it is necessary to use isopropyl alcohol to remove any remaining residue of acetic

acid before it is placed in the furnace.  After 5 more minutes in isopropyl alcohol, the foil is then

dried with nitrogen gas.  Once dry, the copper foil is then ready to be placed inside of the

furnace.  The following detailed process is illustrated below.

Figure 11: Illustration of the cleaning process used for the copper foil. 1) Place copper foil in acetone to remove organic compounds. 2) place foil in isopropyl alcohol to remove any remaining residue of acetone left on the foil. 3) Place foil in acetic acid heated to 50 degrees Celsius to decrease size of grain boundaries. 4) Dry copper foil with nitrogen. 5) Place foil back into isopropyl alcohol to remove remaining acetic acid residue. 6) Dry foil a final time with nitrogen gas before placing in the furnace.

## 4.2: Chemical Vapor Deposition

The method used in the experiments to synthesize graphene was chemical vapor deposition or CVD. The CVD system setup in lab, illustrated below, consists of three mass flow controllers (MFC's), central mass flow controller, high power vacuum, MTI furnace, pressure controller, pressure controller valve, and a quartz tube.
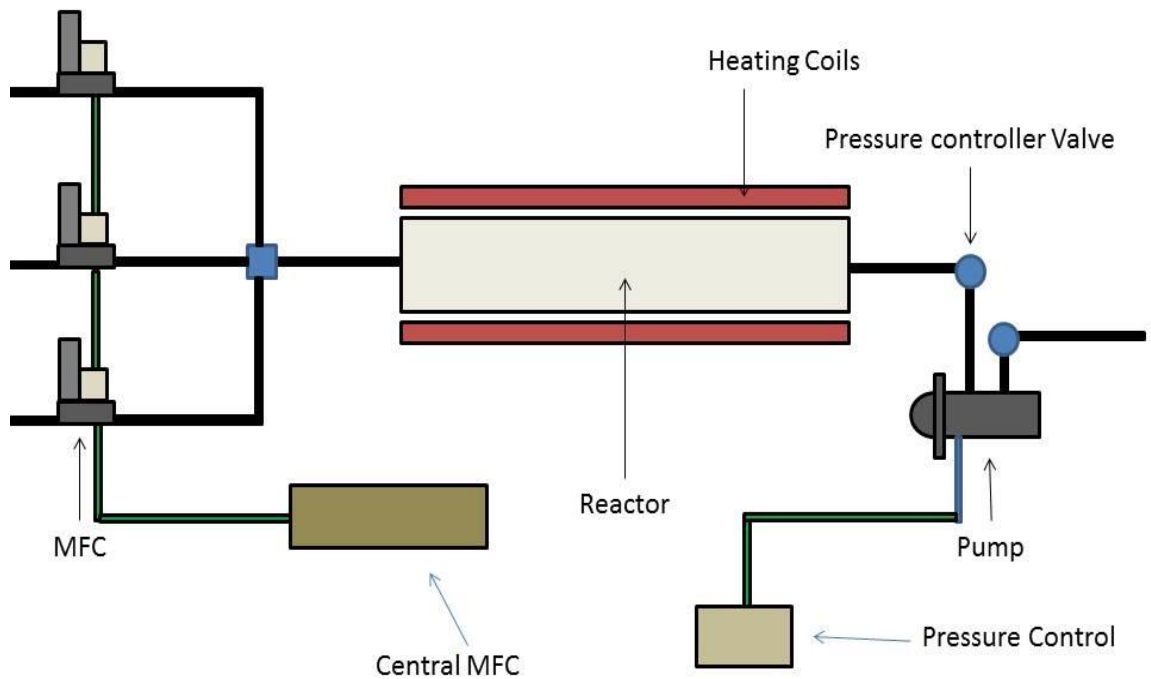
Figure 12: The schematic above illustrates the CVD setup used in the following experiments.

The copper foil is loaded into the furnace where it is sealed at each end by two stainless end

caps. The copper is placed directly in the center of the furnace to avoid any heat loss due to the

heat gradient that exists at each end of the furnace. Once sealed, the furnace is pumped down

to 1.7 torr to remove any air in the system. At the desired pressure, the mass flow controllers

open and release a constant stream of gas into the system to ensure the system is purged of any

remaining air that was not able to be pumped out. There are three tanks hooked up to the mass

flow controllers regulated by the multi gas controller. These three tanks are Methane (CH4)

Hydrogen (H) and Argon (Ar). Methane is a very clean carbon source while hydrogen acts as the

hydrocarbon and carrier gas. Argon's presence in the system is for dilution of the gas ratios.

The two ratios used in the experiments is a 1:1 ratio of hydrogen to argon for annealing with a

40:1 ratio of hydrogen to methane for synthesis of the graphene and a 1:1 ratio of hydrogen to

argon for annealing with a 2:1 ratio of hydrogen to methane for synthesis.  The recipes used to

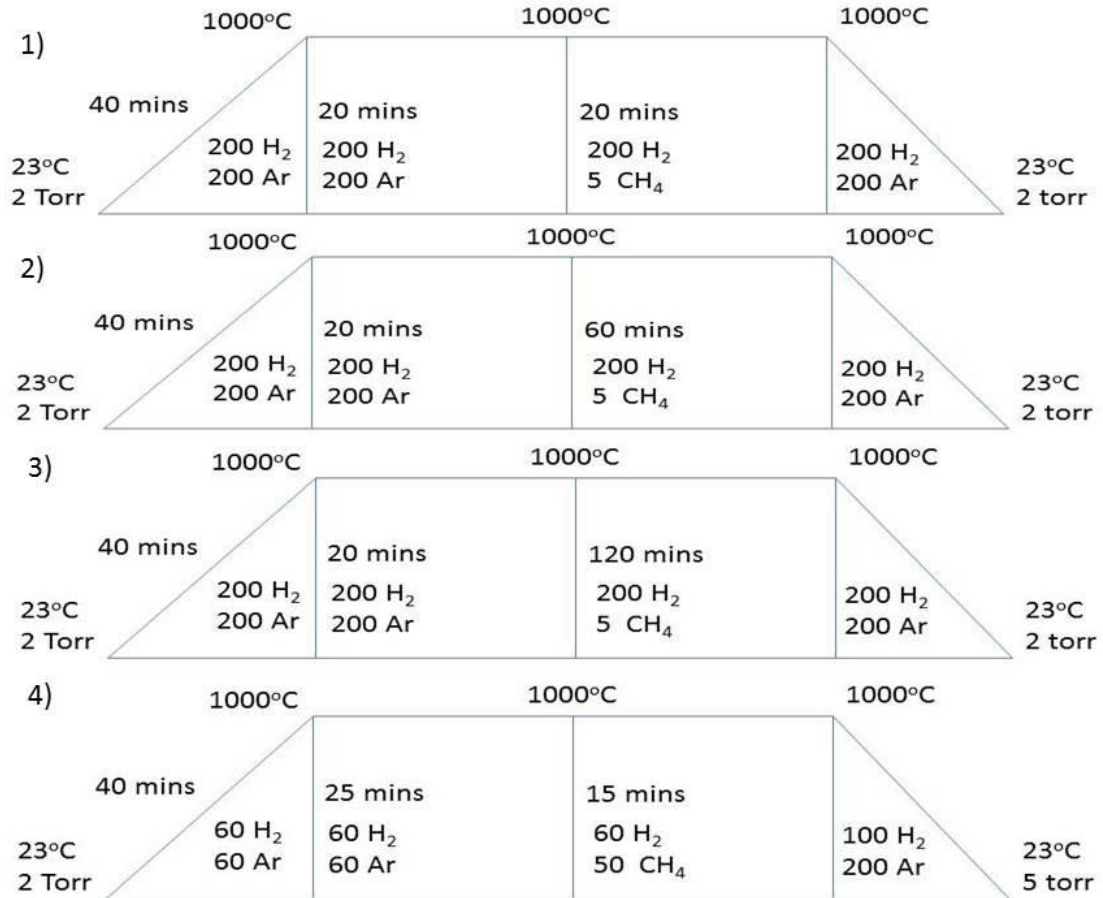synthesize the graphene are illustrated below.



Figure 13:  Illustrations of the four recipes used during the experiments.  The difference in the first three recipes lays within the amount of time used to grow graphene:  1) 20 minutes, 2) 60 minutes 3) 120 minutes. 4) The first recipe used to synthesize graphene when the increase in growth speed was observed

As illustrated in the figure 13 above, there is only a minor difference in the first three recipes.

This was purposeful so as to be able to see what was occurring by altering the fluid mechanics of

the system.  The final recipe is the standard recipe used in lab to grow graphene.  It was initially

observed using recipe (4) that graphene grew at an elevated rate by adjusting the fluid

mechanics.  The results of using recipe (4) with and without the plate are detailed by Raman and

Raman mapping sets forth in the results and discussion.

The plate is composed of aluminum with small holes machined in a honeycomb

structure.  The  honeycomb structure's surface area is smaller than that of the inlet.  This results

in not all the air passing through the plate's holes.  The benefit of this is the resulting turbulent

mixing.  Turbulent mixing forces the gases to achieve a more homogenous state then previously.
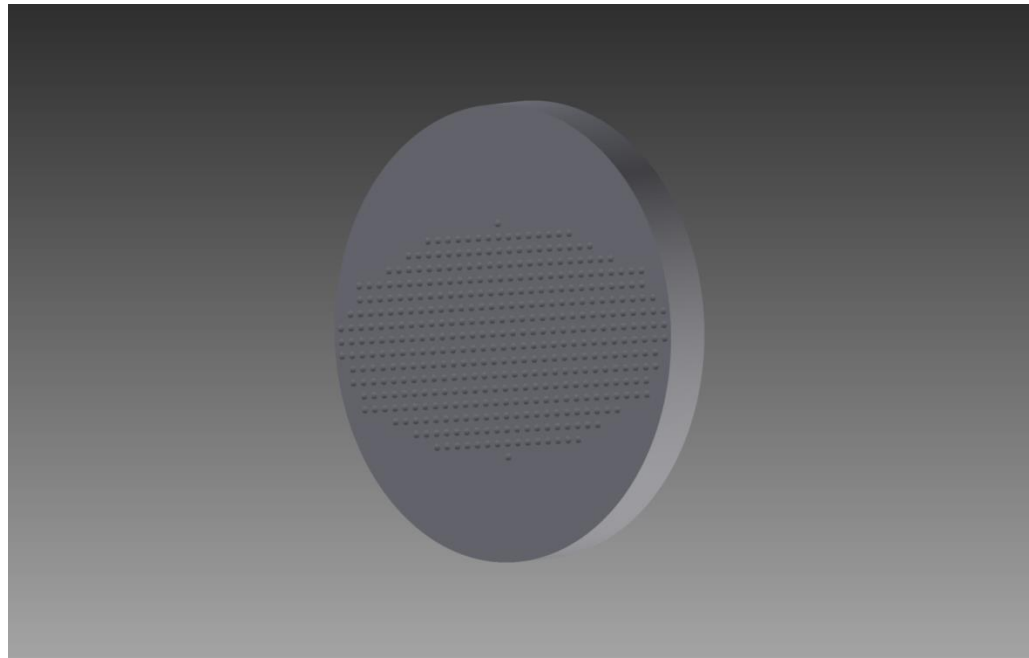
The plate is depicted below in figure 14.



Figure 14: Depiction of plate used in experiments

**4.3: Transfer**

  The transfer process is a time consuming three step process that is extremely involved and occurs after the grapheme growth using the CVD system.  The first step involves spin coating the copper foil with PMMA at 3600 rpms for sixty seconds.  After the foil is spin coated, it is placed on a hot plate at $115^0C$ for 15 minutes to turn the PMMA from liquid phase to solid phase.  Hardening the PMMA ensures that it will not fall off during the second step of the process.  The second step of the process involves exposing the uncoated side of the foil to a solution of 96% ferric chloride and 4% hydrochloric acid.  The copper foil is left in the acid solution overnight to ensure that all the copper is removed leaving only the top layer of graphene that is adhered to the hardened PMMA.  The final step involves removing the acid solution and replacing it with water.  This involves diluting the acid solution several times with diluted water by filling the glass beaker with water than pumping it out.  After several dilutions, the graphene is fished out onto a silicon dioxide wafer.  The wafer is than let to dry before being placed in acetone and isopropyl alcohol to remove the PMMA.  The Transfer process is illustrated in figure 15 below.
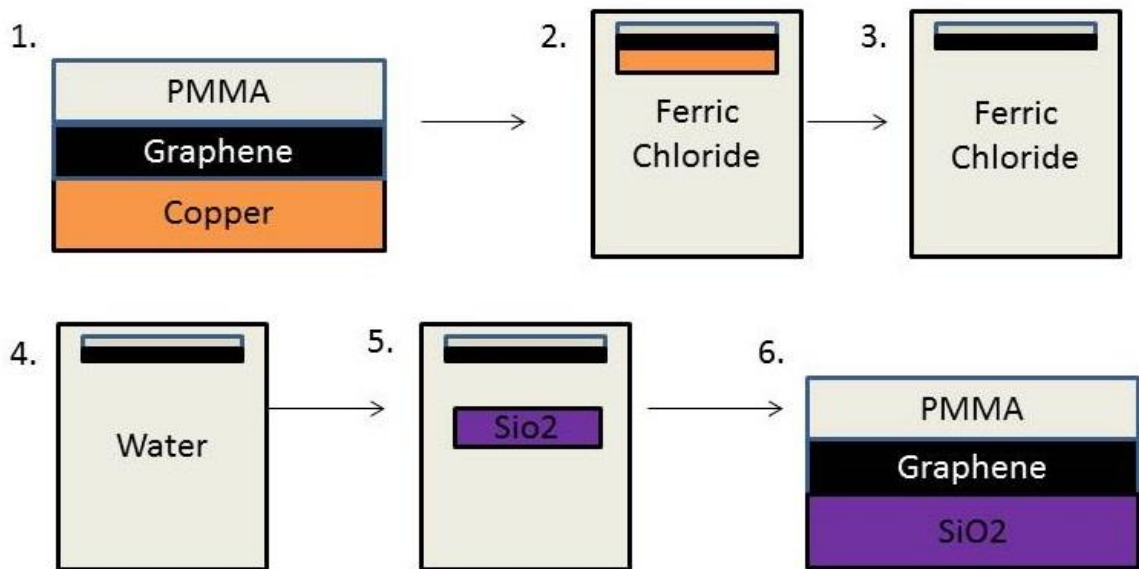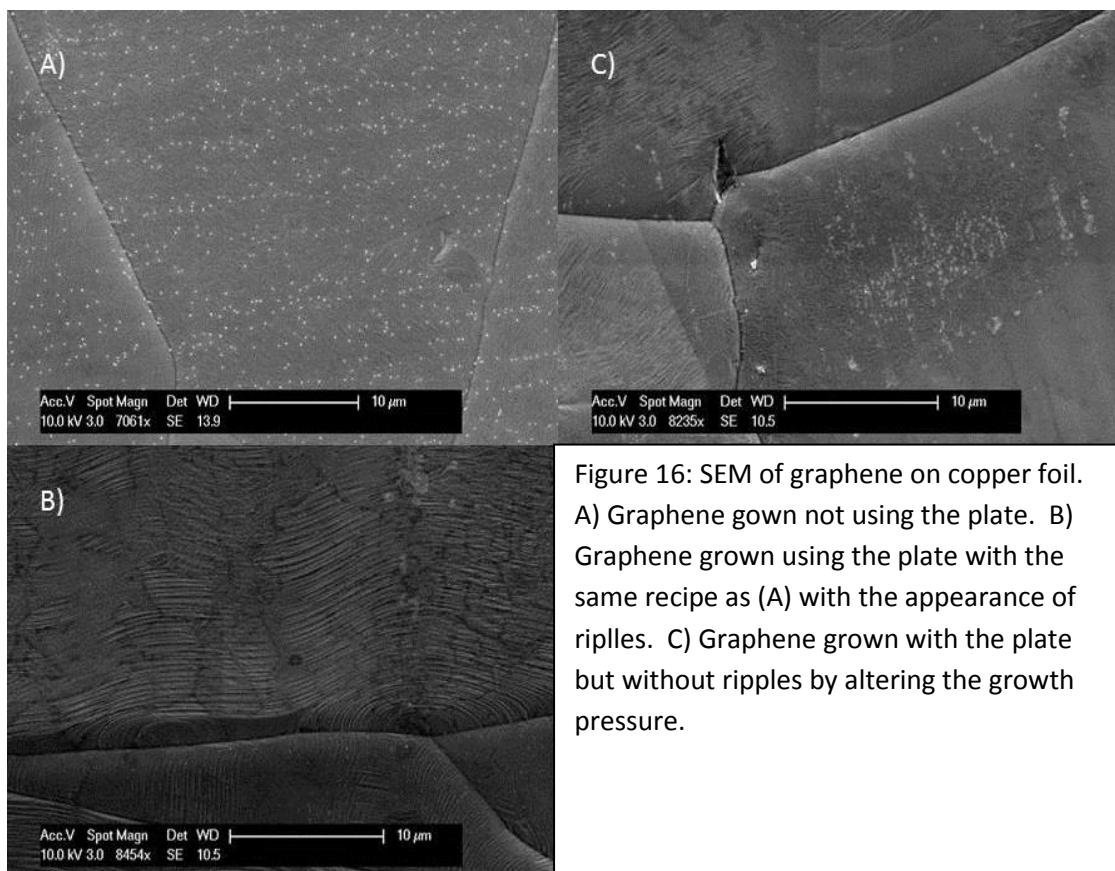
Figure 15:  The graphene transfer process illustrated

## 5: Results and Discussion

The original purpose of modifying the air flow in the CVD system was to decrease

contamination witnessed on top of the graphene under SEM.  The original intent was for the

plate to provide a homogenous air flow throughout the entire furnace thereby minimalizing the

amount of contamination on top of the graphene.  Originally the plate reduced the amount of

contamination that would appear on top of the graphene as depicted in Figure 16.  However, it

was observed that the use of the plate sometimes caused ripples to develop on the graphene.

As a result, growths were carried out altering the recipe used with the intent of alleviating the

problem of ripples forming.  After several experiments, it was determined that pressure was the

cause of the ripples.  Low pressure growths from 2-10 torr resulted in no formation of ripples as

shown in Figure 16.  An issue developed when the contamination reached the same levels as

before the plate.  It was determined that the contamination actually originated from the quartz

tube in the furnace becoming porous due to thermal expansion resulting from high growth

temperatures.  Under cooling the pours would close up trapping in catalysts used during the

graphene growth and then release them during the next growth.  The problem was finally

alleviated by using the graphene that synthesized on the underside of the copper rather the

grapheme that synthesized on the top of the copper.  While trying to remove the

contamination, an observation was made about graphene grown using the plate.  What

appeared to be single layer under SEM actually turned out to consist of multiple layers.  The

multiple layers are confirmed by the Raman spectra analysis shown in figure 17.



Figure 16: SEM of graphene on copper foil. A) Graphene gown not using the plate.  B) Graphene grown using the plate with the same recipe as (A) with the appearance of riplles.  C) Graphene grown with the plate but without ripples by altering the growth pressure.

Shown by the relationship between the G'/G peak being less than 1, the graphene sample

contains multiple layers of graphene.  The existence of multiple layers is a surprise considering

the same recipe used without the plate achieves a single layer as illustrated in figure 16.  The

Raman spectra analysis in figure 17 shows that relationship of the G'/G for no plate is greater

than 1 showing the existence of a single layer graphene.   The hypothesis was that the

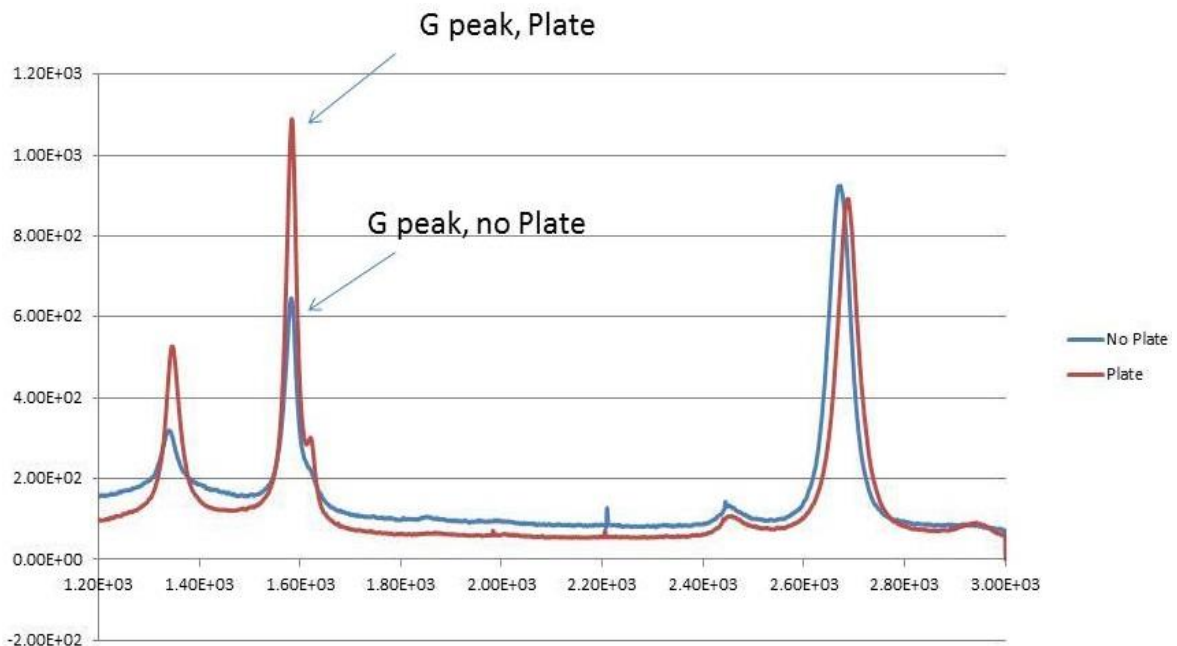introduction of the plate resulted in quicker synthesis of graphene.



Figure 17:  Raman spectroscopy of graphene synthesis using and not using the plate.  The higher G peak indicates the formation of multi-layer when using the plate.

In order to confirm that graphene was synthesizing faster, graphene was first grown using the

original 60 Hydrogen/ 60 Argon/ 30 Methane synthesis recipe.  Instead of growing for 15

minutes though, the synthesis time was reduced by a third to 5 minutes.  The result of dropping

the graphene synthesis time is the formation of a mostly uniform single layer.  The mostly

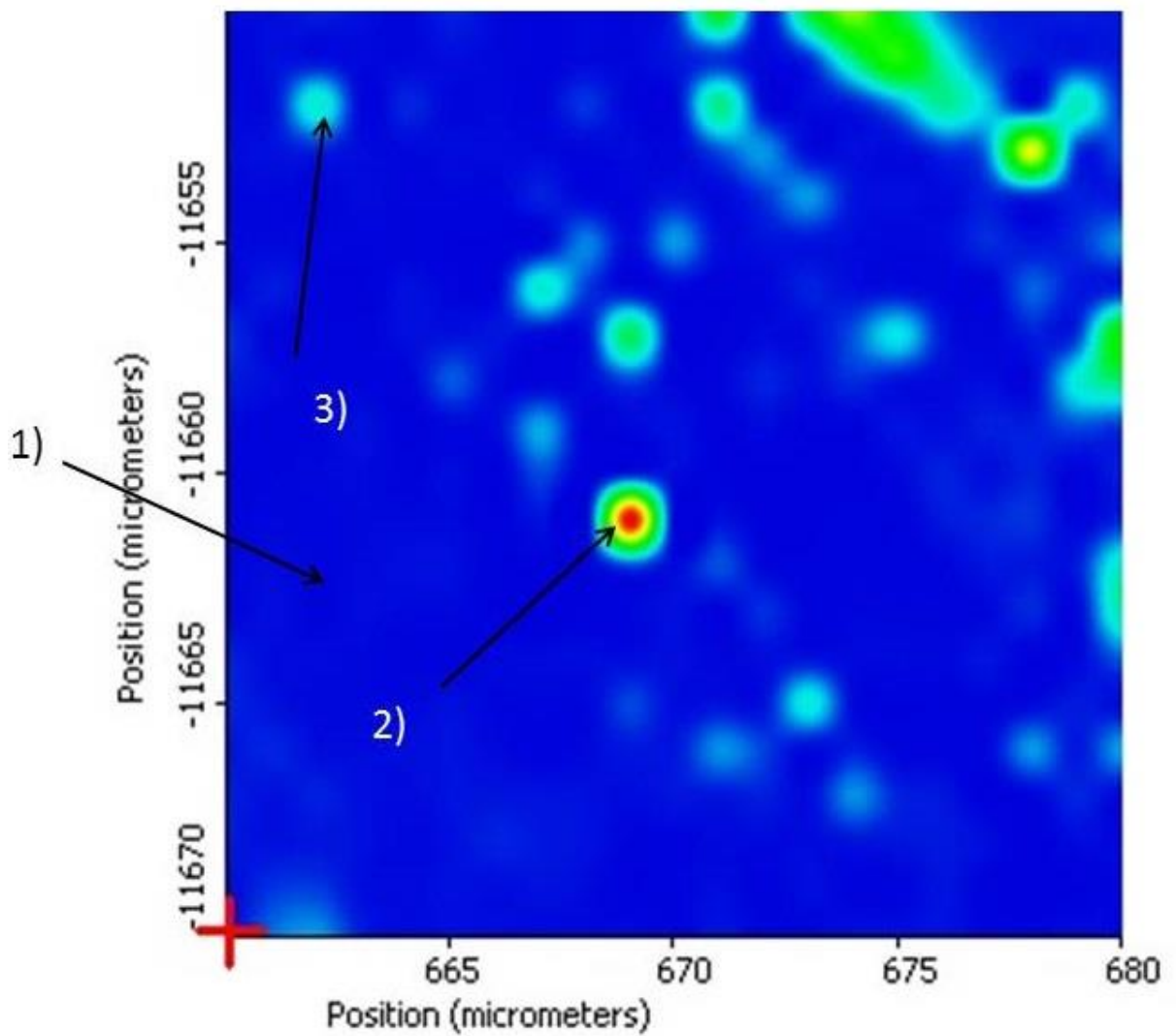uniform single layer is confirmed by Raman mapping illustrated in figure 18.

Figure 18: Raman mapping of graphene grown using the 60 Hydrogen/ 60 Argon/ 30 Methane. 1) predominantly single layer region. 2) Bi layer region 3)Multi Layer region

The blue regions represent single layer region of graphene and since the sample is

predominately uniform it can be deduced that the addition of the plate reduced growth times to

achieve similar results as those obtain not using the plate and synthesizing for 15 minutes. The

red region on the Raman map indicates a point on the graphene that is multilayer. The greenish

blue regions indicated few layers and bi layer regions on the graphene. The layer of the regions

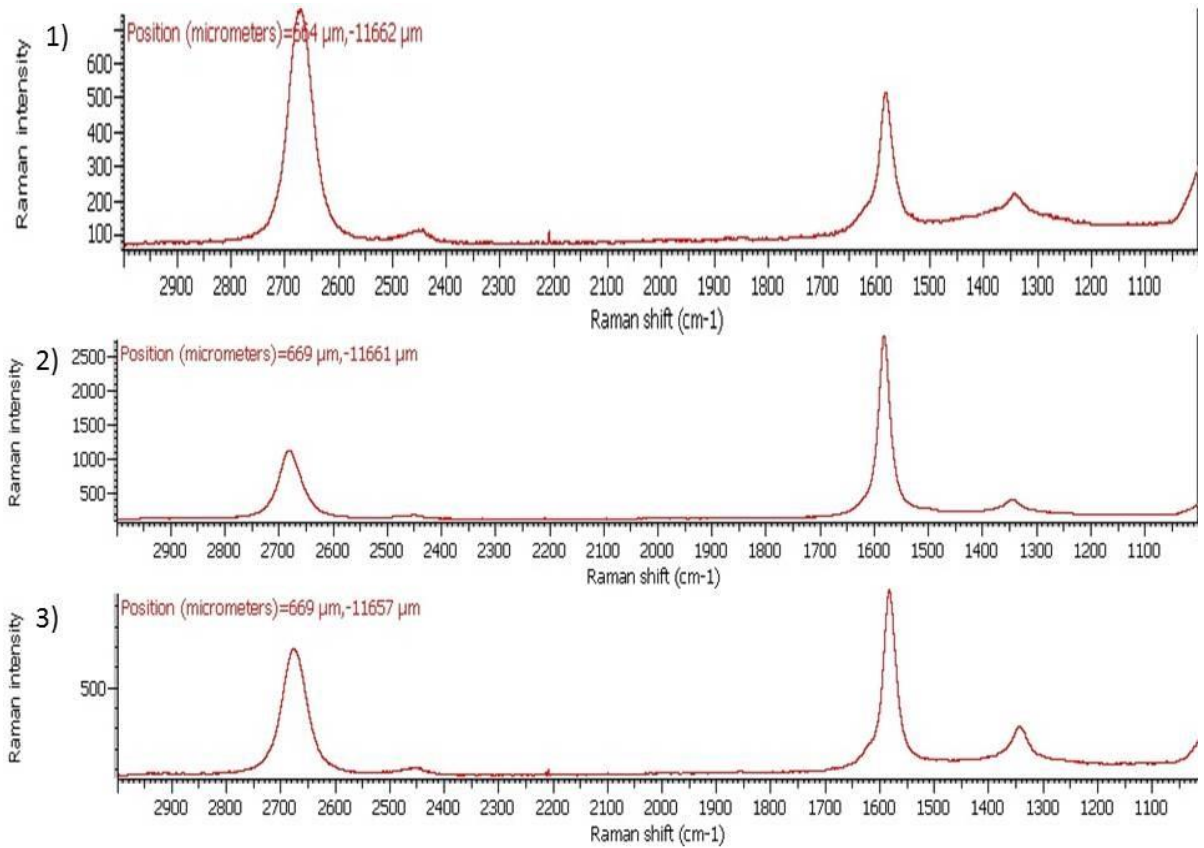is confirmed by Raman spectra analysis shown below in figure 19.



Figure 19: Raman for graphene grown 60 Hydrogen/ 60 Argon/ 30 Methane. 1) Single layer graphene. 2) Multi-layer graphene. 3) Few and bilayer graphene.

The Raman graphs above detail 3 different points on the Raman sample grown using the

60 Hydrogen/ 60 Argon/ 30 Methane.  The time used in this recipe was 5 minutes compared to

the original 15 minutes used to achieve single layer large area uniform graphene.  From the

Raman images above and the use of Raman mapping it can be concluded that 5 minutes is still

too long to achieve uniform single layer.  Therefore, testing has been done to reduce the time

even further to see at what point in comparison to the original recipe use of the plate achieves

uniform single layer.  It was concluded that with use of the plate, graphene would achieve

uniform single layer when synthesized for 3 minutes in the furnace.  The Raman spectra analysis

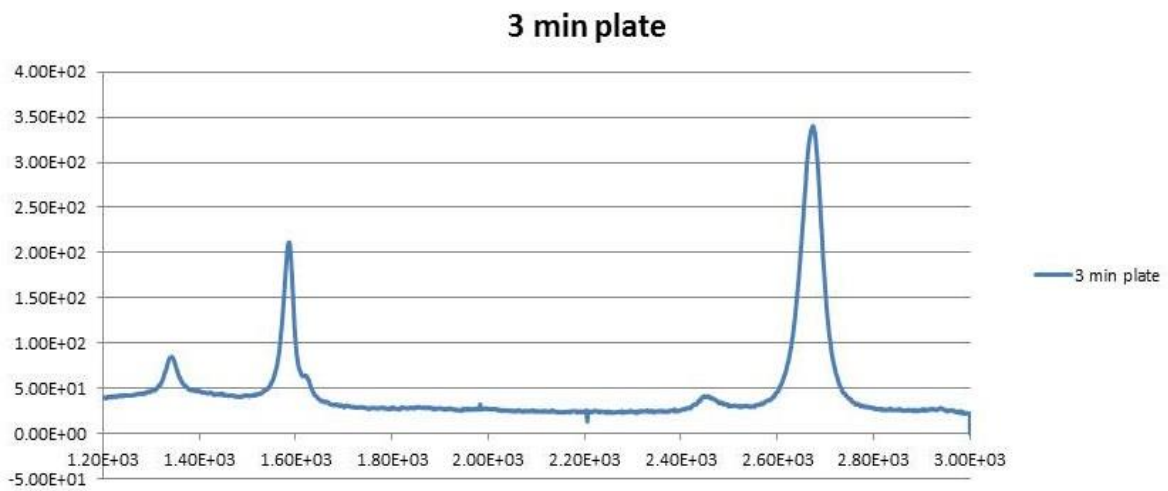for the 3 minute growth is shown in figure 20 below.



Figure 20: Raman for 3 minute graphene growth.

The results of the 3 minute graphene growth prompted a further look into what

mechanics are going on inside the system.  To further understand the mechanics of the system

an experiment was planned with a control that did not use the plate.  The experiment would

slow down the time required to achieve single layer graphene by diluting the hydrogen to

methane ratio of the system.  Diluting the hydrogen to methane ratio of the system is to achieve

uniform single layer graphene requires 120 minutes to synthesize the graphene.  In order to see

the crystal growth, growths times were staggered at 20, 60, and 120 minutes.  The results of

growing graphene for 20 minutes with a 40:1 hydrogen to methane ratio is the clear depiction of

hexagonal graphene crystals.  The hexagonal crystal is depicted in figure: 21 below.  In order to

compare the growths using the plate and not using the plate, an identical growth was done with

the plate to see how it affected the growth.  The 20 minute growth using the plate is depicted
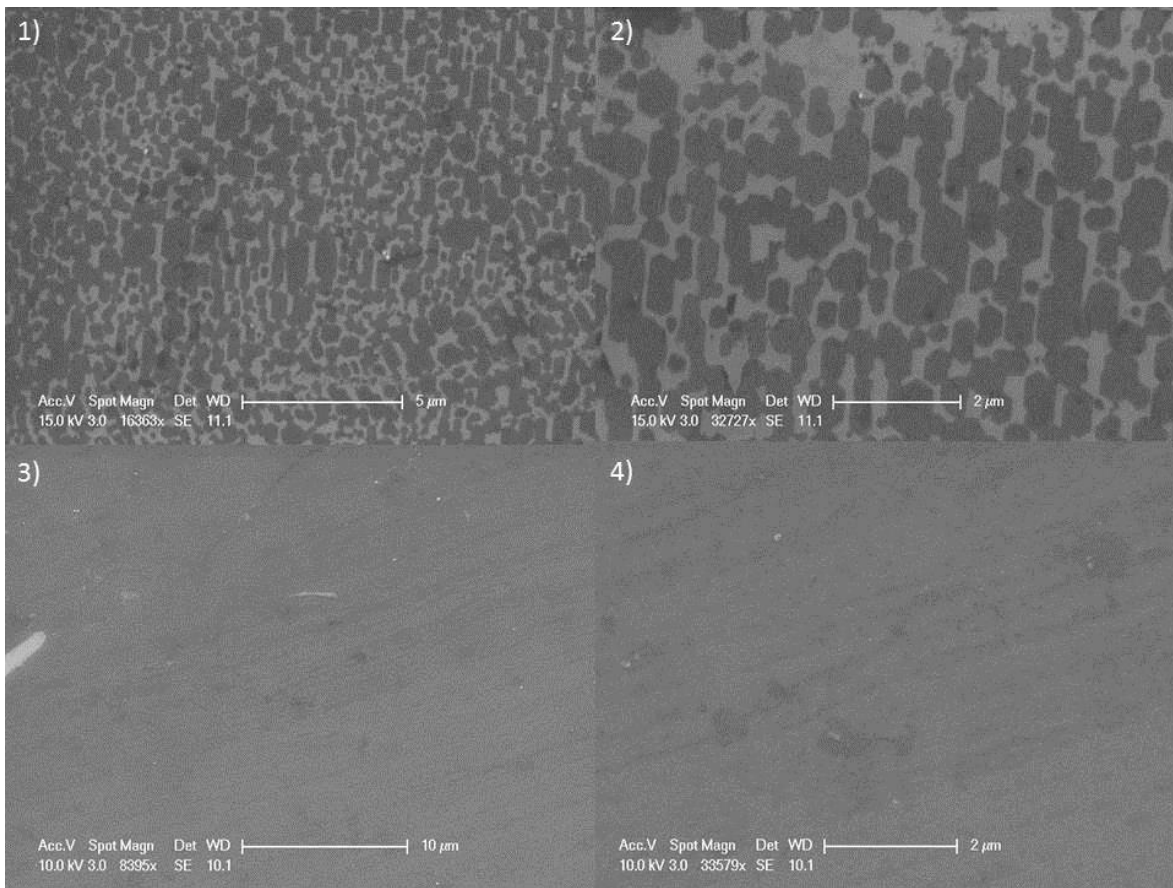
below in figure 21.



Figure 21:  SEM images of graphene growths transferred onto silicon dioxide. 1) & 2) SEM images of the 20 minute growth without the plate.  3) & 4) SEM images  of the 20 minute growth with the plate.

Depicted clearly in images 1) and 2), it is possible to see the hexagonal crystals that were forming during the growth.  In contrast, images 3) and 4) look like sheets of film with no discernible grain boundaries.  Originally it was concluded that nothing had grown or that the grain sizes were very small but things became clearer once Raman was taken.  The Raman spectra analysis showed that the graphene grown using the plate was extremely multilayer.  The Raman spectra analysis depicting the extent to which the 20 minute sample using the plate is multi-layer is shown below in figure 22.
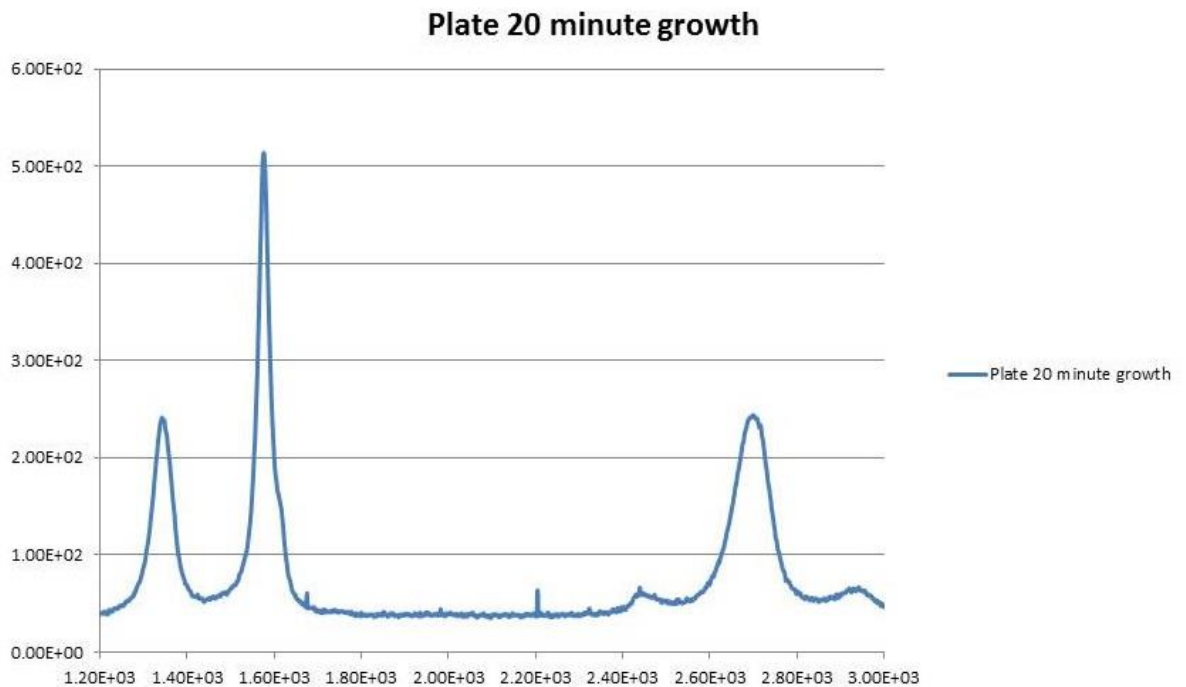


Figure 22: Raman graph of the 20 minute growth using the plate

The Raman above represents the results of the 20 minute growth using the plate.  From the ratio of the G'/G peak it is possible to conclude that the graphene that was synthesized contains several layers.  Another factor to take into account from the Raman is the height of the D peak.  The height of the D peak suggests there are quite a few edge defects on the graphene sample.  This may result from the size of the graphene crystals forming when using the plate.  In comparison to not using the palte, micron size crystals are achieved where as using the plate, only nano size crystals are formed.  This may explain why there is such a high D peak in the Raman results.  The second step at 60 minutes produced similar results as can be seen by the SEM images listed below in figure 23.
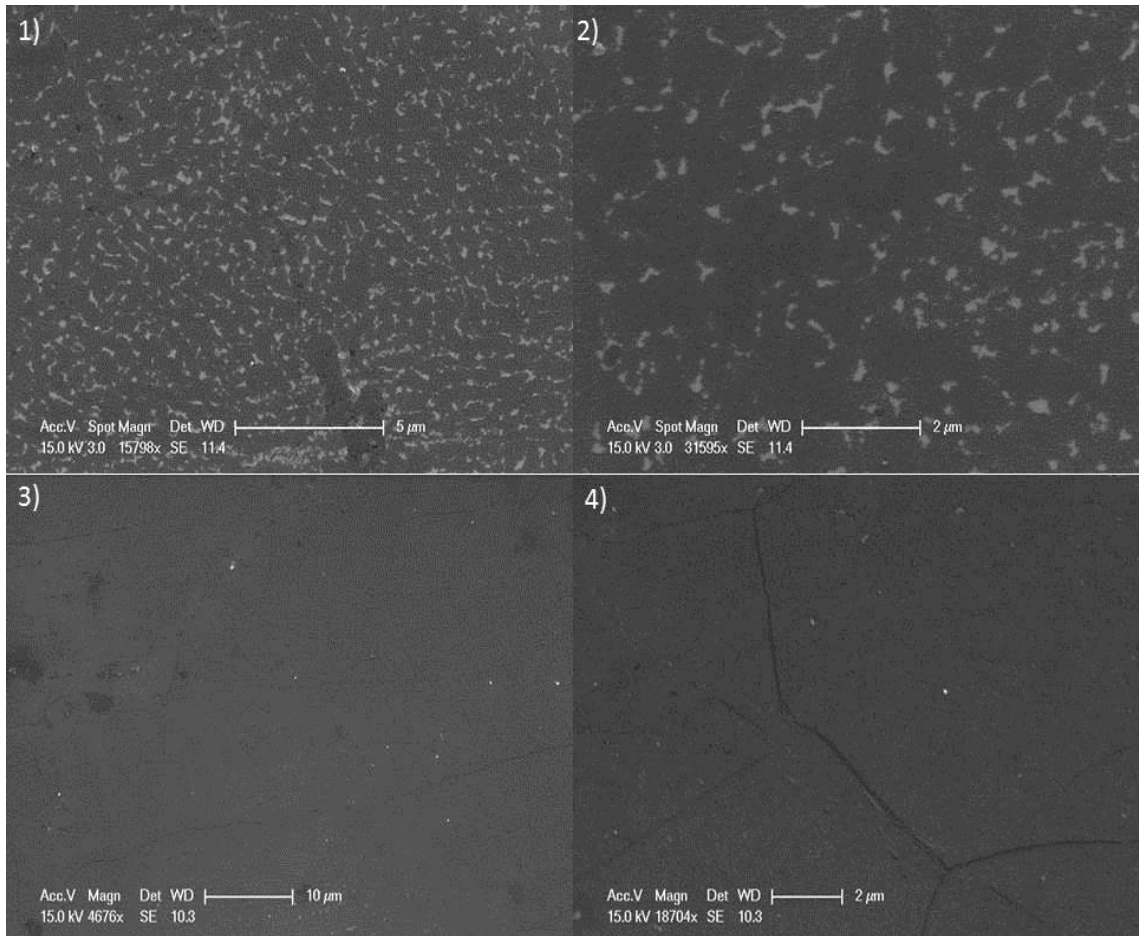
Figure 23: SEM images of graphene growths. 1) & 2)  SEM of the 60 minute growth of graphene without the palte. 3) & 4) SEM of the 60 minute growth of graphene with the plate.

Similar to the 20 minute growth shown previously, the 60 minute growth achieved similar results with minor differences.  Firstly, the 60 minute growth without the plate shows the same hexagonal structures that graphene is known to have still, but the formation of a uniform single layer has not been achieved.  In comparison to the 20 minute growth with the plate, the 60 minute growth without the plate did progress closer to achieving uniform single layer.  The 60 minute growth with the plate is similar to that of the 20 minute growth without it.  The only difference is the number of layer and thickness of the graphene.  From the SEM it is

possible to see the extreme thickness of the graphene when using the plate for the 60 minute growth. Since the 20 minutes growth results show use of the plate results in quicker growths, no growth with the plate for 120 minutes was attempted. However, a growth was done for 120 minutes without the plate in order to ensure that without the plate it takes 120 minutes to grow large area uniform graphene.
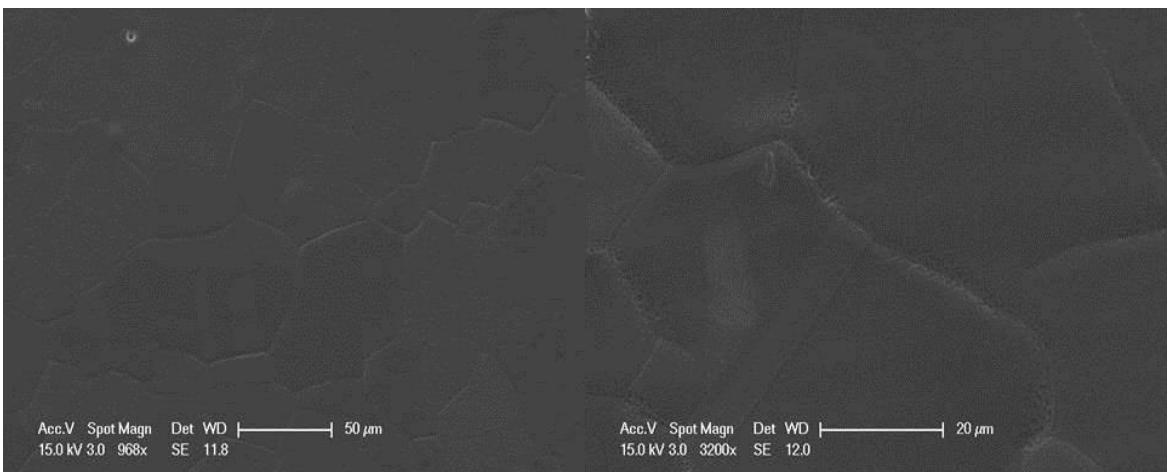


Figure 24: SEM images of the 120 minute growth without the plate

Shown in the SEM image above in figure 24, the graphene grown for 120 minutes without the plate has achieved uniform coverage. Also shown by the image above, the graphene has large grain sizes which can be attributed to the duration at which the graphene has been grown.

**6: Conclusion**

The conclusion that can be drawn from the results is that by altering the fluid mechanics of the system to provide a more uniform homogenous air flow above the sample, there can be many advantages to industry. These advantages include reduced growth times and use of less

precursor gas.  The reduced growth times is a tuning process; currently where it stands in the

experiments above, the crystal grain sizes are too small to be beneficial for electronic circuits.

This being said, if crystal size is not an issue and all that is desired is graphene flakes, than

altering the fluids mechanics of the system with the plate is an easy way to achieve graphene

flakes quickly without over saturation of the sample with carbon precursor.  No testing was

done on using less precursor gas since the current systems set up in the lab could not achieve a

low enough flow of sccm.  As a result it can only be hypothesized that if less methane gas were

to be used than there you could get similar grain size results without having to use so much gas.

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