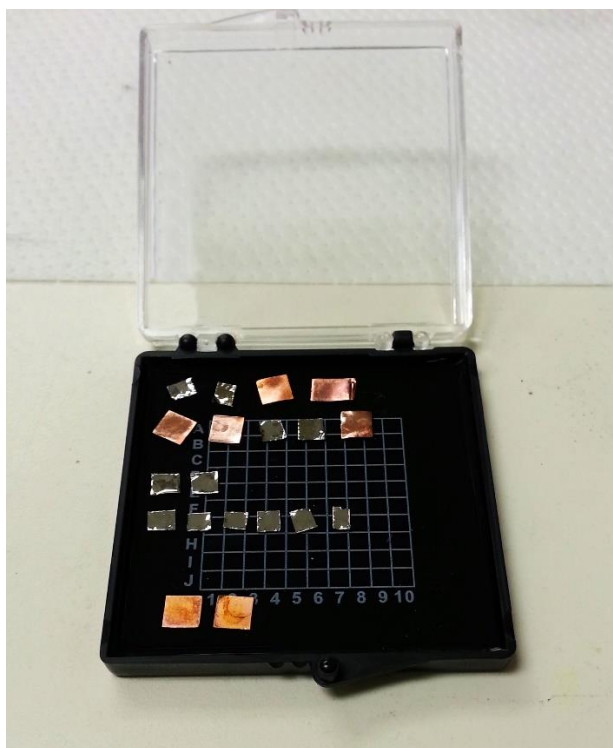


THE UNIVERSITY OF BRITISH COLUMBIA



Synthesis of Single- and Few- Layer Graphene by Chemical Vapor Deposition of Methane on Copper and Platinum



Prepared by: Sanad Aridah ()

Supervised by: Dr. Alireza Nojeh and Andrew Koch

In collaboration with: Dr. Guangrui Xia

ABSTRACT

Graphene has been in the spotlight of research activity for the past decade, this two-dimensional lattice of carbon atoms has strong SP² covalent bonds that give the material characteristics unmatched by any other substance in terms of mechanical strength, electrical and heat conductivity, as well as flexibility. This project explored the synthesis of Graphene using chemical vapor deposition (CVD), a process well known for its ability to produce high quality, defect-free solid materials. The system was modified to chemically deposit Methane onto Platinum and Copper catalysts at temperatures nearing 1040° C. The resulting samples were characterized using Raman Spectroscopy, the Raman spectrums provide essential information regarding the number of layers in the Graphene structure and whether or not the structure is free of defects. The analyzed Raman spectrums of Graphene on platinum indicate that the relationship between the flow rate and the intensity peak ratio of the 2D/G bands as well as the growth time and the location of the G-band are linear, however, the growth time seems to have less of a clear influence on the intensity peak ratio due to factors like the high solubility of carbon in Pt, the deposition of amorphous carbon near the grain boundaries and the size of the carbon grains themselves. The Raman spectrums of two of the copper samples show G- and 2D-bands that are fitted in the shape of a Lorentzian function, the bands are located near 2710 CM⁻¹ and 2712 CM⁻¹ with line widths of 36 CM⁻¹ and 34 CM⁻¹ respectively, the G-bands are located near 1590.3 CM⁻¹ and 1589 CM⁻¹, with 2D/G intensity peak ratios of ~1.22 and ~1.92 respectively. The D/G intensity peak ratios of both samples were near ~0.07 which is a clear sign that the Graphene structure formed on the surface is defect-free.

TABLE OF CONTENTS

ABSTRACT	2
TABLE OF CONTENTS	3
LIST OF FIGURES	4
LIST OF TABLES.....	5
GLOSSARY	6
LIST OF ABBREVIATIONS.....	7
1.0 INTRODUCTION	8
2.0 EQUIPMENT AND METHODOLOGY.....	11
2.1 Chemical Vapor Deposition	11
2.1.1 Two-Zone CVD setup	13
2.2 Digital Flow Controllers.....	15
2.3 Raman Spectroscopy	17
3.0 IMPLEMENTATION AND EXPERIMENTING.....	19
3.1 Platinum Foil.....	19
3.1.1 Pre-treatment.....	20
3.1.2 Growth Parameters.....	20
3.2 Copper Foil.....	21
3.2.1 Pre-treatment.....	21
3.2.2 Growth Parameters.....	22
4.0 RESULTS.....	24
5.0 CONCLUSION	30
5.1 Recommendations	30
REFERENCES	31

LIST OF FIGURES

FIGURE 1 GRAPHENE STRUCTURE	8
FIGURE 2 GRAPHENYLENE STRUCTURE	9
FIGURE 3 CVD SETUP.....	11
FIGURE 4 CVD REACTION INSIDE THE QUARTZ CHAMBER	12
FIGURE 5 CVD SINGLE-ZONE SETUP.....	13
FIGURE 6 CVD TWO-ZONE SETUP	14
FIGURE 7 HEATED SILICON SUBSTRATE AT 1041° C	14
FIGURE 8 BEFORE AND AFTER SNAPSHOTS OF THE PT FOIL CRUMBLING	14
FIGURE 9 DISCOLORATION OF CERAMACAST 645N.....	15
FIGURE 10 HORIBA STEC DIGITAL FLOW CONTROLLERS	15
FIGURE 11 MKS VACUUM GAUGE MEASUREMENT AND CONTROL SYSTEM	16
FIGURE 12 SEC-N100 USER INTERFACE.....	16
FIGURE 13 LABRAM HR RAMAN SPECTROSCOPE	17
FIGURE 14 RAMAN SPECTRUM SHOWING THE DIFFERENT BANDS ⁵	18
FIGURE 15 25 BY 25MM PT FOIL	19
FIGURE 16 ARI ULTRASONIC CLEANER	21
FIGURE 17 UNTREATED VS TREATED COPPER FOIL	22
FIGURE 18 MICROSCOPIC IMAGE OF THE COPPER SURFACE,	22
FIGURE 19 RAMAN SPECTRUMS OF ALL 8 PT SAMPLES	24
FIGURE 20 MICROSCOPIC IMAGES OF THE SCANNED LOCATION ON THE PT SAMPLES	24
FIGURE 21 A PLOT OF THE FLOW RATE VS PEAK RATIO FOR SAMPLES 1, 2 AND 4.....	25
FIGURE 22 A PLOT OF THE GROWTH TIME VS PEAK LOCATION RATIO	27
FIGURE 23 A PLOT OF THE GROWTH TIME VS PEAK RATIO	27
FIGURE 24 A 2-D RAMAN MAPPING OF SAMPLE 6, SHOWING POSSIBLE SINGLE-LAYER GRAPHENE	27
FIGURE 25 RAMAN SPECTRUMS OF ALL 4 CU SAMPLES	28

LIST OF TABLES

TABLE 1 PT FOIL SAMPLES AND THEIR CORRESPONDING GROWTH PARAMETERS	20
TABLE 2 CU FOIL SAMPLES WITH THEIR CORRESPONDING GROWTH PARAMETERS.....	23
TABLE 3 PT. SAMPLES AND THEIR RAMAN PEAK RATIOS OBSERVED DURING 7 MINUTES OF GROWTH TIME.....	25
TABLE 4 ANALYSIS OF THE GROWTH TIME, PEAK RATIO AND THE G-PEAK LOCATION OF THE PT. SAMPLES.....	26
TABLE 5 ANALYSIS OF THE 2D/G PEAK RATIO AND POSSIBLE NUMBER OF GRAPHENE LAYERS.....	29

GLOSSARY

Graphene : A 2D mono-layer array of Carbon atoms which are hexagonally bonded in SP2 hybridization orbitals.

Graphenylene : A 2D mono-layer array of non-delocalized SP2 Carbon atoms, made of Cyclohexatriene elements with two C-C bonds within a hexagonal C ring.

LIST OF ABBERRIATIONS

CVD	- Chemical Vapor Deposition
RS	- Raman Spectroscopy
C	- Celsius
Nm	- Nanometer
Pt	- Platinum
Cu	- Copper
Ar	- Argon
H ₂	- Hydrogen
Si	- Silicon
CH ₄	- Methane
SCCM	- Standard Cubic Centimeters per Minute

1.0 INTRODUCTION

This report is concerned with a project whose purpose was to modify an existing CVD system in order to synthesize mono-layer Graphene by chemically depositing Methane (CH_4) on Copper and Platinum foil.

Graphene is a two-dimensional, single-layered lattice of Carbon atoms. These Carbon atoms are bonded together with SP^2 orbitals in a hexagonal pattern.¹ Research on Graphene has expanded significantly over the past few years, especially since the structure was first mechanically exfoliated using adhesive tape in 2004 by Andre Geim and Konstantin Novoselov at The University of Manchester which had earned them a Nobel Prize in Physics for their groundbreaking work on the material later in 2010.² With its single atom thinness and its strong SP^2 covalent bonds, Graphene is so far the strongest material known to mankind, it's also remarkably light weight, highly flexible and has the highest current density and intrinsic mobility at room temperature, making it the perfect heat and electricity conductor.³ Once Graphene is synthesized, its applications influence numerous fields including medical (drug delivery systems, microbial and virus diagnosis devices)⁴, electrical (transistors⁵, integrated circuits and processors, sensors, quantum dot cells⁶) and energy (solar cells, super-capacitors, batteries)⁷.

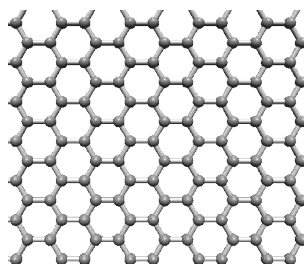


Figure 1 Graphene Structure

(<http://www.nano-enhanced-wholesale-technologies.com/images/structure-graphene.gif>)

The ultimate goal of this project is only the first step towards synthesizing Graphenylene (or Porous Graphene) which is also a two-dimensional, single-layered lattice of Carbon atoms, but that lattice has non-delocalized SP² bonds and is composed of Cyclohexatriene units with two unique Carbon-Carbon bonds within a Benzene ring. The nano-scaled pores in that Carbon lattice gives the material properties different than that of pure Graphene and the porous nature of Graphenylene opens up potential for applications such as gas separation and purification, energy storage (as the anode in Lithium-ion batteries, super-capacitors) as well as DNA sequencing ⁸.

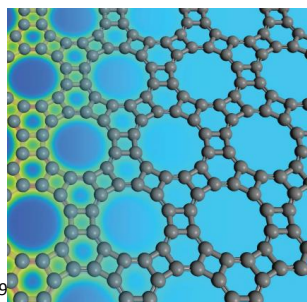


Figure 2 Graphenylene structure ⁹

The methods that were considered for synthesizing Graphene in this project were: mechanical exfoliation using adhesive tape, liquid-phase exfoliation, drawing with a highly-ordered graphite pencil onto a silicon wafer and CVD. Out of the options mentioned above, CVD was chosen because the process is well-known for producing continuous, highly pure and high performance samples. Also, because the only real limiting parameter for the size of the Graphene flake that can be produced is the size of the furnace used in the setup.

The CVD experiments were conducted on two types of catalysts, Pt and Cu, Pt being the favorable catalyst because the substrate can be repeatedly used without any limitations. Also, because the process of transferring Graphene from Pt onto other substrates using water electrolysis based bubbling proved to be much less challenging than that of the chemical etching

of Cu¹, and since the ultimate goal of this project was to synthesize a Graphene sheet which will later be used to synthesize a nanometer-scale area of Graphenylene, the grain size and the nucleation density of Carbon atoms in the lattice were not a major issue.

The remainder of this project report is divided into the following sections:

Section 2 is concerned with equipment and methodology.

Section 3 is concerned with implementation and experimenting.

Section 4 is concerned with results.

Conclusions that were reached and recommendations for further work regarding this project are offered in Section 5 of this report.

2.0 EQUIPMENT AND METHODOLOGY

The main focus of this section is to discuss the modifications made to an already existing CVD system, in order to grow Graphene, which consists of three gas cylinders containing Ar (a noble carrier gas), H₂ (a carrier gas that is also used in the annealing process) and CH₄ (a precursor gas and our Carbon source), a Thermo LINDBERG/BUEMEL furnace capable of reaching temperatures as high as 1,200° C, a fused Quartz tube to contain the reaction, a fused Quartz boat as a sample holder, both with softening points nearing 1,665° C, a HORIBA STEC SEC-N112 MGR digital flow controller, two floating-ball flowmeters, a high performance DC power supply and a thin Silicon wafer.

2.1 Chemical Vapor Deposition

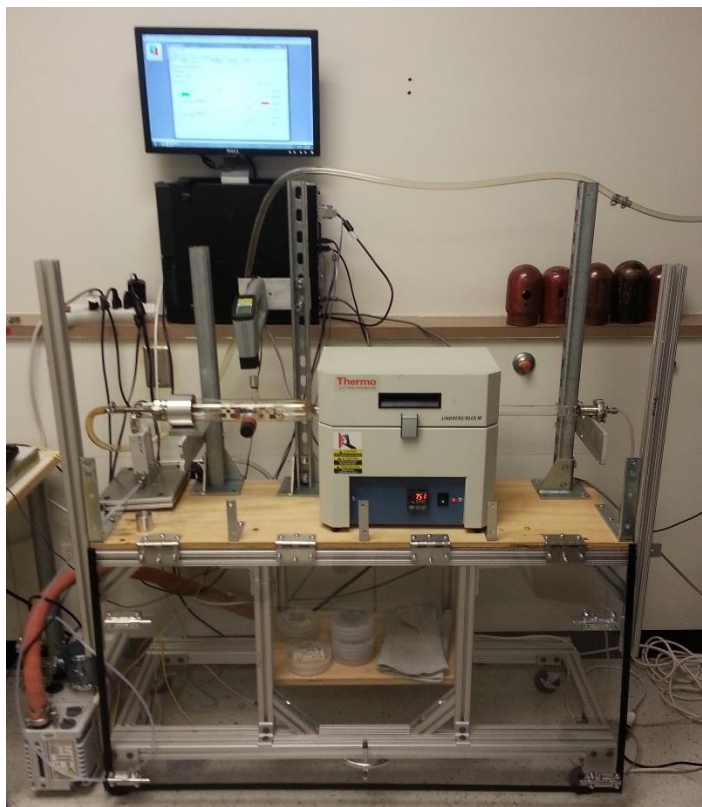


Figure 3 CVD setup

CVD is a chemical process where gases get broken down at relatively high temperatures and then deposited onto a wafer or a catalyst in order to produce high purity, high performance solid materials.

Prior to introducing Methane, which is the Carbon source necessary for the growth of Graphene, both of the metal catalysts (Pt and Cu) had to undergo an annealing process in the presence of Hydrogen, which is a heat treatment that changes some of the physical and chemical properties of the material like increasing its ductility, rearranging its structure and making it more homogeneous, as well as removing any possible residues of Carbon and organic substances on its surface.

After the annealing process is completed, CH_4 is introduced, the high temperature inside the furnace results in the pyrolysis of the gas causing it to break down into disassociated Carbon atoms inside the Quartz reaction chamber. The disassociated Carbon atoms are deposited inside the Quartz boat where the samples are contained (Figure 4), but in order for the Carbon atoms to form a nucleation site for Graphene, extreme temperatures (well over $2,000^\circ\text{C}$) are needed which is why the metal catalyst is crucial to this stage. The catalyst reduces the temperature needed for the reaction to occur by almost one half ($\sim 1,000^\circ\text{C}$). However, the problem with using a catalyst is that it introduces extra compounds into the reaction chamber, which affect the reaction in a way that can cause the carbon atoms to dissolve into the metal once the substrate is cooled down.

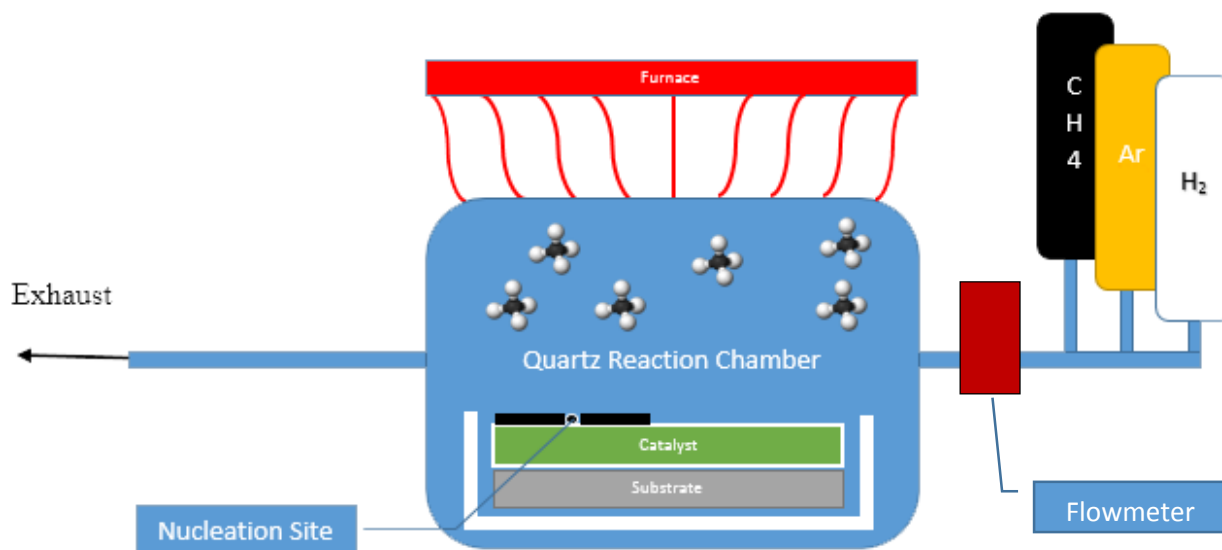


Figure 4 CVD reaction inside the Quartz chamber

2.1.1 Two-Zone CVD setup

The most common and established CVD setup involves a single-zone furnace (Figure 5), inside of which the gases break down and react with the catalyst in the same location. In an attempt to control the pyrolysis temperature of Methane independently of the temperature of the substrate on which the metal catalyst is placed, the concept of a two-zone furnace was inspected.

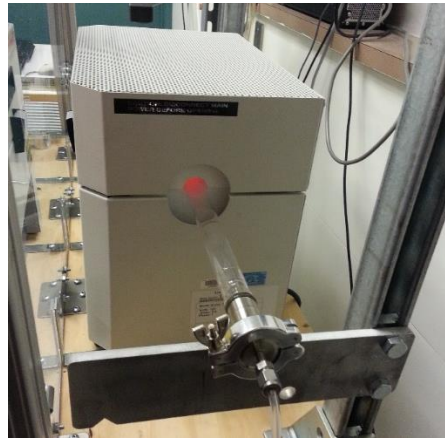


Figure 5 CVD single-zone setup

The two-zone CVD setup consists of the furnace from the single-zone setup alongside a secondary Quartz chamber (Figure 6) which contains a 7 by 1 cm, 250 μ m thick Silicon wafer mounted on a ceramic sample holder and connected to a high performance DC power supply. The power supply provides the current necessary to heat up the silicon wafer. The electrical resistance of the silicon wafer can be described by this relationship:

$$R = \frac{\rho * L}{A}$$

With ρ being the electrical resistivity constant, L the length of the wafer and A the cross-sectional area of the wafer. The resistance of our wafer was measured to be nearing 3.0 Ω . Due to the low resistance of the silicon wafer, we were able to push the temperature of the substrate up to 1041 $^{\circ}$ C by supplying around 320 Watts of power.

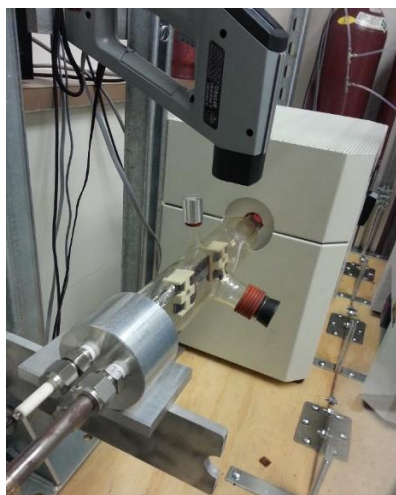


Figure 6 CVD two-zone setup



Figure 7 Heated Silicon substrate at 1041° C

However, problems quickly arose from using the Silicon wafer as our secondary heater, because placing a conductive metallic catalyst on top of the Si substrate in order to heat it up causes a short circuit therefore creating a dead-spot in the temperature gradient leading the substrate to break. In an attempt to solve this problem, Ceramacast 645N, which is a ceramic potting compound used to encapsulate high temperatures and electrically insulate the substrate from the catalyst was used. However, at $\sim 800^{\circ}\text{C}$, the fused silica in the Ceramacast compound triggers a chemical reaction that causes the Pt foil to melt and crumble on itself despite the fact that Pt has a melting point of $1,772^{\circ}\text{C}$ (as shown in Figures 8 and 9). The discoloration (shown in Figure 10) is also a clear indication of the reaction mentioned above.



Figure 8 Before and after snapshots of the Pt foil crumbling



Figure 9 Discoloration of Ceramacast 645N

2.2 Digital Flow Controllers

In order to accurately control the flow rate of Methane in the system, a HORIBA STEC SEC-N112 MGR digital flow controller was used. The controller is capable of controlling flows as low as 12 SCCM and as high as 2500 SCCM, which falls within the range of the flow rates needed for this project.



Figure 10 HORIBA STEC Digital Flow Controllers

The Methane gas cylinder was connected to the flow controller (Figure 10), and the flow controller was then connected to the MKS control system (Figure 11) which was linked to the lab computer via USB. The control system provided the voltage needed to control the digital valve, as well as the ability for the user to set the desired flow point and an instant stream of important information like the current flow and the valve voltage (Figure 12).

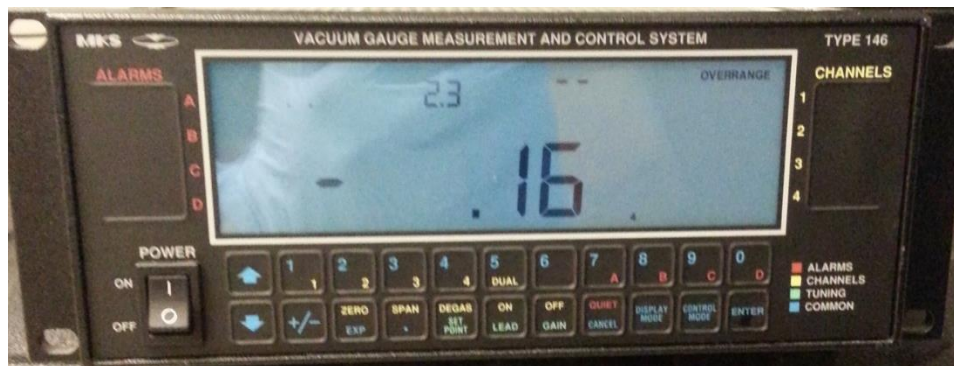


Figure 11 MKS vacuum gauge measurement and control system

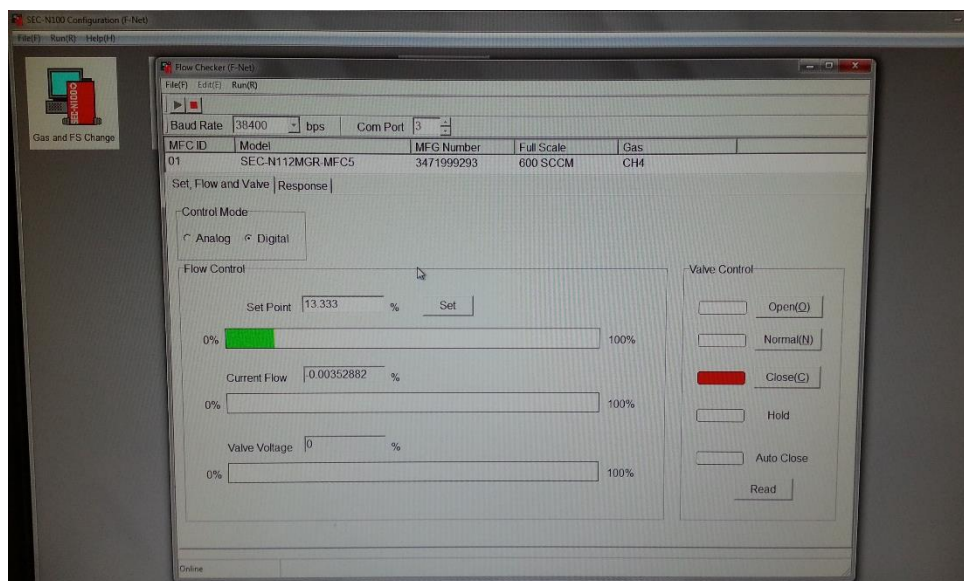


Figure 12 SEC-N100 user interface

2.3 Raman Spectroscopy

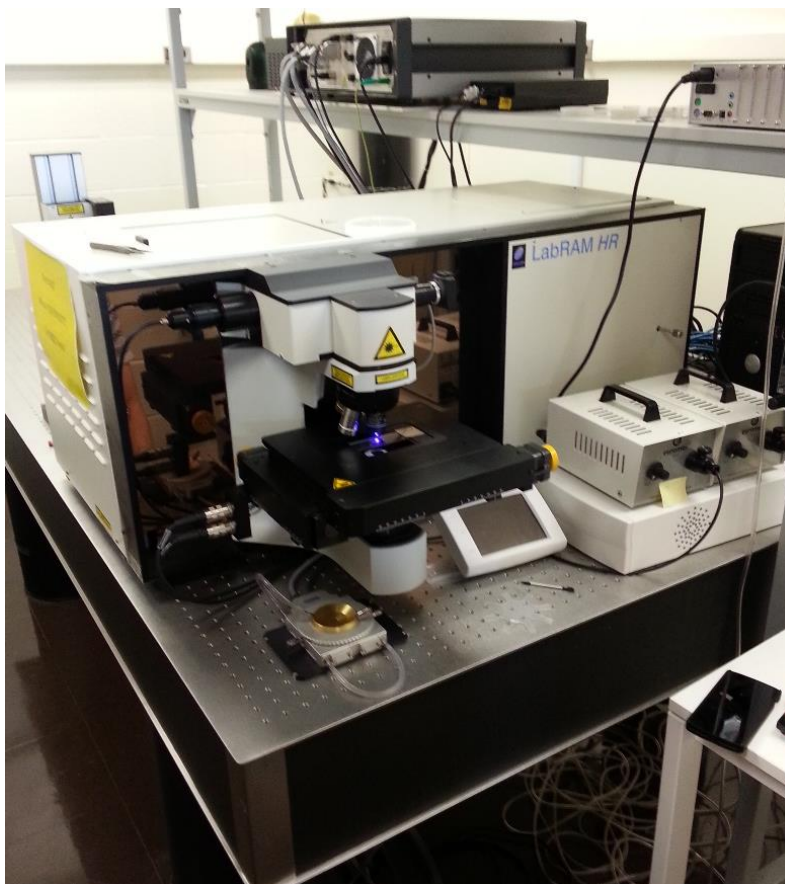


Figure 13 LabRAM HR Raman Spectroscop

There are many methods to characterize Graphene such as Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM) and Raman Spectroscopy (RS) (Figure 13). All of which have their own advantages and disadvantages, but RS was chosen as our method of characterization because it requires no sample preparation. Also, because not only can RS determine the number of layers in the sample structure, but also can determine whether or not the structure of Graphene is free of defects.¹⁰

Using Raman Spectroscopy, we are able to characterize carbon structures of SP2 and SP3 hybridization orbitals, like Graphene, Graphite and carbon nanotubes. All of the structures mentioned above have their own unique Raman ‘fingerprint’. RS is a technique which involves the inelastic scattering of a Helium Cadmium laser beam, of wavelength ~ 442 nm, which interacts with the molecular vibrations in the material and then is reflected off of its structure. This interaction causes a shift in the beam’s energy, this shift is registered and plotted against the spectrum’s intensity, providing information about the material’s vibrational modes.

In a Raman Spectrum (Figure 14), the G-band appears from the stretching of the Carbon-Carbon bond in graphitic materials, the position of the G-band is highly sensitive to the amount of layers in the sample and to the amount of strain on the Carbon bonds in the structure. The D- and D'-bands appear when there's a disorder in the structure of graphene, thus a defect-free graphene sheet will show no sign of the D-band.

Finally, the 2D-band appears in the Raman spectrum as a result of a two phonon vibrational process, the shape and position of the band can be strongly affected by the number of graphene layers and the level of laser excitation. For example, an increase in the number of layers would cause the shape of the band to broaden.¹¹

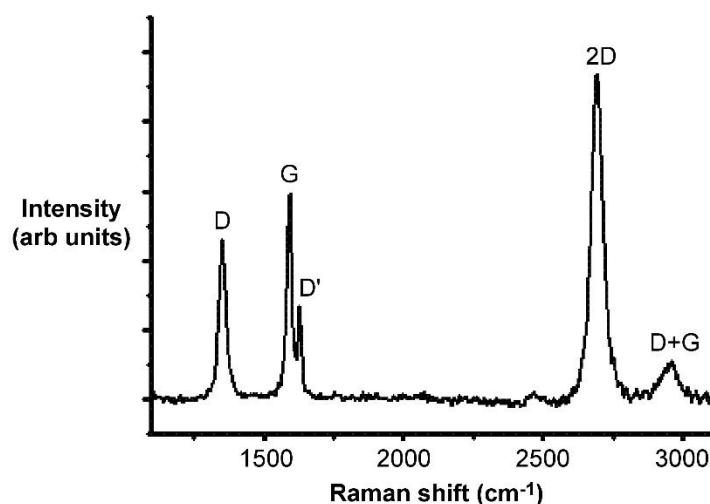


Figure 14 Raman spectrum showing the different bands ¹¹

3.0 IMPLEMENTATION AND EXPERIMENTING

In order to achieve the objective of this project, CVD experiments were ran on two types of metal catalysts, Platinum and Copper. Apart from the process of catalyst pre-treatment, the method of growing Graphene on either of those two catalysts is essentially the same.

However, there are many growth parameters to account for, such as the gas flow rate, gas concentration, chamber pressure, substrate temperature, and most importantly, growth time. This section is divided into two sub-sections for Pt and Copper and will address, in details, the growth parameters used for each of the metal catalyst.

3.1 Platinum Foil



Figure 15 25 by 25mm Pt foil

The platinum that was used in the experiment had the following properties: a melting point of 1772°C , dimensions of 25 by 25 by 0.025 mm, and was of 99.9% purity (trace metals basis). The foil was subdivided using a pair of scissors into multiple 2.5 by 2.5 mm square pieces.

3.1.1 Pre-treatment

Prior to introducing the carbon source necessary for the growth of Graphene, the platinum foil had to undergo the annealing process described in section 2.2 of this report. The foil was loaded into a fused silica boat, which was inserted into the fused silica chamber that runs through the furnace. Then, the furnace was heated up to 1040° C in the presence of Ar, which was flowing at a rate of 1000 sccm. Ar is an inert gas, it was used during the heating of the furnace in order to carry oxygen and other potentially combustible gas molecules out of the chamber and through the exhaust. Once the furnace was at 1040° C, H₂ was introduced at a flow rate of 700 sccm for 10 minutes in order to remove any possible residues of Carbon and organic substances on the surface of the foil. Since the Pt foil had an extremely smooth surface, no chemical or mechanical polishing was needed.

3.1.2 Growth Parameters

Using Pt as the metal catalyst, two different growth parameters were varied while keeping all of the other parameters constant, gas flow rate and growth time. Following is a detailed account of all the unchanged growth parameters:

- The pressure inside the growth chamber was near atmospheric pressure.
- Immediately after the foil was annealed for 10 minutes, Ar was cut off and CH₄ was introduced at the flow rates and for the growth times shown in Table 1.
- As soon as the specified growth time has passed, the furnace was shut off and the sample was left to cool down to 650° C, after which CH₄ was cut off, followed by H₂. Then the sample was removed from the chamber once the temperature reached ~200° C. The average cooling time of our system was around 2° C/s.

Table 1 Pt foil samples and their corresponding growth parameters

Sample Number	CH₄ flow rate (sccm)	Growth Time (minutes)
1	200	7
2	60	7
3	80	5
4	80	7
5	80	9
6	80	11
7	80	13
8	80	15

3.2 Copper Foil

The copper that was used in the experiment had the following properties: a melting point of 1083.4° C, dimensions of 50 by 50 by 0.25 mm, and was of 99.98% purity (trace metals basis). Since the copper foil was 10 times thicker than the platinum foil, it was subdivided using shears into 100, 5 by 5 mm square pieces.

3.2.1 Pre-treatment

Unlike the Pt foil, annealing alone wasn't enough for the Cu foil. Metal polishing was needed because the surface of the Cu sheet was quite rough compared to the surface of Pt. The polishing process was necessary in order to clean and remove the impurities in the catalyst's surface, it also eliminated scratches and wrinkles, helping smoothen the surface of the metal. There are numerous means for polishing a metal, for example, electrochemical polishing¹², but for the purposes of this project, a two-step process was used. First, using nitric acid (HNO_3) which is known to react strongly with copper, removing the layer of copper oxide on the surface and also reducing the thickness of the copper foil by almost one half (0.125 mm). Next, the foil was placed in an acetic acid solution (CH_3COOH) inside the digitally heated ultrasonic cleaner shown in (Figure 16), ultrasonic cleaners are known for using high frequency sound waves to generate pressure in the cleaning solution, this pressure creates strong forces which thoroughly attack contaminants adhered on the surface of the substrate. The differences between the untreated and the treated copper samples can be noted visually (Figure 17), the untreated copper is slightly darker and has a brown shade to it because of the oxidization on the surface. Figure 18 shows the differences on the micro-scale, the untreated foil has a far rougher surface than that of the treated foil.



Figure 16 ARI ultrasonic cleaner

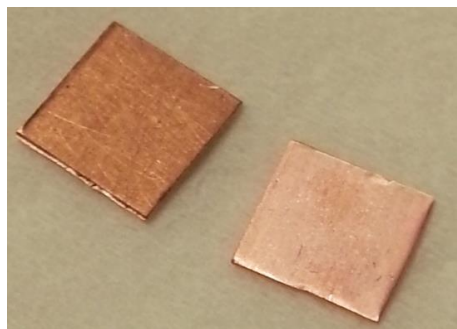


Figure 17 Untreated vs treated copper foil

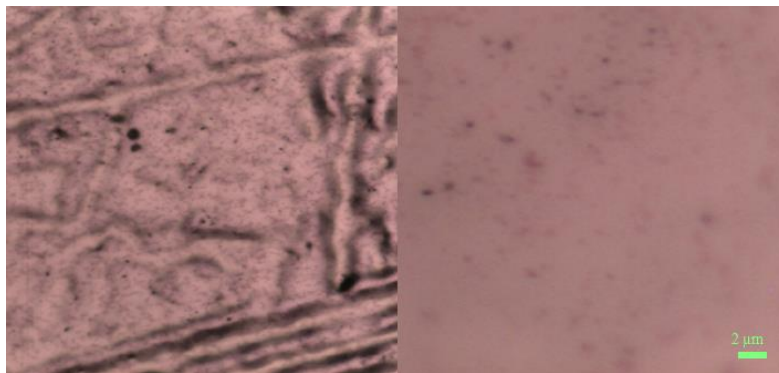


Figure 18 Microscopic image of the copper surface,
Pre- and post- treatment (100x)

Subsequently, the polished copper foil was annealed in a process similar to that of Pt. The foil was loaded into a fused silica boat, which was inserted into the fused silica chamber that runs through the furnace. Then, the furnace was heated up to 1000°C in the presence of Ar, which was flowing at a rate of 1000 sccm. Once the furnace was at 1000°C , H_2 was introduced at the flow rates shown in Table 2 for 30 minutes in order to remove any possible residues of Carbon and organic substances on the surface of the foil.

3.2.2 Growth Parameters

Using Cu as the metal catalyst, the focus of our study was on the effects that the pre-treatment procedure has on the growth of Graphene on copper. Following is a detailed account of all the growth parameters:

- The pressure inside the growth chamber was near atmospheric pressure.
- Immediately after the foil was treated using the parameters shown in Table 2, Ar was cut off and CH_4 was introduced at the flow rates and for the growth times shown in Table 2.
- As soon as the specified growth time has passed, the furnace was shut off and the sample was left to cool down to 500°C , after which CH_4 was cut off, followed by H_2 . Then the sample was removed from the chamber once the temperature reached $\sim 200^{\circ}\text{C}$. The average cooling time of our system was around 5°C/s .

Table 2 Cu foil samples with their corresponding growth parameters

Sample number	Pre-treatment	CH₄ flow rate (sccm)	Growth time (minutes)
1	<ul style="list-style-type: none"> - Acetic acid ultrasonic cleaning for 5 minutes. - 15 sccm of H₂ for 30 minutes. 	50	5
2	<ul style="list-style-type: none"> - Machine sanding - Acetic acid ultrasonic cleaning for 5 minutes. - 15 sccm of H₂ for 30 minutes. 	50	5
3	<ul style="list-style-type: none"> - Nitric acid etch for 40 seconds. - 15 sccm of H₂ for 30 minutes. 	50	5
4	<ul style="list-style-type: none"> - Nitric acid etch for 40 seconds. - Acetic acid ultrasonic cleaning for 10 minutes. - 15 sccm of H₂ for 30 minutes. 	50	5

4.0 RESULTS

The results observed from the chemical vapor deposition of Methane on Pt and Cu foil were exactly, and in some cases very close, to the expected outcomes. As mentioned in section 2.3 of this report, Raman Spectroscopy was the chosen method of characterization, Figures 19 and 25 show, respectively, a superimposed images of all of the Raman spectrums detected on our Pt and Cu samples. Note that the letter S followed by the number in the graph's legend denote the samples mentioned in Tables 1 and 2. In addition, the intensity of the Raman peaks are of arbitrary units, and the ratio between the peaks provides much more useful information about the sample at hand than the intensity level at which the peak is at. Also note that the peak showing near $\sim 2330 \text{ CM}^{-1}$ is nothing more than Nitrogen in the atmosphere.

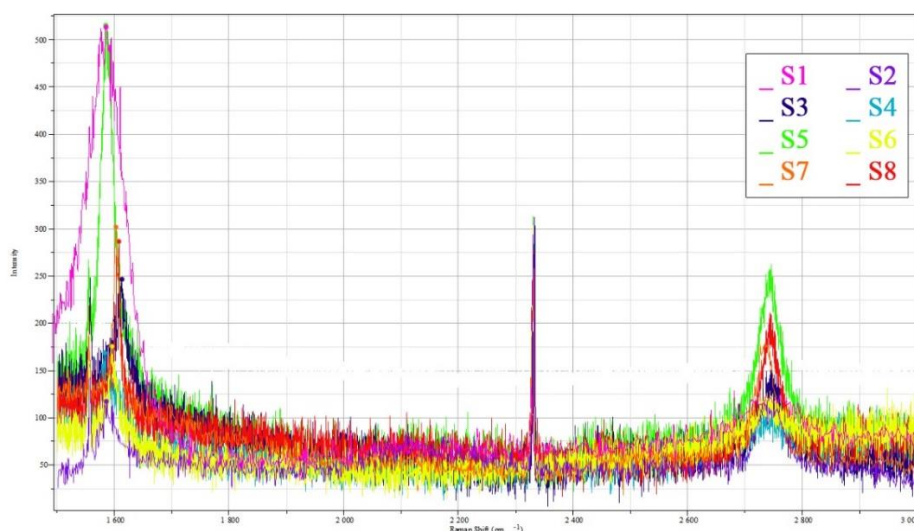


Figure 19 Raman Spectrums of all 8 Pt samples

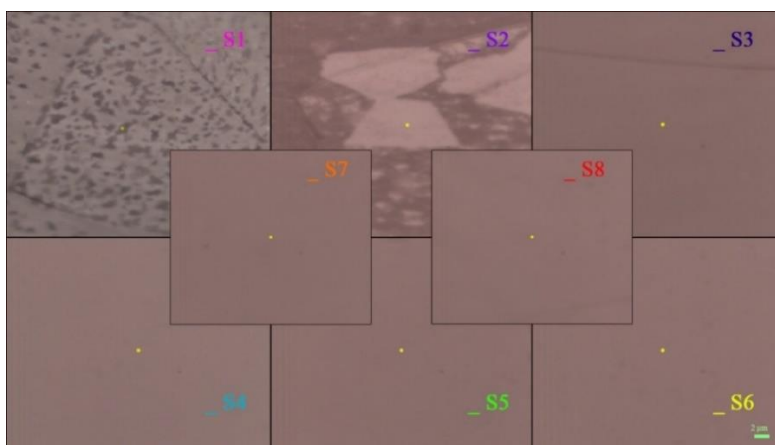


Figure 20 Microscopic images of the scanned location on the Pt samples

Using platinum as our catalyst, we were able to conduct various mini-studies on the different effects the growth parameters have on the carbon structure and the number of Graphene layers in the sample. Beginning with the first phase of tests which involved investigating the relationship between the flow rate of CH₄ and the intensity peak ratio of the 2D/G bands. By keeping the growth time constant at 7 minutes, we were able to analyze samples number 1, 2 and 4 as per Table 3. The measured data was then plotted (Figure 21) and the relationship between the flow rate and the peak ratio was found to be inversely linear, as expected.

Table 3 Pt. samples and their Raman peak ratios observed during 7 minutes of growth time

Sample #	Flow Rate	G Peak	2D Peak	2D/G Peak Ratio	# of Layers
2	60	22.27	22.5	1.010327795	~2
4	80	42	37.5	0.892857143	~2-3
1	200	43	6	0.139534884	>6

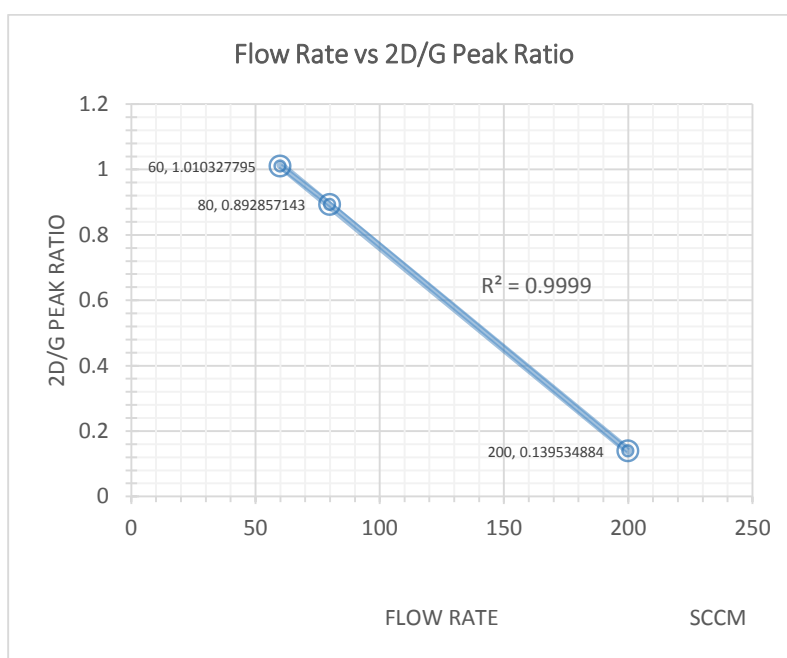


Figure 21 A plot of the Flow Rate vs Peak Ratio for samples 1, 2 and 4

The second series of tests involved studying the relationship between the growth time and the location of the G-peak, as well as the intensity peak ratio of the 2D/G bands, respectively. The flow rate in both scenarios was kept constant at 80 sccm, varying only the growth time in the process. Table 4 shows the samples and their corresponding ratios and G-band locations as well as the possible number of Graphene layers grown on the surface. Once the Raman measurements were analyzed and plotted, it was evident through Figure 22 that the relationship between the growth time and the location of the G-band is linear, because the longer the sample was exposed to Methane during the CVD process, the higher the chances are that the disassociated carbon atoms would bind with the nucleation site and form more layers, and the higher the number of layers formed, the larger the shift in the peak. The increase in the shift is due to the sensitivity of the G-band with respect to the strain put on the carbon-carbon bonds in a layer by the interactions between the carbon atoms from another layer in the Graphene structure.

On the other hand, the growth time had a less clear effect on the peak intensity ratio of the 2D/G bands (Figure 23), this is due to a possible number of factors such as the relatively high solubility of carbon in Pt ¹, especially when the substrate is being cooled down, the deposition of amorphous carbon near the grain boundaries (clearly visible in S1 and S2 of Figure 20), as well as the size of the carbon grains themselves. This study was taken one step further by inspecting a 2-D cumulative Raman scan of a 20μm by 20μm area of sample number 6 (Figure 24). The spectrum shows encouraging results that point towards the existence of single-layered Graphene, the colored scale on the far right represents the intensity peak ratio of the 2D/G bands, regions of peak ratios greater than 2 are promising locations where single- or dual- layered Graphene flakes might exist.

More information on controlling factors of the grain size and recommendations for further work will be included in section 5.1 of this report.

Table 4 Analysis of the Growth Time, Peak Ratio and the G-Peak location of the Pt. samples

Sample #	Growth Time	G Peak	2D Peak	2D/G Peak Ratio	G Peak Location	# of layers
3	5	69.25	68.5	0.989169675	1604	~1,2
4	7	42	37.5	0.892857143	1577.5	~2-3
5	9	209.25	112	0.535244922	1585	~4
6	11	48.75	25	0.512820513	1594.5	~4
7	13	93	62.25	0.669354839	1603.5	~3-4
8	15	101.25	75.75	0.748148148	1610.1	~2,3

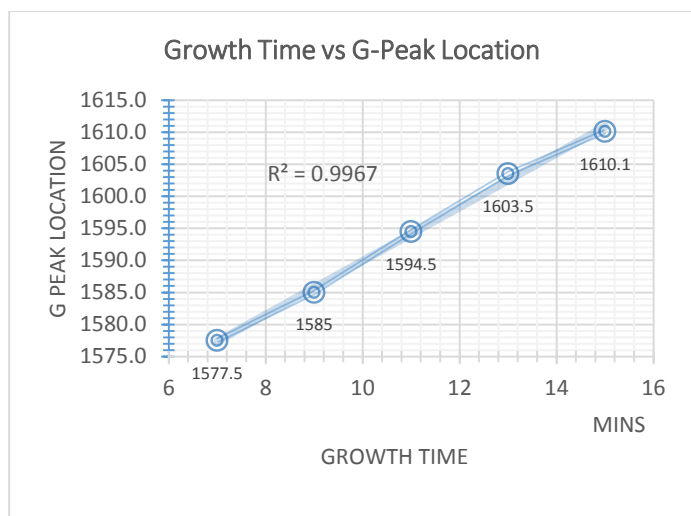


Figure 22 A plot of the Growth Time vs Peak Location

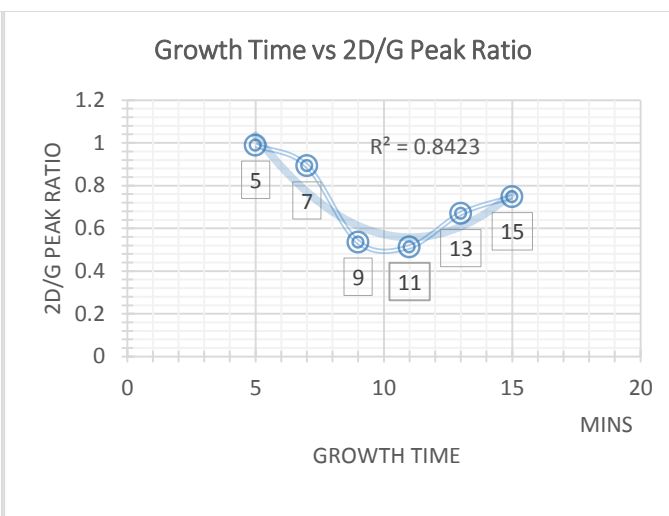


Figure 23 A plot of the Growth Time vs Peak Ratio

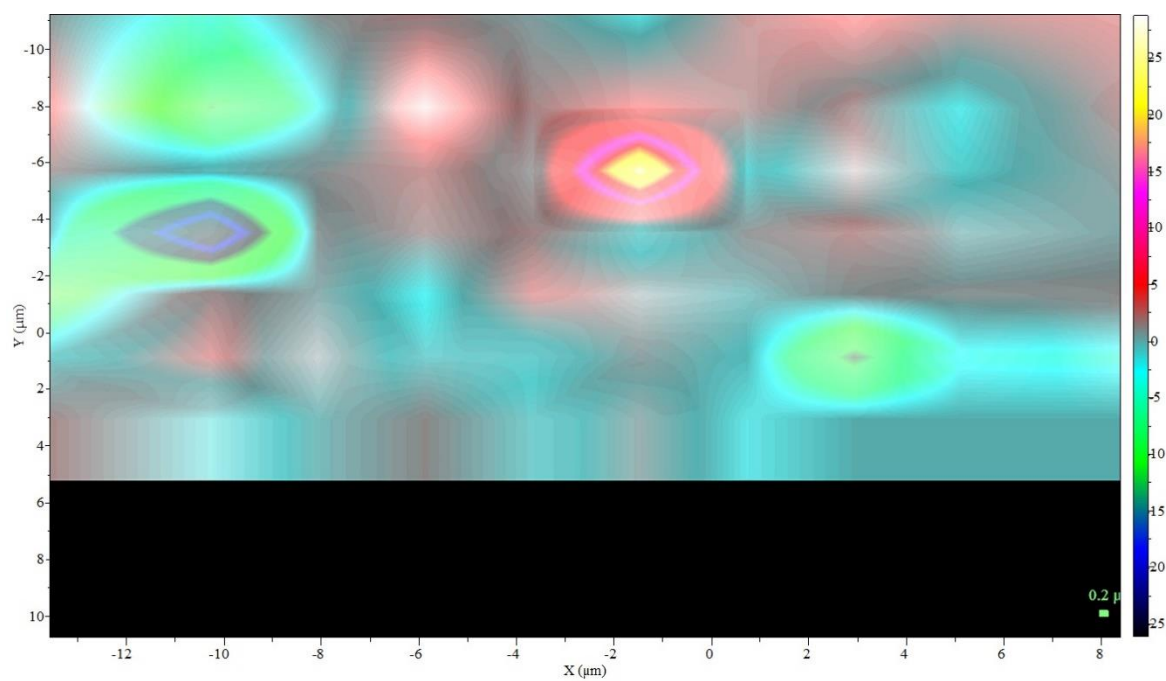


Figure 24 A 2-D Raman mapping of sample 6, showing possible single-layer Graphene

Using copper as our metal catalyst was to investigate the effects surface roughness has on the growth of Graphene. As discussed in section 3.2.2, all the growth parameters were kept the same across all four Cu samples, the only difference being the pre-treatment process. The surface roughness, defects and impurities all play an important role in the process of forming nucleation grains of single- and few- layer graphene. The processes of chemical and mechanical polishing resulted in changing the density and growth rate of those nucleation sites which impacts the number of Graphene layers in the structure¹³, as shown in Table 5. Samples 1 and 2 were pre-treated ultrasonically and with machine sanding respectively, both of these methods involve scratching and getting rid of thin layers of oxide on the surface of the catalyst, however, that proved to be insufficient for the growth of highly pure single-layer Graphene and it is only when etching with Nitric acid etching is done (in samples 4 and 5) does the surface become smooth and defect-free to a high degree, which is evident in the Raman spectrums shown in Figure 25.

The Raman spectrums of S4 and S5 indicate the presence of highly pure, single-layered Graphene on the surface of the Cu foil. The spectrums show a G-band and a 2D-band that are fitted in the shape of a Lorentzian function. The 2D bands are located near 2710 CM^{-1} and 2712 CM^{-1} with line widths of 36 CM^{-1} and 34 CM^{-1} respectively, the G-bands are located near 1590.3 CM^{-1} and 1589 CM^{-1} with 2D/G intensity peak ratios of ~ 1.22 and ~ 1.92 respectively. In addition, the D/G intensity peak ratios of both samples were near ~ 0.06 which is a clear sign that the Graphene structure formed on the surface is defect-free.

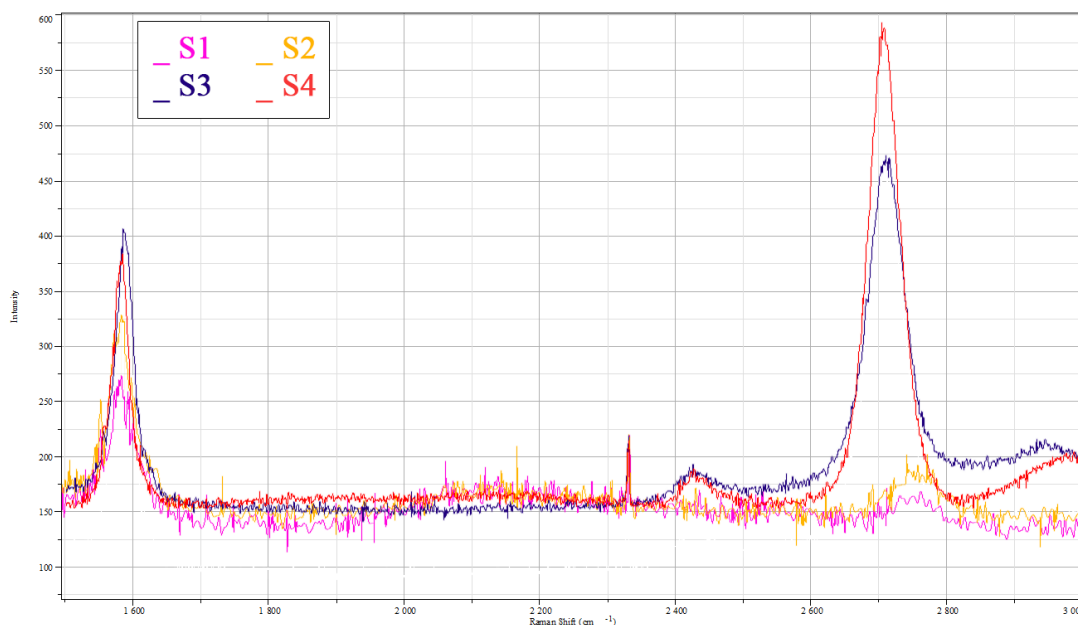


Figure 25 Raman Spectrums of all 4 Cu samples

Table 5 Analysis of the 2D/G Peak Ratio and possible number of Graphene layers

Sample Number	G Peak	2D Peak	2D/G Peak Ratio	# of layers
1	39.4	10.0	0.253807107	>5
2	54.3	19.1	0.35174954	~3,4
3	82.2	100.6	1.223844282	~1,2
4	79.5	152.6	1.919496855	1

5.0 CONCLUSION

This report discussed the process and experimental setup of Chemical Vapor Deposition (CVD) and its use in satisfying the objective of this project which was to synthesize single- and few- layer Graphene on copper and platinum substrates. The CVD setup was capable of pushing the temperature of the substrates as high as 1040° C, while digitally controlling the flow rate of gases at a range between 12 and 2500 SCCM. When examining the different growth parameters associated with CVD growth of Graphene on platinum, it was found that varying the flow rate of Methane while keeping the other parameters constant had a clear, inverse, relationship on the intensity peak ratio of the 2D-/G- bands, which strongly relates to the number of layers in the Graphene structure. In addition to the flow rate, the relationship between the growth time and the shift in the location of the G-band was investigated and clearly found to be linear, this is because the location of the band is very sensitive to the strain put on the carbon-carbon bonds within a certain layer by the interactions that occur with carbon atoms from a different layer in the Graphene structure. However, the effect growth time has on the intensity peak ratio of the 2D-/G- bands was less evident and requires more investigation. The surface roughness and existence of impurities in the material all contribute significantly to the number of layers in the Graphene structure, when it came to using copper as a metal catalyst. We were able to grow a single-layered, highly pure structure of Graphene on the surface.

Ultimately, the success of this project is only a stepping stone towards enhancing the quality of CVD-synthesized Graphene samples. Graphene samples which we hope to be later used to create porous Graphenylene structures, a material of promising characteristics that can be used in energy as well as medical applications.

5.1 Recommendations

There are numerous improvements that can be incorporated into the CVD setup. In the case of using a two-zone CVD system, it is a feasible option to replace the CERAMACAST 645N compound with another, more chemically inert compound, such as the RESBOND 904. Additionally, recommendations can be made towards establishing a more uniform laminar flow inside the fused quartz chamber by creating a low pressure environment has been shown to improve the homogeneity of the Graphene layers forming on the surface of the catalysts.

REFERENCES

- ¹ L. Gao, W. Ren, H. Xu, L. Jin, Z. Wang, T. Ma, L. P. Ma, Z. Zhang, Q. Fu, L. M. Peng, X. Bao, and H. M. Cheng, *Nature communications* **3**, 699 (2012).
- ² M. S. Dresselhaus and P. T. Araujo, *ACS nano* **4** (11), 6297 (2010).
- ³ G. Tsoukleri, J. Parthenios, K. Papagelis, R. Jalil, A. C. Ferrari, A. K. Geim, K. S. Novoselov, and C. Galiotis, *Small* **5** (21), 2397 (2009).
- ⁴ R. Tkacz, R. Oldenbourg, S. B. Mehta, M. Miansari, A. Verma, and M. Majumder, *Chemical communications* **50** (50), 6668 (2014).
- ⁵ F. Chen, Q. Qing, J. Xia, and N. Tao, *Chemistry, an Asian journal* **5** (10), 2144 (2010).
- ⁶ L. A. Ponomarenko, F. Schedin, M. I. Katsnelson, R. Yang, E. W. Hill, K. S. Novoselov, and A. K. Geim, *Science* **320** (5874), 356 (2008).
- ⁷ M. D. Stoller, S. Park, Y. Zhu, J. An, and R. S. Ruoff, *Nano letters* **8** (10), 3498 (2008).
- ⁸ Yang JiXiang Xu PengTao, WANG KeSai, ZHOU Zhen, SHEN PanWen, *Chinese Science Bulletin* **57**, 8 (2011).
- ⁹ Bing Wang Qi Song, Ke Deng, Xinliang Feng, ManfredWagner, Julian D. Gale, Klaus M"ullen and Linjie Zhi, *Journal of Materials Chemistry* **C** (2012).
- ¹⁰ M.A. Pimenta L.M. Malard, G. Dresselhaus, M.S. Dresselhaus, *Physics Reports* **473** (2009).
- ¹¹ Andrew R. Barron Zheng Yan, (2006).
- ¹² Z. Yan, J. Lin, Z. Peng, Z. Sun, Y. Zhu, L. Li, C. Xiang, E. L. Samuel, C. Kittrell, and J. M. Tour, *ACS nano* **6** (10), 9110 (2012).
- ¹³ G. H. Han, F. Gunes, J. J. Bae, E. S. Kim, S. J. Chae, H. J. Shin, J. Y. Choi, D. Pribat, and Y. H. Lee, *Nano letters* **11** (10), 4144 (2011).