UC Riverside

UC Riverside Electronic Theses and Dissertations

Title

Low Temperature Direct Growth of Graphene Films on Transparent Substrates by Chemical Vapor Deposition

Permalink

https://escholarship.org/uc/item/0vw8m3g9

Author

Antoine, Geoffrey Sandosh Jeffy

Publication Date

2013

Peer reviewed|Thesis/dissertation

eScholarship.org Powered by the California Digital Library
University of California

UNIVERSITY OF CALIFORNIA
RIVERSIDE

Low Temperature Direct Growth of Graphene Films on Transparent Substrates by Chemical Vapor Deposition

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

Master of Science

in

Electrical Engineering

by

Geoffrey Sandosh Jeffy Antoine

June 2013

Thesis Committee:

- Dr. Mihrimah Ozkan, Chairperson
- Dr. Cengiz Ozkan
- Dr. Kambiz Vafai
- Dr. Alexander Khitun

Copyright by
Geoffrey Sandosh Jeffy Antoine
2013

The Thesis of Geoffrey Sandosh Jeffy Antoine is approved:

Committee Chairperson

University of California, Riverside

ACKNOWLEDGEMENTS

This thesis is written to emphasize the need for ease in the synthesis of graphene in today's electronics world. I would like to thank my professors Dr. Mihrimah Ozkan and Dr. Cengiz Ozkan for the opportunity to work in this project. I would also like to thank everyone in my group especially Aaron and Isaac who trained and helped me in mastering the use of all the necessary tools and equipment for this project and who will also continue my work in future.

ABSTRACT OF THE THESIS

Low Temperature Direct Growth of Graphene Films on Transparent Substrates by Chemical Vapor Deposition

by

Geoffrey Sandosh Jeffy Antoine

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

Graphene, two dimensional sheet of carbon atoms has recently gained attention as some of its properties are very useful for electronics, optoelectronics and photovoltaic applications. Its high mobility makes it useful in radio-frequency applications and its transparency makes it useful as transparent electrodes in photovoltaic applications. It is known that chemical vapor deposition (CVD) is one of the techniques that can be used to synthesize graphene. A lot of work has been done on selecting appropriate substrates and hydrocarbon sources. Nickel, having a high solubility at high temperatures has

been in focus lately. Ethylene which has a lower breaking point compared to other hydrocarbons has a good efficiency in the synthesis of graphene. Complexity associated with graphene synthesis and transfers onto transparent substrates constitute the major obstacles to using this material for photovoltaic and optoelectronic applications. Here we show a novel method of obtaining graphene directly on glass via chemical vapor deposition (CVD) using ethylene as the hydrocarbon source and nickel as the catalyst. The low cracking temperature of ethylene which is 542.8 °C permits us to use glass substrates directly in the CVD furnace. To improve the thickness of graphene, a good manipulation of pressure and hydrogen during the growth process will be useful. We introduce a novel catalyst etching technique after the growth results in graphene settling down on the glass substrate in a transfer-free process. Raman spectroscopy indicated good uniformity and high quality before and after the etching process.

CONTENTS

Acknowledgements.....IV

Abstract of the Thesis….....V

List of Figures……..…X

CHAPTER 1

LITERATURE SURVEY ON GRAPHENE

1.1 Graphene and its structure.....1

1.2 Properties of graphene……2

1.2.1. Mechanical.....2

1.2.2. Electronic.....2

1.2.3. Optical.....3

1.3 Synthesis methods of graphene……...3

1.3.1. Mechanical exfoliation.....3

1.3.2. Epitaxial growth.....5

1.3.3. Chemical Vapor Deposition.....5

References.....7

CHAPTER 2

DETAILED DESCRIPTION OF CHEMICAL VAPOR DEPOSITION

2.1 The CVD system.....8

2.2 Factors impacting CVD growths.....11

2.2.1. Pressure.....12

2.2.2. Hydrocarbon source.....12

2.2.3. Temperature.....13

2.2.4. Hydrogen.....14

2.2.5. Metal substrate.....18

References.....21

CHAPTER 3
NOVEL PROCEDURE FOR GRAPHENE SYNTHESIS

3.1 Experimental Procedure.....22

References.....30

CHAPTER 4

CHARACTERIZATION TECHNIQUES OF GRAPHENE

4.1 Raman scattering.....32

4.2 Raman spectra of graphene.....33

4.3 Four-point electrical resistivity measurement……..34

References……37

CHAPTER 5
RESULTS AND DISCUSSION

5.1 Raman spectra of synthesized low temperature graphene…….....38

5.2 Transparency…….....50

5.3 Improving the technique……..52

References.....56

CONCLUSION……..57

LIST OF FIGURES:

Fig. 1 Graphene cell structure……1

Fig. 2 Graphene obtained through mechanical exfoliation……..……4

Fig. 3 CVD system……..10

Fig. 4 Chemical vapor deposition process in CVD……...……10

Fig. 5 (a) Methane molecules diffuse and adsorb on nickel surface. (b) Methane pyrolysis to carbon ad-atoms on nickel surface. (c) Carbon ad-atoms dissolve in bulk nickel. (d) Carbon atoms precipitate back to nickel surface at low temperature and graphene is formed…….……..……20

Fig. 6 Schematic diagram of the sample prior to graphene synthesis……..…….……22

Fig. 7 Schematic diagram of Nickel evaporated on glass by e-Beam evaporation..……25

Fig. 8 Schematic diagram of Graphene grown on nickel using CVD……26

Fig. 9 Schematic diagram of PMMA addition……..26

Fig. 10 Schematic diagram showing the after-etching results……..27

Fig. 11 Schematic diagram showing the final stage of graphene on glass……...……27

Fig. 12 Feynman diagram……32

Fig. 13 Raman spectrum of multi-layer and single layer graphene……..33

Fig. 14 Comparison of graphene samples with varying number of layers……34

Fig. 15 Schematic diagram of van der Pauw Method……35

Fig. 16 Raman spectrum of graphene with recipe [A]…….. …….39

Fig. 17 Raman spectrum of graphene with recipe [B]……..…….41

Fig. 18 Raman spectrum of graphene with recipe [C]……42

Fig. 19 Optical image of graphene……43

Fig. 20 Raman spectrum of graphene with recipe [D]……45

Fig. 21 Raman spectrum of graphene with recipe [E]……46

Fig. 22 Pressure vs quality of sample plot……47

Fig. 23 Pressure vs I_G/I_{2D}……47

Fig. 24 Pressure vs I_{2D}/I_G……48

Fig. 25 Temperature vs I_D/I_G……...49

Fig. 26 Temperature vs I_{2D}/I_G…….……49

Fig. 27 Temperature vs I_G/I_{2D}……..50

Fig. 28 Picture of the sample consisting of graphene on top of glass….51

Fig. 29 Diagram showing Different cooling rates giving different amounts of graphene layers……..……52

Fig. 30 Raman spectra showing Different cooling rates giving different amounts of graphene layers……..……53

Fig. 31 (Fig.A) Graphene grown on nickel before etching……55

Fig. 31 (Fig.B,C,D,E) Destruction of sample due to improper coverage with PMMA during etching or due to lack of optimal drying time in the evaporation chamber……..55

Fig. 31 (Fig.F) The bending of the glass shows the intolerance at a temperature of 700°C……..……55

CHAPTER 1: LITERATURE SURVEY ON GRAPHENE

1.1 Graphene and its structure:

Graphene, the material made of widely abundant carbon, has a unique structure which gives it unique mechanical, optical and electrical properties. It was discovered and named so in 1962 by Hanns-Peter Boehm. It is a single layer of sp2-bonded carbon atoms that are packed in a honeycomb lattice.

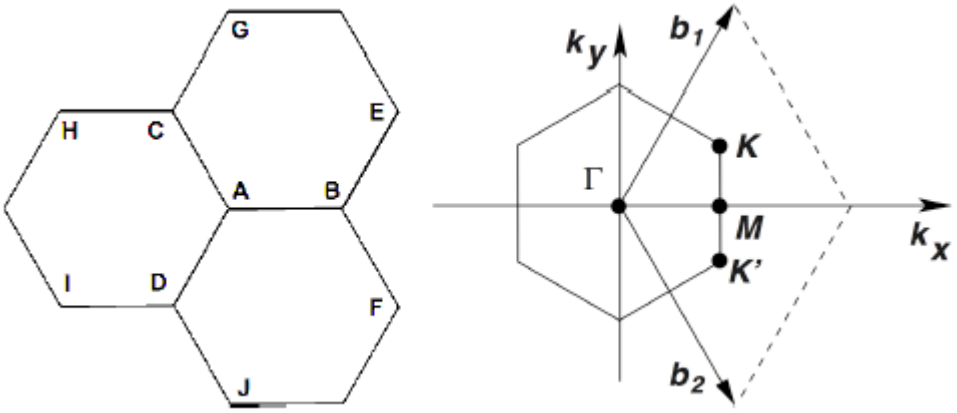


Figure 1: Hexagonal crystal structure of a graphene primitive cell and its neighbors; First Brillouin zone of graphene and its symmetry points. Adapted from [1].

1.2 Properties of graphene:

1.2.1. Mechanical:

Graphene is one of the strongest materials ever tested. It is also the first 2-D crystal ever discovered. It is very light, weighing only about 0.77 milligrams per square meter. It has a spring constant in the range 1–5 N/m and the Young's modulus is 0.5 TPa. These high values make graphene very strong and rigid. It is harder than diamond and about 300 times harder than steel. These intrinsic properties could lead to using graphene for MEMS applications such as pressure sensors and resonators [4]. It is also a bendable material and hence can take any form or shape.

Like all other materials, regions of graphene are subject to thermal and quantum fluctuations in relative displacement. It has a good thermal conductivity of about 3000 W/m-K in plane and about 2 W/m-K out of plane.

1.2.2. Electronic:

Intrinsic graphene is a semi-metal or zero-gap semiconductor. Experimental results from transport measurements show that graphene has a remarkably high electron mobility at room temperature, with reported values in

excess of 15,000 $cm^2 \cdot V^{-1} \cdot s^{-1}$. [5] The mobility of holes and electrons is nearly the same.

Defect scattering is the dominant scattering mechanism. The conductivity is based on ballistic electron transfer which is the transport of electrons in a medium with negligible electrical resistivity due to scattering resulting in high mobility.

1.2.3. Optical:

Graphene absorbs 2.3% of white light. Though it may absorb some light at certain wavelengths, it would still be transparent to the naked eye. It can even be tuned electronically to further improve the transparency which makes it suitable for a wide range of applications that require an electrically conductive and transparent medium.

1.3 Synthesis methods of graphene:

1.3.1 Mechanical exfoliation:

This is the oldest method used to obtain single layer graphene. In this method, Individual graphene sheets are separated from graphite. In 2004, scientists Andre Geim and Konstantin Novoselov of University of Manchester used Scotch Tape and stuck it on graphite. This resulted in the peeling off of

many layers. Next, they used a second piece of tape to peel a few graphite layers off of the first piece of tape. The process continued for some time until the last piece of tape was stuck to a flat silicon wafer. It was later peeled off. The layers remaining on the wafer were a single atom thick–graphene. This process involves a simple and low budget.

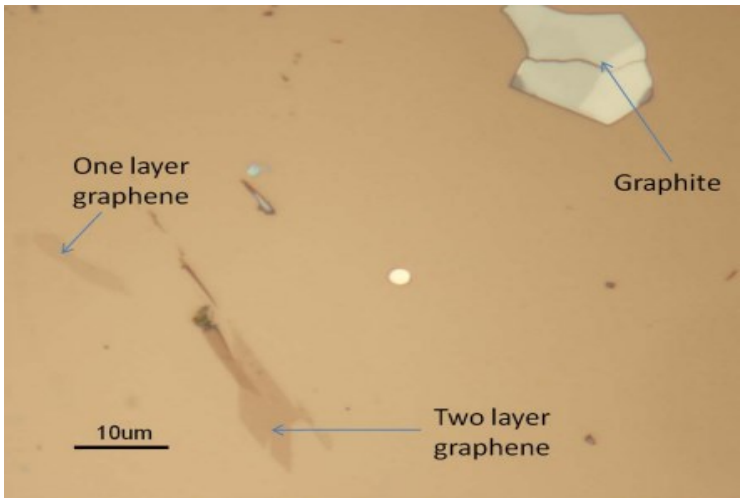


Figure 2: Graphene obtained by mechanical exfoliation. (Photo credit: Nathaniel Safron, University of Wisconsin – Madison).

The issues however with this method are that it is very difficult to control the uniformity of the layers especially when the requirement is continuity in layers. It is regarded as a crude fabrication process. The graphene sample is irregularly shaped and has limited commercial and electronic applications. Though this method is usually used for obtaining quick graphene samples, it is

not feasible for industry applications and mass production of graphene samples due to the enormous amount of manual work required.

1.3.2. Epitaxial growth on silicon carbide:

This involves heating silicon carbide at very high temperature and high vacuum so that it gets reduced to graphene [6]. This method makes it easy for layer control. But it is difficult to obtain large area sheets of graphene.

1.3.3. Chemical Vapor Deposition:

The mechanism behind the growth of Graphene using Chemical Vapor Deposition (CVD) is deposition of vapor species from various chemical reactions. The chemical reactions play a vital role and acts as one of the distinctive features of this process. CVD growths have largely proved to be a successful means for growing uniform and large area graphene.

This method is used for large-scale and high quality graphene samples. The traditional drawback has been the need for transfer onto a different substrate which leads to folding, tearing and wrinkles in the graphene sample. This is a straightforward process and considered to be the most reliable for continuous, large area graphene.

The process is based on three simple steps. One, the substrate is exposed to volatile precursors. Two, the precursors react and/or decompose on the substrate's surface. Finally, by-products and extra materials are removed by gas flow out of the system.

Other methods that can be used:

- Graphite oxide reduction,
- Growth from metal-carbon melts,
- Pyrolysis of sodium ethoxide,
- From nanotubes
- From graphite by sonication.

Of all the specified methods, the most popular ones are the mechanical exfoliation method for its simplicity and the CVD method for large area, continuous and scalable graphene synthesis possibilities.

References:

[1] Angela Jones and Nathaniel Safron, “Exfoliation to Make Graphene and Visualization”, University of Wisconsin, Madison, Mechanical

[2] Dodd Gray, Adam McCaughan, Bhaskar Mookerji, “Crystal Structure of Graphite, Graphene and Silicon”, 6.730, Physics for Solid State Applications

[3] Congquin Miao, Churan Zheng, Owen Liang, Ya-Hong, “Chemical Vapor Deposition of Graphene”.

[4] Frank, I. W., et al. (2007). “Mechanical properties of suspended graphene sheets”, AVS.

[5] Geim, A. K. and Novoselov, K. S. (2007), “The rise of Graphene”, *Nature Materials* 6 (3): 183–191

[6] Sutter, P. (2009), “Epitaxial graphene: How silicon leaves the scene”, *Nature Materials* 8 (3): 171–2

CHAPTER 2: DETAILED DESCRIPTION OF CHEMICAL VAPOR DEPOSITION

2.1 The CVD system:

CVD is a very promising technique of growing large area and high quality graphene with the much needed compatibility with silicon-based integrated circuits[1].

The CVD is composed three basic stages:

1. Gas delivering system:

There are mass flow controllers that deliver the required gas. In the event of several gases passed at the same time, they are mixed properly before being fed into the reacting system (quartz tube). The amount of every gas flow is regulated by unit called 'standard cubic centimeter per minute' (sccm). The gases fed in get involved in chemical reactions and deposition occurs on the material on which a process is conducted (substrate) at high temperature and low pressure of the quartz tube.

2. Reacting system:

It is usually a quartz tube though there can be variations in this choice. A quartz tube's melting temperature is as high as 1670 °C (β tridymite) and 1717 °C (β cristobalite) which makes a suitable material of choice for sustaining high temperatures.

The quartz tube is mounted onto the CVD furnace and care is ensured that it is exactly at a center point of the furnace. This is to ensure that temperature is evenly distributed on both sides of the tube. This temperature variance within the tube is of paramount importance since every chemical process is triggered at different temperatures.

3. Gas removal system:

The removal system involves a vacuum pump connected opposite to the end of the quartz tube where the gas inlet flow controllers are connected. This pump sucks out the necessary amount of air or gas from the tube to keep it under the stated pressure level. The required pressure varies from substrate to substrate as well as from various requirements of graphene properties, layers and uniformity. There are several factors that influence the required pressure for a growth.

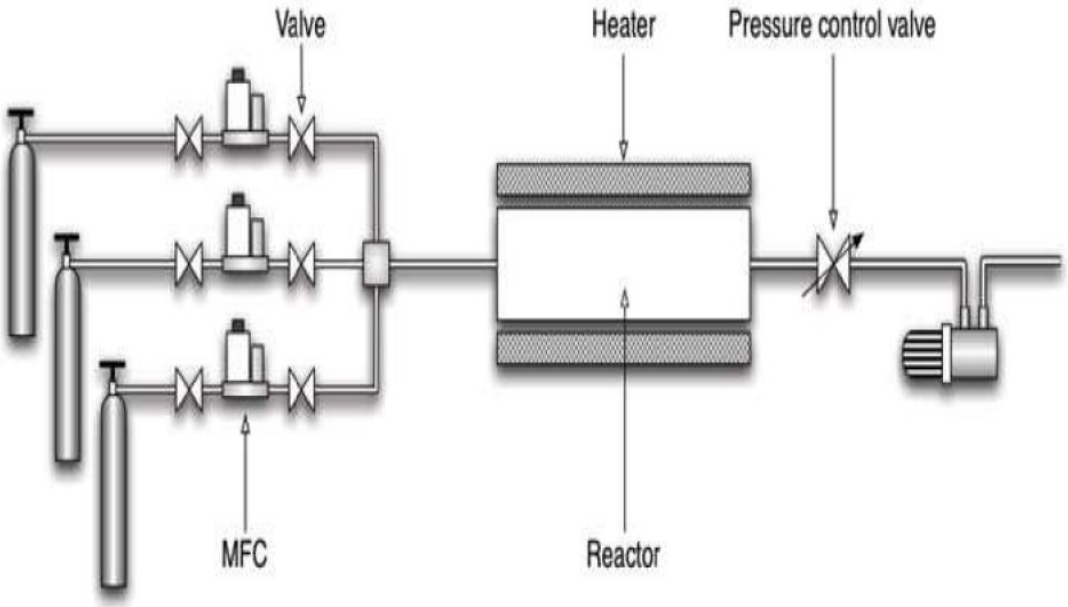


Figure 3: Schematic of typical CVD system. (Adapted from [2])

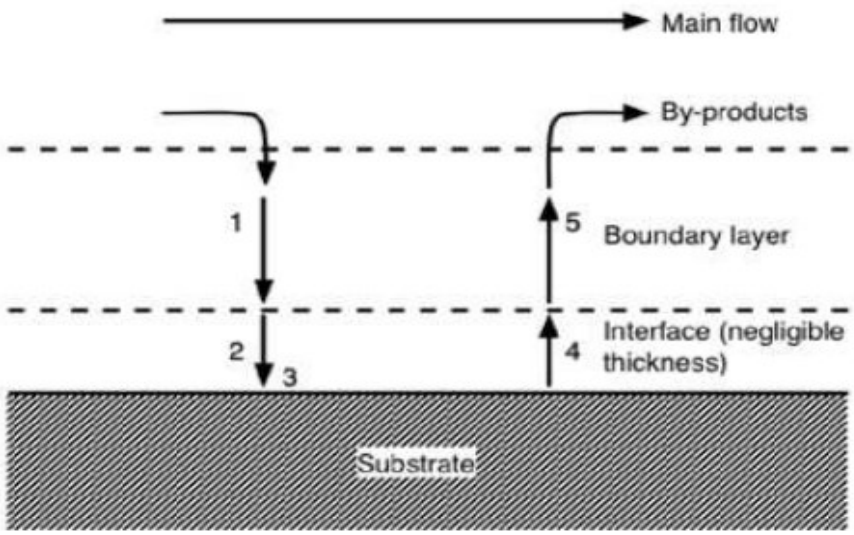


Figure 4: The chemical deposition process in CVD: *1. Reactants diffuse through the boundary layer, 2. Reactants are adsorbed onto substrate surface, 3. Chemical reaction occurs on the surface, 4. The by-products of the reaction are desorbed from the surface, 5. The by-products diffuse through the boundary layer. Adapted from [2].*

2.2 Factors impacting CVD growths:

The major factors that impact the graphene growth in the chemical vapor deposition technique are as follows:

2.2.1. Pressure

2.2.2. Hydrocarbon source

2.2.3. Temperature

2.2.4. Hydrogen

2.2.5. Metal substrate

Each of these factors has a different impact on every substrate. For example, if copper is used as the substrate, the mechanism involved is different from the mechanism involved if nickel is used as the substrate. There are several metal substrates that can be used in this CVD process for graphene growths though copper has proven to be efficient in several ways.

2.2.1. Pressure:

Low pressure has been preferred traditionally for single or bilayer graphene growths [3]. There are few high pressure large area graphene growths also made in the past [4]. Though the thermodynamics are the same at any pressure level, the kinetics may still vary. High pressure usually releases the source gas at a higher turbulence whereas low pressure tends to provide a smooth flow of the source gas with lower turbulence. This leads to better

interaction between the gases and the substrate contrary to the high pressure scenario where the turbulence would result in collisions which in turn results in abrupt deposition or lesser efficient interactions between the substrate and the gases. Therefore high pressure growths usually result in a lower quality graphene when compared to a low pressure growth.

2.2.2. Hydrocarbon source:

Every hydrocarbon source undergoes similar thermodynamics during a CVD growth. At a certain cracking temperature, the carbon and hydrogen atoms get separated and the carbon atoms interact with the substrate to form graphene. Different hydrocarbon sources have different cracking temperatures. The lower the cracking temperature, the better it is for low temperature growths.

Methane:

Methane is a hydrocarbon gas with the chemical formula CH_4. The molecules contain only single bonds. It is the simplest alkane, the main component of natural gas, and probably the most abundant organic compound on earth. The relative abundance of methane makes it an attractive fuel. It is one of the most commonly used source gas to obtain graphene using the CVD technique. Methane usually requires a high temperature of 1000°C irrespective of the substrates used for the graphene growth.

***Ethylene*:**

Ethylene is an organic compound, a hydrocarbon with the formula C_2H_4. It is a colorless and flammable gas. It is the simplest alkene and the simplest unsaturated hydrocarbon after acetylene. Ethylene is widely used in chemical industry, and its worldwide production (over 109 million tons in 2006) exceeds that of any other organic compound. Ethylene has a much lower cracking temperature when compared to methane. It can be used to do growths at temperatures as low as 550°C and hence it is very suitable for low temperature growths. It is also a very clean source and does not leave much residue in the CVD furnace. At temperatures below 500°C, a competing surface carbide forms and this impedes the growth of graphene [5].

2.2.3. Temperature:

The temperature to be used is dependent on both the substrate and the hydrocarbon being used. There has been low temperature graphene synthesis made with various hydrocarbons. Hydrocarbons like benzene have yielded graphene at temperatures as low as 300°C [6]. However, due to the health concerns over benzene, the safest yet productive hydrocarbon gases are ethylene and methane. However, methane would require high temperatures of about 1000°C whereas ethylene would only require 550°C. The lower the temperature, the better it is for industry and mass production applications.

2.2.4. Hydrogen:

The presence of hydrogen is a must in the growth of graphene using the CVD technique. Without hydrogen, it is not possible to obtain graphene on any substrate. Hydrogen acts differently with Cu and Ni. It readily diffuses in Cu, while it recombines on the Ni surface. Both these actions take place in agreement with the different hydrogen diffusion coefficients with Cu and Ni.

***Hydrogen has three major purposes*:**

1. Graphene formation:

It helps in the breaking down process of the hydrocarbon gas into hydrogen and carbon [7], [8]. This process is called 'dehydrogenation'. There exists a competition between the "dissociative chemisorption" nature of H_2 and the "dissociative dehydrogenation" of CH_4 on the surface sites. This H_2 competition plays a kinetic inhibitor role mainly for graphene growth on Cu. These two competing actions are represented by the following equations:

$H_2 + 2(s) \rightarrow H(s) + H(s)$

$CH_4 + (s) \rightarrow CH_4(s)$

Without the presence of hydrogen gas in the reaction mixture, methane has to chemisorb on the copper surface to form active carbon species, that is, $(CH_3)_s$, $(CH_2)_s$, $(CH)_s$,or C_s, which subsequently react to produce graphene but the instability involved makes it unreliable [7].

The sticking coefficient of hydrogen is lower for Ni than it is for Cu. That is why hydrogen tends to interact more on the surface of Cu by dissociative chemisorption. The catalytic role of hydrogen in activating carbon is represented by the following equations [7]:

$Cu + H_2 \leftrightarrow 2H_s$

$Cu + CH_4 \rightarrow CH_3(s) + H(s)$ --- slow

$Cu + CH_4 \leftrightarrow (CH_4)_s$

$(CH_4)_s + H_s \leftrightarrow (CH_3)_s + H_2$

Dehydrogenation of hydrocarbons is represented by the following equations:

$CH_4(s) + (s) \rightarrow CH_3(s) + H(s)$

$CH_3(s) + (s) \rightarrow CH_2(s) + H(s)$

$CH_2(s) + (s) \rightarrow CH(s) + H(s)$

$CH(s) \rightarrow C(s) + H(s)$ where (s) represents surface sites.

This dehydrogenation is impeded by the surface hydrogen in the case of Cu. The surface hydrogen acts as an inhibitor and the increase of hydrogen could drastically reduce the amount of graphene formation on the surface of Cu. In the case of nickel, the hydrogen desorption can also contribute to the dehydrogenation of CHx (x = 1–3) according to the additional processes:

$CHx(s) + H(s) \rightarrow CHx-1(s) + s + H_2\uparrow$

In nickel, hydrogen re-surfacing occurs unlike the case of copper. This results in hydrogen quickly migrating to the surface and recombining with subsurface hydrogen. This favors dissociative chemisorption of CHx (x = 1–3). In the case of CH_4, dehydrogenation is also represented by the following equations:

$CH_4(s) + (s) \rightarrow CH_3(s) + H(s)$

$CH_3(s) + (s) \rightarrow CH_2(s) + H(s)$

$CH_2(s) + (s) \rightarrow CH(s) + H(s)$

$CH(s) \rightarrow C(s) + H(s)$ where (s) represents surface sites.

The hydrogen desorbs from a Ni surface at low temperatures of 350K due to the unique recombination reaction of subsurface with the surface hydrogen [8].

$H(s) + H(s) \rightarrow H_2\uparrow + 2_s$

Therefore, though these four above equations are valid for both Cu and Ni growths, but the only difference is that in the Ni case, the hydrogen that tends to comes out to the surface aids the dehydrogenation of the hydrocarbons, whereas in the case of Cu, the same hydrogen tends to combine with surface hydrogen and stays on the surface itself, this impedes the

dehydrogenation of hydrocarbons and hence a careful amount of hydrogen is to be used for growths on Cu.

2. <u>Layer control</u>:

It removes excess layers of carbon from the substrate [7], [8]. Hydrogen resurfacing and surface combination aid in keeping sites on the Ni surface free for the CHx (x = 1–4) dehydrogenation, yielding diffusion/segregation of carbon. So optimizing the hydrogen level results in graphene with no or less D-peak on polycrystalline Ni.

The graphene etching using H_2 is done because they hybridization takes place. The sp^2 is converted to sp^3 and it leaves as a hydrocarbon at a particularly low pressure, high temperature and considerable amount of H_2 flow. Therefore, hydrogen likely acts not only as a catalyst for carbon activation by dehydrogenation of methane but also participates in controlling the graphene size as depicted in the following equation:

$$H_s + \text{graphene} \rightarrow (\text{graphene-C}) + (CH_x)_s$$

On Cu, the etching occurs noticeably at temperatures no less than 850°C. That is why annealing is usually done at 1000°C [7].

3. <u>Oxide layer removal prior to growth</u>:

The H_2 during the ramp up is done because of the need to remove oxides. Hydrogen likes Oxygen and hence it takes the oxygen molecule away from the metal which in this case is nickel. The oxygen appears on the metal because during e-Beam evaporation, a thin oxide layer is inevitably formed. This process facilitates the growth of graphene.

2.2.5. Metal substrate:

Transition metal substrates in graphene CVD growths may include one or more of the following substances: copper, nickel, iron, cobalt, platinum, iridium, ruthenium, the like, and/or combinations thereof[9].

<u>Copper</u>:

Copper has almost zero carbon solubility. The dehydrogenated hydrocarbon gas in the presence of a carrier gas and hydrogen at low pressure and high temperature interacts with the Cu substrate and deposits carbon onto the surface of Cu. Islands of graphene are formed on the surface of Cu which in turn result into flakes upon further deposition. These flakes tend to combine and form a layer of graphene. Further accumulation results in multilayer graphene.

Nickel:

Nickel has non-negligible carbon solubility. There is a stronger graphene-metal interaction and lattice match compared to copper. There are no tilt grain boundaries in nickel as there is in copper. During cooling, the solubility of nickel is reduced and therefore the excess dissolved carbon is precipitated to the surface and that is when it forms graphene. When the carbon atoms precipitate out of the nickel, they do not arrange themselves in a uniform manner.

The carbon atoms instead pick the high surface energy areas like grain boundaries and even rough areas and that is why uniformity is absent in nickel graphene. Surface carbide prevents the nucleation of graphene but not its growth once it is nucleated. So the solubility of nickel with carbon is the property which makes the growth mechanism unique. The growth is done during the cooling stage rather than the annealing stage.

Care must be ensured to do optimal cooling. Quick cooling results in less graphene because there is not enough time for carbon precipitation to occur. Slow cooling has nothing on the surface in that carbon atoms diffuse deep into the bulk catalyst [2].

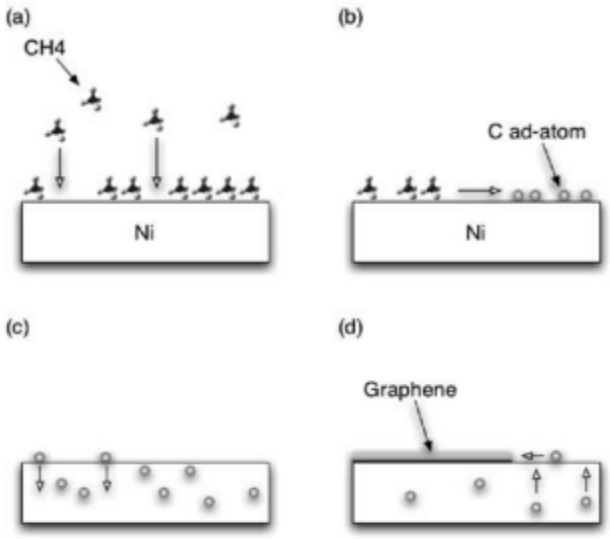


Figure 5: (a) Methane molecules diffuse and adsorb on nickel surface. (b) Methane pyrolysis to carbon ad-atoms on nickel surface. (c) Carbon ad-atoms dissolve in bulk nickel. (d) Carbon atoms precipitate back to nickel surface at low temperature and graphene is formed. Adapted from [2].

References:

[1] Yagang Yao, Ching-ping Wong, *carbon 2002, "*Monolayer graphene growth using additional etching process in atmospheric pressure chemical vapor deposition".

[2] Congquin Miao, Churan Zheng, Owen Liang, Ya-Hong Xie, "Chemical Vapor Deposition of Graphene".

[3] Li, X., et al. (2011), "Large-Area Graphene Single Crystals Grown by Low-Pressure Chemical Vapor Deposition of Methane on Copper", Journal of the American Chemical Society 133(9): 2816-2819.

[4] Ivan Vlassiouk, Pasquale Fulvio, Harry Meyer, Nick Lavrik, Sheng Dai, Panos Datskos, Sergei Smirnov (2013), "Large scale atmospheric pressure chemical vapor deposition of graphene".

[5] Addou, R., et al. (2012). "Monolayer graphene growth on Ni(111) by low temperature chemical vapor deposition." Applied Physics Letters 100(2): 021601-021603.

[6] Li, Z., et al. (2011). "Low-temperature growth of graphene by chemical vapor deposition using solid and liquid carbon sources." ACS Nano 5(4): 3385-3390.

[7] Vlassiouk, I., et al. (2011). "Role of Hydrogen in Chemical Vapor Deposition Growth of Large Single-Crystal Graphene." ACS Nano 5(7): 6069-6076.

[8] Losurdo, M., et al. (2011). "Graphene CVD growth on copper and nickel: role of hydrogen in kinetics and structure." Physical Chemistry Chemical Physics 13(46): 20836-20843.

[9] Wassei, J. K., et al. (2012). "Chemical Vapor Deposition of Graphene on Copper from Methane, Ethane and Propane: Evidence for Bilayer Selectivity." Small 8(9): 1415-1422.

CHAPTER 3: NOVEL PROCEDURE FOR GRAPHENE SYNTHESIS

3.1 Experimental Procedure of the growth:

A 100 nm layer of pure nickel is evaporated onto glass using E-beam evaporation. The substrate is then placed inside the CVD furnace.

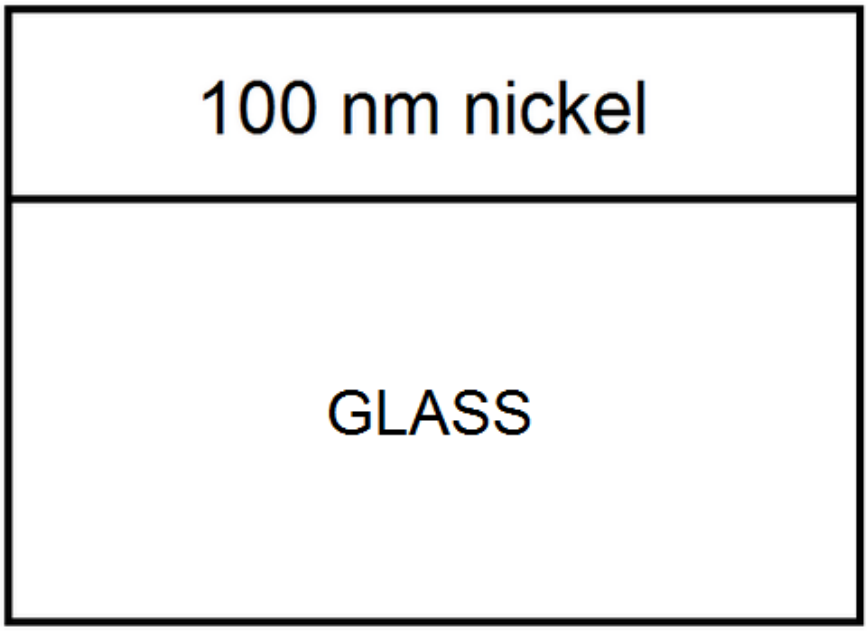


Figure 6: A 100 nm layer of nickel evaporated onto a glass substrate.

When the catalyst used is nickel, there is a stronger graphene metal interaction. The hydrocarbon decomposes and the inflow of hydrogen at this stage also plays an important part in the growth mechanism[1].

Main stages in the growth mechanism:

1. Dissociation of the hydrocarbon into at high temperature on the surface of nickel,
2. Dissolution of carbon into nickel,
3. Precipitation of graphene at the surface of nickel during cooling.

The dissociation of the hydrocarbon results into carbon and hydrogen. The carbon seeps through nickel because of the high solubility of nickel at high temperatures. Upon cooling, the solubility of nickel reduces and hence the excess dissolved carbon is therefore precipitated to the surface. This forms a two-dimensional arrangement of graphene [2].

Ethylene (C_2H_4) has a low cracking temperature. The analysis of the Raman spectra shows low D-peak at temperatures as low as 700℃. At 600℃, the the D/G peak ratio is still less than 0.5, indicating the growth of high quality few-layer graphene at low temperatures.

The low temperature growth makes it possible for borosilicate glass to be used directly in the furnace. It can sustain a maximum temperature of 600℃ but results in deformations slightly beyond that value. Below a certain temperature, a competing nickel carbide phase impedes graphene formation. Therefore, a good choice of temperature is 600℃.

The sample is heated to a temperature of 600℃ at a pressure of 500 Torr, in the presence of argon (800 sccm) and hydrogen (100 sccm). Following a two minute annealing at a pressure of 20 Torr, ethylene (10 sccm) is then made to flow for about 10 minutes after which it is turned off and the sample is cooled at a rate of 200℃/min. Poly (methyl methacrylate) (PMMA) is spin-coated on the graphene before baking it on a hotplate at 100℃ for 15 min.

With a lot of care, the PMMA is selectively removed as shown in Fig. 9 by dipping the sample appropriately in acetone. The sample is then immersed in 20% HCl solution which acts as the etchant. The duration is for 10 hours but it is expected to vary if a different etchant is used. The duration varies based on the strength and concentration of the etchant used. For example, Marble's reagent can show results in just few minutes.

The selective removal of PMMA is carried out to provide gaps for any etchant to pass through and etch the underlying nickel away. This gap forms due to the buoyancy of PMMA in liquids. Therefore, the PMMA provides a gap for the etchant to etch away the nickel while PMMA is still attached to the glass in the places where selective removal with acetone was not done.

This mechanism paves the way for obtaining graphene directly on glass in a transfer free process with each step shown in Fig. (7-11). The sample is

completely dried in a vacuum chamber for about 12 hours and the remaining PMMA is removed by completely immersing it in acetone followed by isopropyl alcohol. Thus graphene can be obtained directly on glass in a transfer free process which is highly suitable for scalable production.

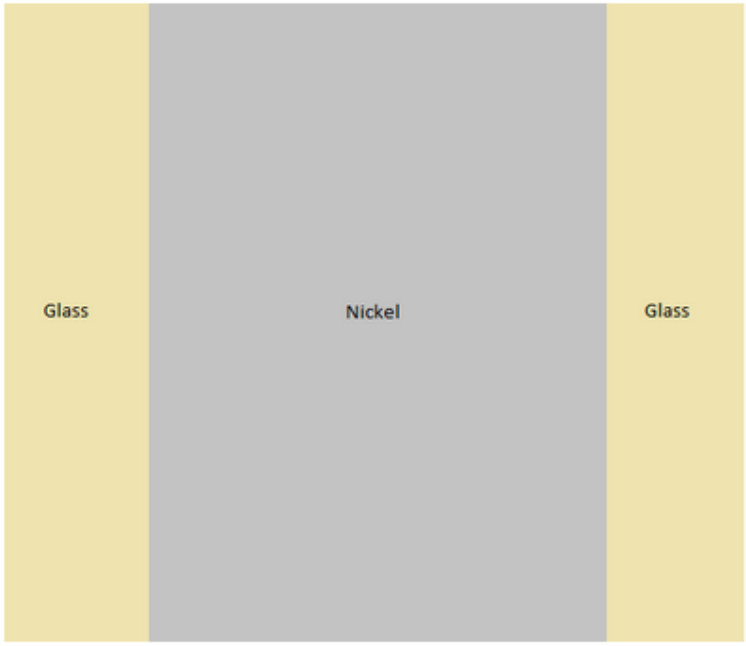


Figure 7: Nickel evaporated on glass by e-Beam evaporation

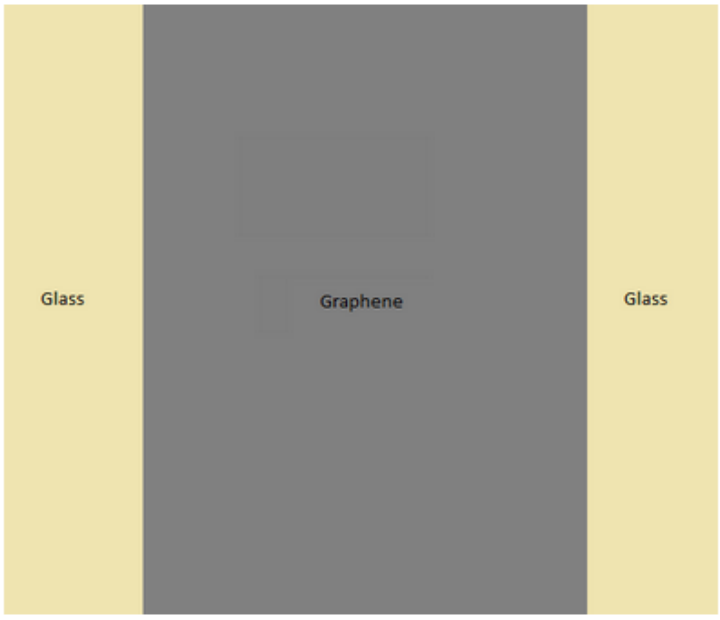


Figure 8: Graphene grown on nickel using chemical vapor deposition

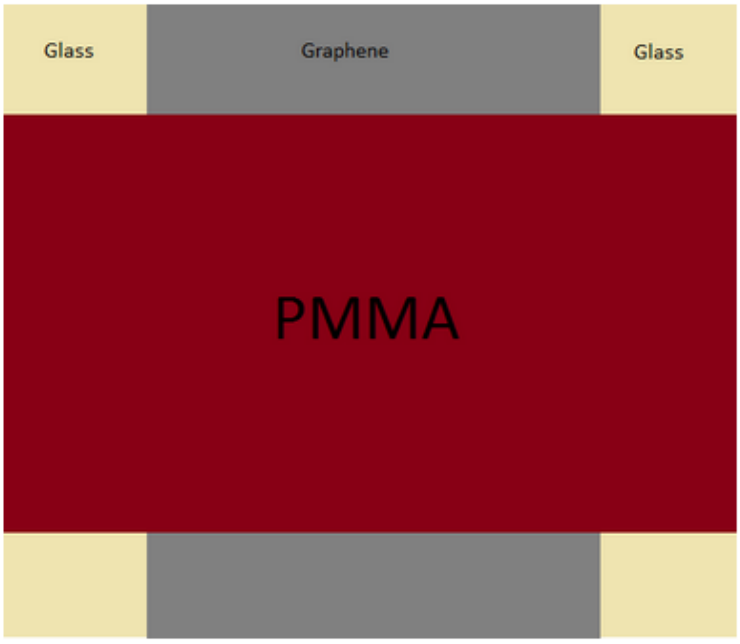


Figure 9: PMMA added on the sample to allow selected regions to be exposed

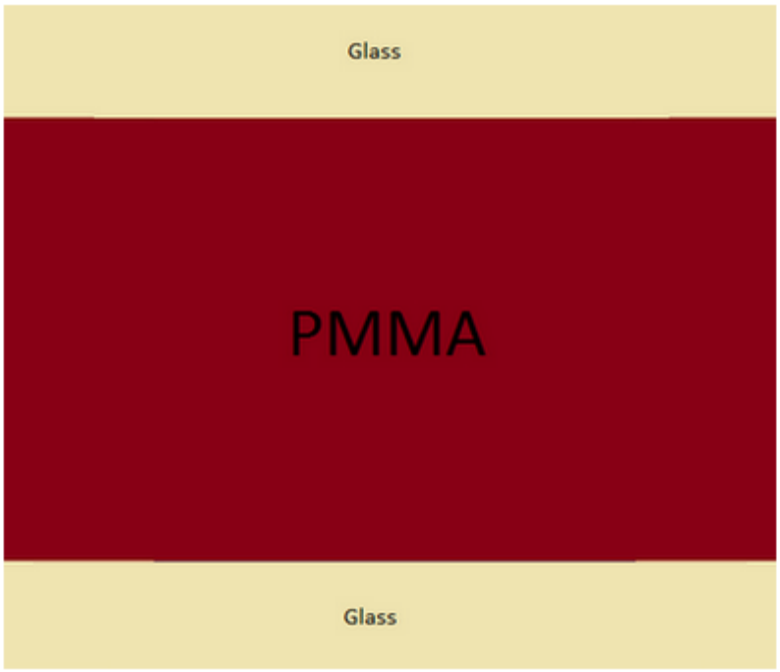


Figure 10: After etching nickel using Marble's reagent or Hydrogen Chloride

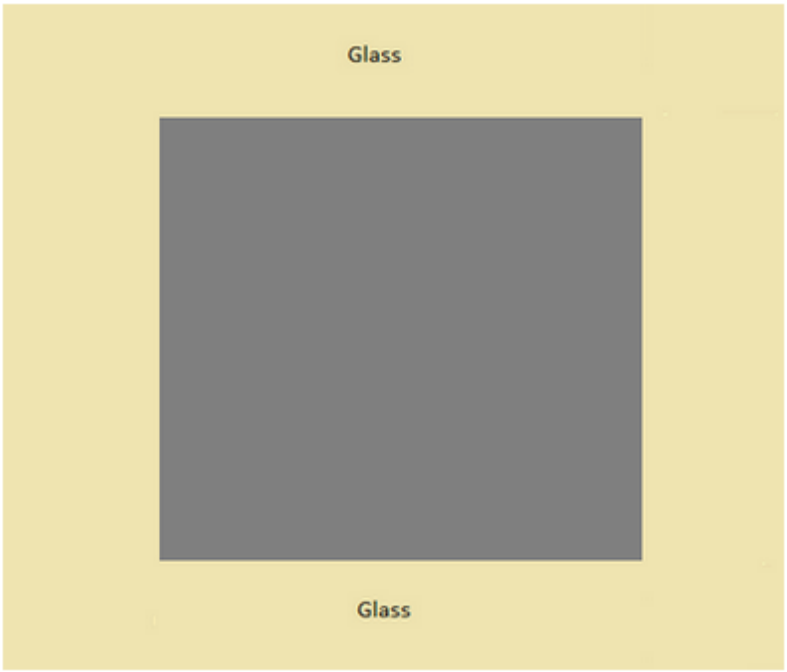


Figure 11: After removing the PMMA using acetone, we get graphene on glass

The transition from the sample shown in Fig.10 to the sample shown in Fig.11 is a very delicate one. A lot of care must be ensured not to disturb the sample much. In Fig.10, the sample is shown as having graphene sandwiched between glass and PMMA. At this point, the sample is still immersed in the etching solution.

The sample should now be cleaned from the solution with water. But removing the sample from the etchant and immersing it again into a container of distilled water is not possible because of two major reasons. One, the graphene is still not fixed to the glass substrate. There is still a gap between the glass and the graphene which is created by the etching of the nickel layer which was there prior to the etching. Two, the liquid present between glass and graphene will act as a barrier and will not allow graphene to attach to glass unless it is cleaned up.

The sample must therefore not be removed at any time from the etchant solution but instead an attempt to replace the liquid with water must be adopted. For that purpose, a pipet is used to suck out a small portion of the etchant solution and another pipet is used to add a similar amount of distilled water. At no point during this process, the lowest level of liquid should be below the top layer of the sample as the pressure is what causes ruptures on the

graphene sample due to buoyancy. A repetition of this process will ensure over time that the liquid is transformed from etchant solution to water.

After considerable cleaning is done, the water removal must take place. The water is sucked out completely from the container containing the immersed sample. At this point, the sample is neither immersed nor floating but is still wet and humid. A considerable amount of drying must happen to completely remove the humidity in the entire sample. A vacuum evaporator is used for that purpose. The sample is kept for about 12 hours and then taken out.

At this point, the graphene is completely stuck on glass because the drying procedure described removes the humidity completely. Now the sample is almost ready and the only remaining part is the removal of PMMA. This is simply done by immersing the sample in acetone, followed by isopropyl alcohol in order to remove the stains caused by acetone. It should be noted that after drying, the sample can be immersed in any solvent with no fear of possible ruptures or damages. The sample obtained in this manner is transparent and well stuck on glass. Other replacement for glass can also be used. Those also include flexible electronics but the condition of feasibility with temperature as high as 600℃ must be ensured. This is a major breakthrough in the advent of graphene usage in flexible electronics and also in organic photovoltaic applications.

References:

[1] Losurdo, M., et al. (2011). "Graphene CVD growth on copper and nickel: role of hydrogen in kinetics and structure", Physical Chemistry Chemical Physics 13(46): 20836-20843.

[2] Reina, A., et al. (2008). "Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition", Nano Letters 9(1): 30-35.

[3] Vlassiouk, I., et al. (2011). "Role of hydrogen in chemical vapor deposition growth of large single-crystal graphene", ACS Nano 5(7): 6069-6076.

[4] Losurdo, M., et al. (2011). "Graphene CVD growth on copper and nickel: role of hydrogen in kinetics and structure", Physical Chemistry Chemical Physics 13(46): 20836-20843.

[5] Kyle, J. R., et al. (2011). "Centimeter-Scale High-Resolution Metrology of Entire CVD-Grown Graphene Sheets", Small 7(18): 2599-2606.

[6] Wang, W., et al. (2013). "Three dimensional few layer graphene and carbon nanotube foam architectures for high fidelity supercapacitors", Nano Energy 2(2): 294-303.

[7] Guo, S., Ghazinejad, M., Qin, X., Sun, H., Wang, W., Zaera, F., Ozkan, M. and Ozkan, C. S. (2012), “Tuning Electron Transport in Graphene-Based Field-Effect Devices using Block Co-polymers”, Small, 8: 1073–1080.

[8] Pleskot, Dennis L., et al. "Large-area Metrology of CVD-grown Graphene Layers on Copper Foil Substrates", *MRS Proceedings*. Vol. 1451. No. 1. Cambridge University Press, 2012.

[9] Li, X., et al. (2009). "Transfer of Large-Area Graphene Films for High-Performance Transparent Conductive Electrodes", Nano Letters 9(12): 4359-4363.

[10] De Arco, L. G., et al. (2009). "Synthesis, Transfer, and Devices of Single- and Few-Layer Graphene by Chemical Vapor Deposition", Nanotechnology, IEEE Transactions on 8(2): 135-138.

[11] Liu, W., et al. (2010). "Chemical vapor deposition of large area few layer graphene on Si catalyzed with nickel films", Thin Solid Films 518 (6, Supplement 1): S128-S132.

[12] Suk, J. W., et al. (2011). "Transfer of CVD-Grown Monolayer Graphene onto Arbitrary Substrates", ACS Nano 5(9): 6916-6924.

CHAPTER 4: CHARACTERIZATION TECHNIQUES OF GRAPHENE

4.1 Raman scattering:

The Raman Effect represents the inelastic scattering of a photon. Scattered photons could be either elastically or inelastically scattered. Elastic scattering is also called Rayleigh scattering. In this case, the scattered photons have the same energy, wavelength and frequency as that of the incident ones. If there is a difference (usually lower), it is called Raman scattering.

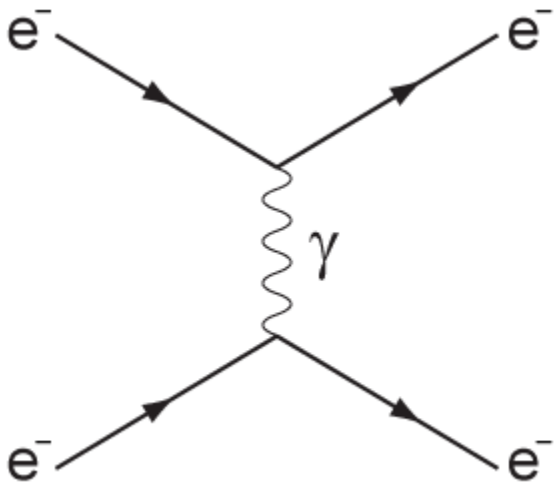


Figure 12: Feynman diagram of scattering between two electrons by emission of a virtual photon (Source: Wikipedia - Raman scattering)

4.2 Raman spectra of graphene:

Raman spectroscopy is a successful technique to analyze the number of layers in a sample.

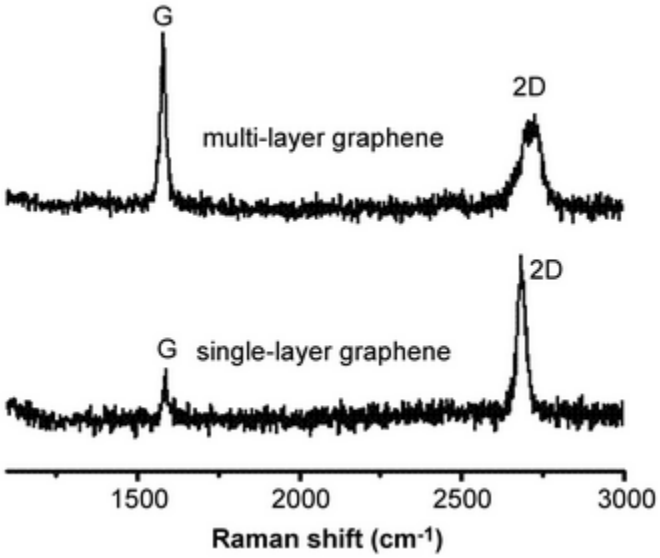


Figure 13: Typical Raman spectrum of multi-layer and single layer graphene (Source: Reference [1])

The G peak being higher than the 2D peak indicates multi-layer graphene. The G peak being lower than the 2D peak indicates few layer or single layer graphene. The D-peak is the defect peak, the lower and the better the quality of the sample.

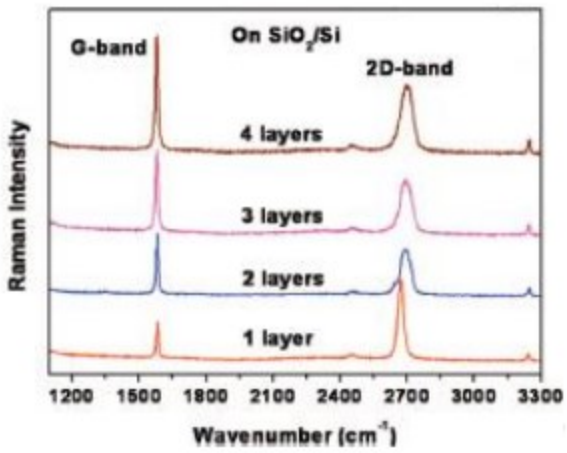


Figure 14: Comparison of graphene samples with varying number of layers (Adapted from: [2])

The most prominent line is the G-band at 1580 cm^{-1}. The G peak is due to certain phonons in the Gamma brillouin zone. The 2D peak is due to transverse optical phonons associated with K-Brillouin zones. Those form a canonical structure wrt graphene sheets. The 2D band's line shape and position depend on the number of layers and it represents the second order of zone-boundary phonons which in turn do not satisfy the Raman fundamental selection rule[3].

4.3 Four-point electrical resistivity measurement:

For low resistivity, the best method is the four-point probe method otherwise called as the "van der Pauw Method". This method is chosen because we are dealing with a two dimensional sample. Its ability to accurately

measure the properties of a sample of any arbitrary two dimensional sample has made this a very reliable method. A current is sent to two probes and the voltage is measured through the other two. Then using Ohm's law, the resistivity can be calculated. This measurement is essential to determine how electrically conductive is the graphene sample when used as a transparent electrode [4].

The properties of a sample that can be calculated are:

1. The resistivity
2. The doping type
3. The number of majority carriers per unit area
4. The mobility of the majority carrier

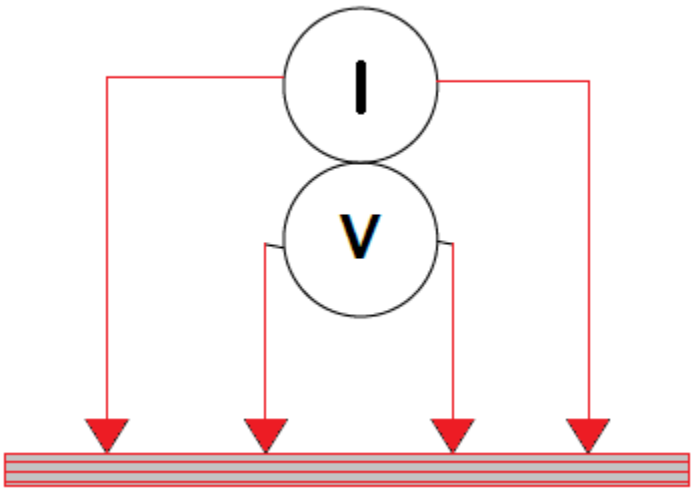


Figure 15: Four-point probing schematic

As shown in Figure 15, two probes are connected to a current source (I) and the voltage (V) is measured across the remaining two. But care must be ensured to remove the graphene surrounding the four contacts. This is to ensure correct measurement. Plasma etching is a popular method used to remove graphene. This is a drawback in this method as testing the resistivity of a large number of samples can make this expensive. All the samples cannot be tested using this technique as going through the procedure of removing some graphene can affect various other parameters and the usability of the sample.

References:

[1] Zheng Yan and Andrew Barron, "Characterization of Graphene by Raman Spectroscopy", Connexions, June 29, 2010.

[2] Amílcar R. Torres Quijano, "Raman spectroscopy for the identification of Graphene layers", Department of Physics, College of Natural Sciences, University of Puerto Rico, Río Piedras, Puerto Rico.

[3] Zhenhua Ni, Yingying Wang, Ting Yu, and Zexiang Shen, "Raman Spectroscopy and Imaging of Graphene", Nano Res (2008)1:273-291.

[4] A method of measuring specific resistivity and Hall Effect of discs of arbitrary shape Philips Res.Rep, Vol. 13, No. 1. (1958) by L. J. van der Pauw.

CHAPTER 5: RESULTS AND DISCUSSION

5.1 Raman spectra of synthesized low temperature graphene:

The laser used for all Raman data is a 532 nm laser. Figure 16 shows the Raman spectra of the graphene synthesized using ethylene, at high pressure and temperature. It is a known fact that the use of nickel as the catalyst will often yield multi-layer graphene. This is confirmed by observation of the G to 2D peak ratio.

The parameters used for all growths are shown below in various recipes, where the gases are expressed in units of 'Standard Cubic Centimeters per Minute'. Regarding the Raman spectra, if the 2D/G ratio is less than 1, then it is multi-layer graphene. . If the 2D/G ratio is greater than 1, then it is single-layer graphene. If the 2D/G ratio is equal to 1, then it is two-layer graphene. The ratio between the D-peak and the G-peak is also important. If the D/G ratio is less than 0.5, the sample is regarded as considerable good quality.

Recipe [A]:

Argon (sccm)	Hydrogen (sccm)	Ethylene (sccm)	Pressure (Torr)	Temperature (℃)
800	100	10	500	700

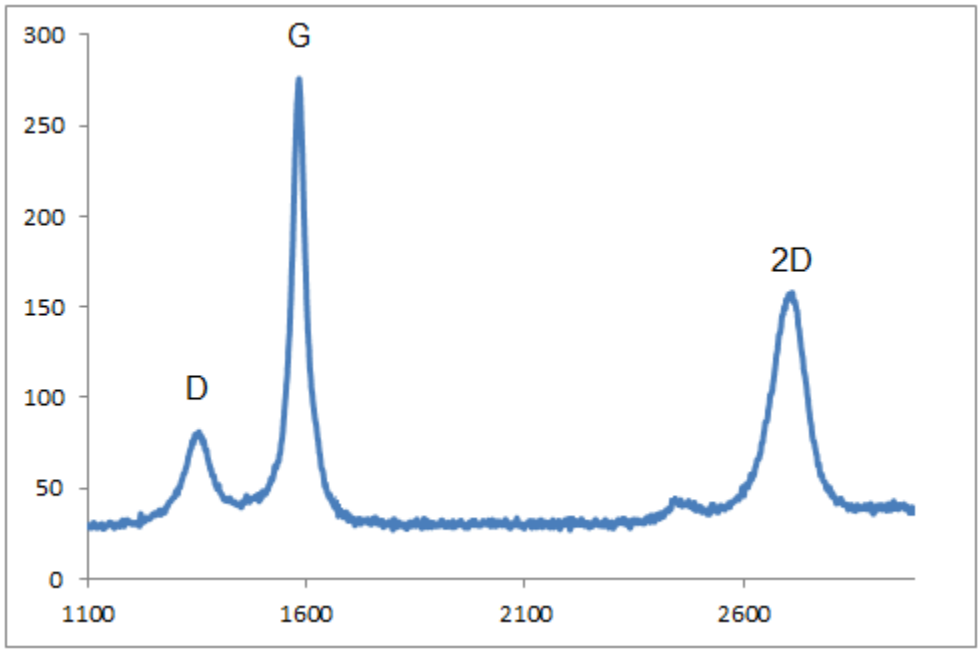


Figure 16: Raman spectra of Graphene, Recipe [A]

I_D/I_G = 44.5/239 = 0.186 (Offset = 30)

I_{2D}/I_G = 124/239 = 0.52

The lower the pressure, the more continuity is expected with the graphene structure. This is because the gas flow is more uniform and with low turbulence level. So the molecules can interact better with the metal substrate. Since the discontinuities reduce, the D-peak also reduces drastically as seen in figure [17].

It is seen that the D-peak is very low and can be further lowered if the temperature is increased further than 700℃. However, since the goal is to grow graphene at low temperatures since glass will not be able to withstand temperatures higher than 600℃, growths done at temperatures higher than 700℃ have been omitted from this report.

Recipe [B]:

Argon (sccm)	Hydrogen (sccm)	Ethylene (sccm)	Pressure (Torr)	Temperature (℃)
800	100	10	20	700

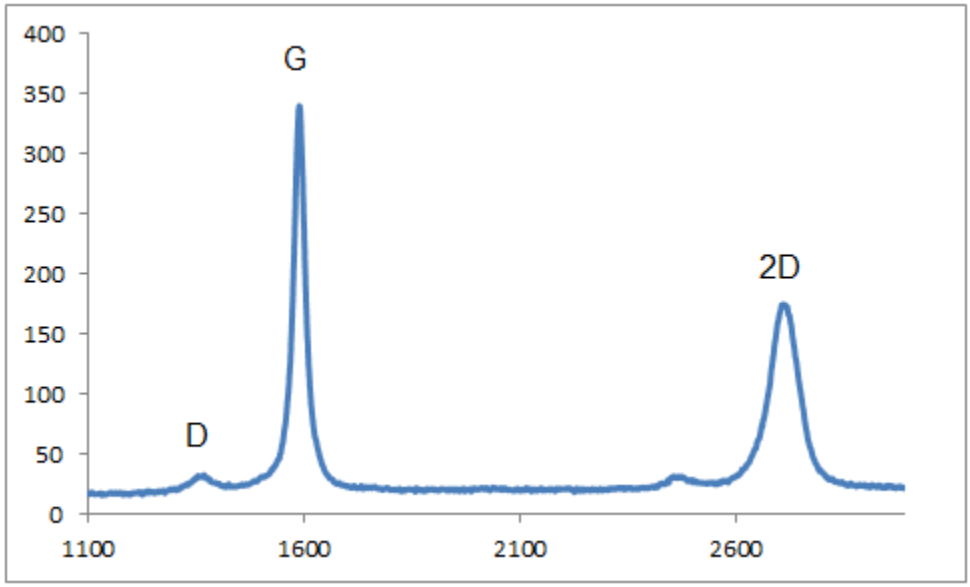


Figure 17: Raman spectra of Graphene, Recipe [B] thinner

I_D/I_G = 11.3/317 = 0.03 (Offset = 17)

I_{2D}/I_G = 156/317 = 0.49

The higher the temperature, the lower the D-peak is expected. This is because of the ethylene tends to break up more efficiently at high temperatures and interact better with the metal substrate. This means that the D-peak tends to increase as the temperature reduces. This is seen in figure [18].

Recipe [C]: (On Glass)

Argon (sccm)	Hydrogen (sccm)	Ethylene (sccm)	Pressure (Torr)	Temperature (°C)
800	100	10	20	600

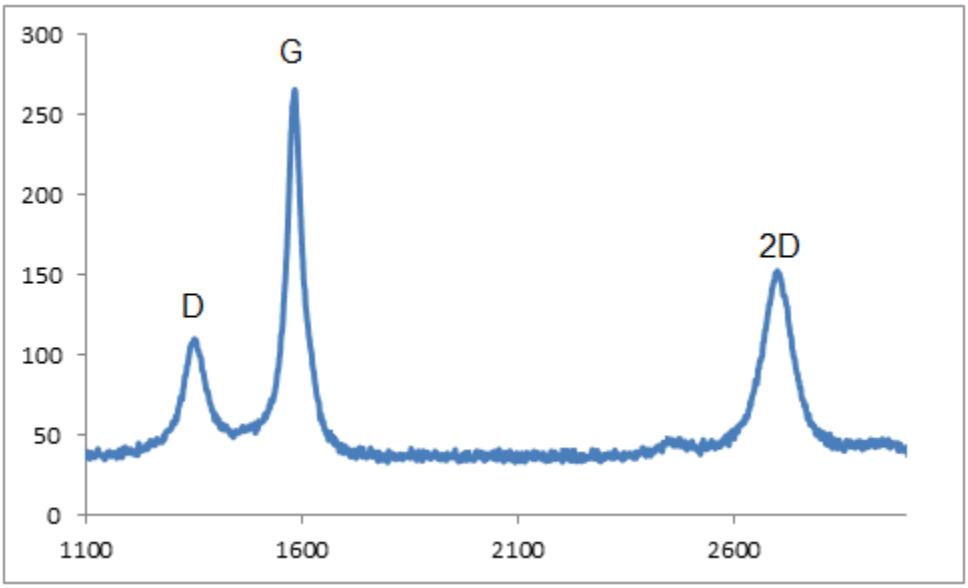


Figure 18: Raman spectra of Graphene on glass, Recipe [C]

I_D/I_G = 72/228 = 0.31 (Offset = 32)

I_{2D}/I_G = 117/228 = 0.51

Though it is possible to obtain few-layer or single layer graphene using hydrogen etching as described in chapter 2, it is not feasible in this situation as high temperature is required for the etch to take place. Since borosilicate glass cannot tolerate temperatures higher than 600℃ and the etching process requires much higher temperatures, it is not a good option to try the etching process in this synthesis technique. It is therefore important to try to minimize the layers during the graphene growth itself even if it is difficult to get single layer graphene with a nickel substrate.

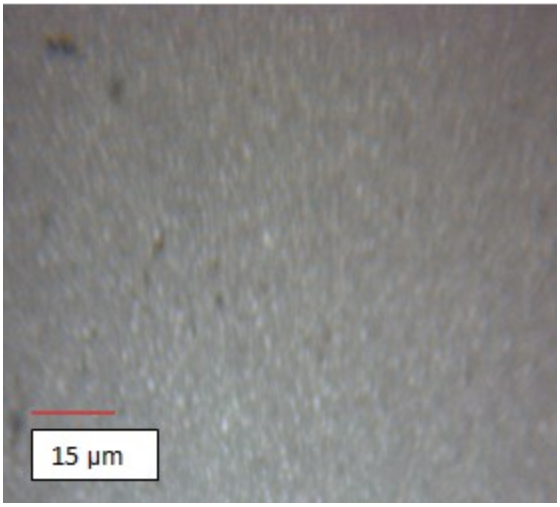


Figure 19: Optical image of graphene grown on nickel substrate.

Using nickel as the catalyst and glass as the substrate:

- The graphene is multi-layered
- Glass can directly be used in the furnace
- Optimal temperatures as low as 600℃ can be used
- Temperature lesser than 600℃ results in high D-peak
- Temperature higher than 600℃ results in melting of the glass substrate

To show that graphene of good quality can be synthesized at temperatures no less than 600℃, the Raman data of graphene synthesized at 550℃ has been included to show that the quality is considerably which limits the amount by which the temperature can be reduced for growths. The D-peak is more than half of the G-peak as seen in figure 20.

Recipe [D]:

Argon (sccm)	Hydrogen (sccm)	Ethylene (sccm)	Pressure (Torr)	Temperature (℃)
800	100	10	20	550

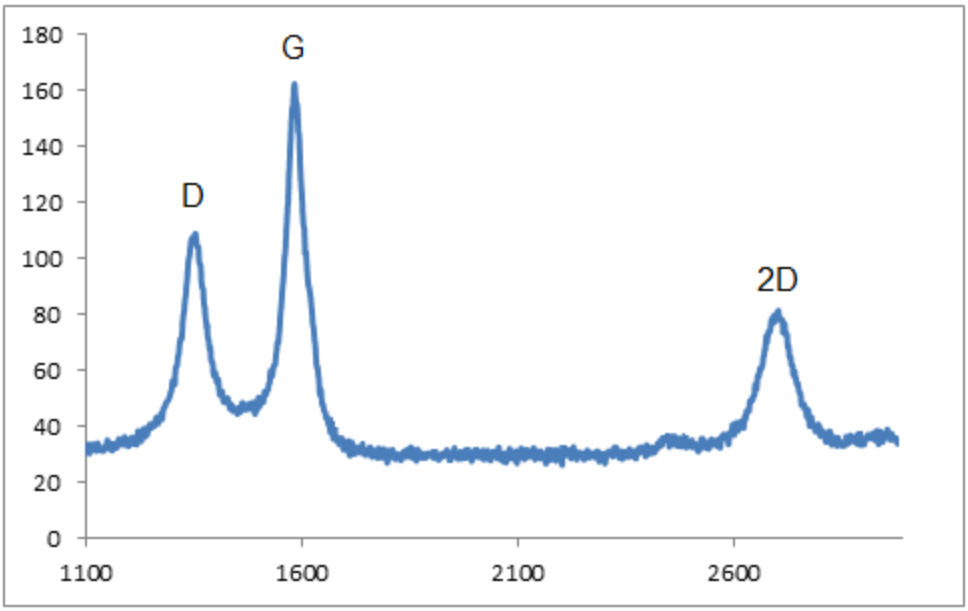


Figure 20: Raman spectra of Graphene on glass, Recipe [D], (High D-peak at a temperature of 550°C)

I_D/I_G = 78/130 = 0.6 (Offset = 29)

I_{2D}/I_G = 50.8/130 = 0.39

Recipe [E]

Argon (sccm)	Hydrogen (sccm)	Ethylene (sccm)	Pressure (Torr)	Temperature (℃)
800	100	10	300	700

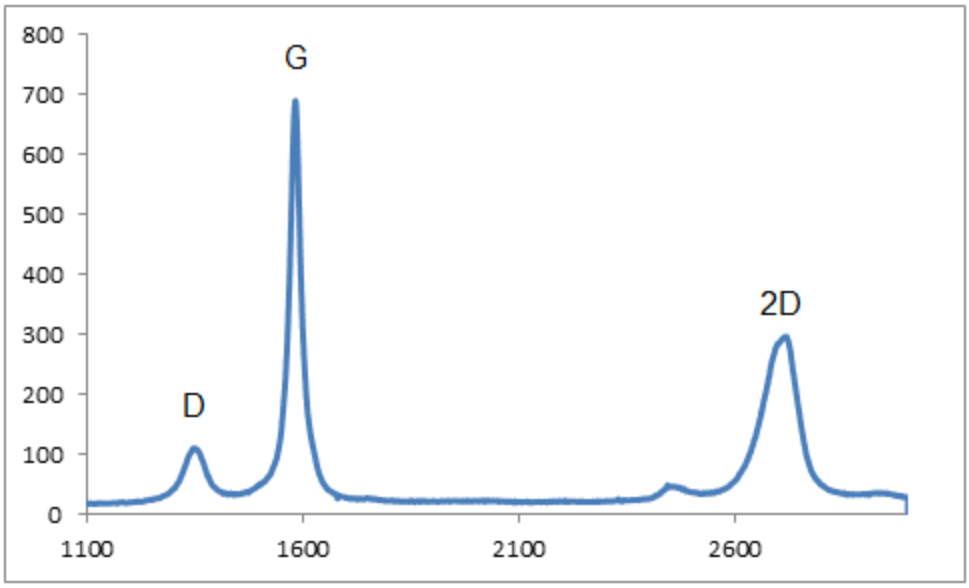


Figure 21: Raman spectra of Graphene (Medium pressure point)

I_D/I_G = 84/678 = 0.12 (Offset = 19)

I_{2D}/I_G = 269/678 = 0.39

Effect of pressure variation:

Temperature	Pressure	I_D/I_G	I_{2D}/I_G	I_G/I_{2D}
700	**500**	0.19	0.52	1.92
700	**300**	0.12	0.50	2.00
700	**20**	0.03	0.49	2.03

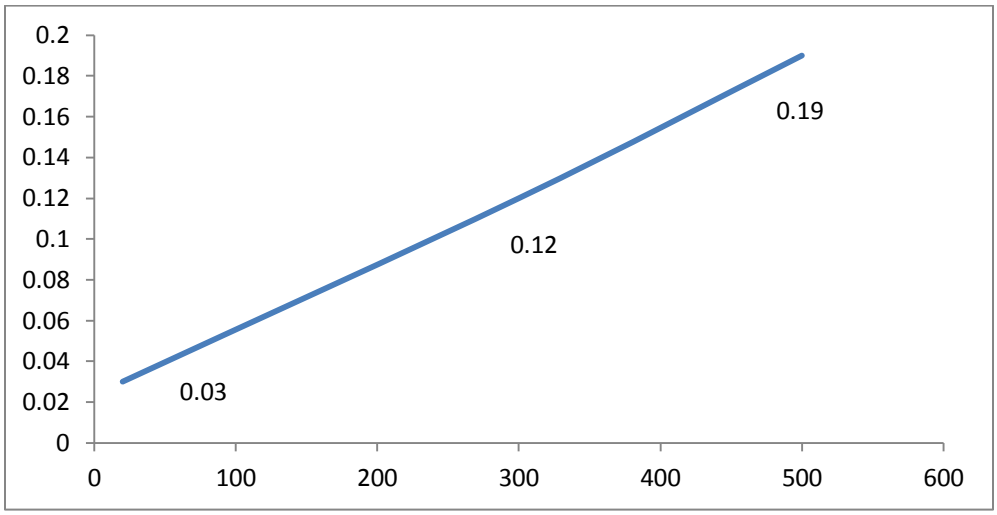


Figure 22: Pressure Vs. Quality of sample

Pressure mainly has an effect on the quality of the sample. The lower the pressure, the higher the quality of the sample becomes. This is a result of more uniformity in carbon deposition.

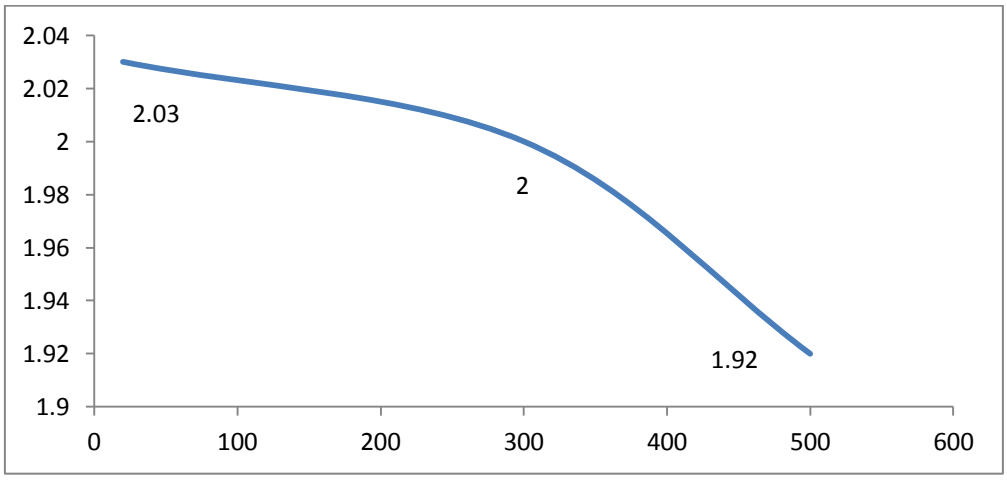


Figure 23: Pressure Vs. I_G/I_{2D}

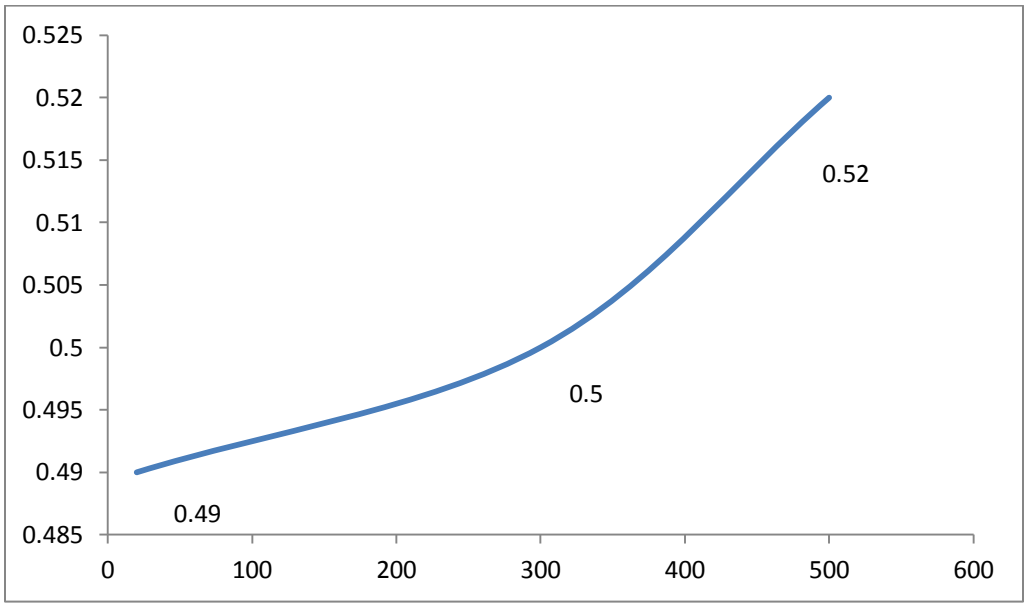


Figure 24: Pressure Vs. I_{2D}/I_G

Effect of temperature variation:

Temperature	Pressure	I_D/I_G	I_{2D}/I_G	I_G/I_{2D}
700	20	0.03	0.49	2.03
600	20	0.31	0.51	1.95
550	20	0.6	0.39	2.56

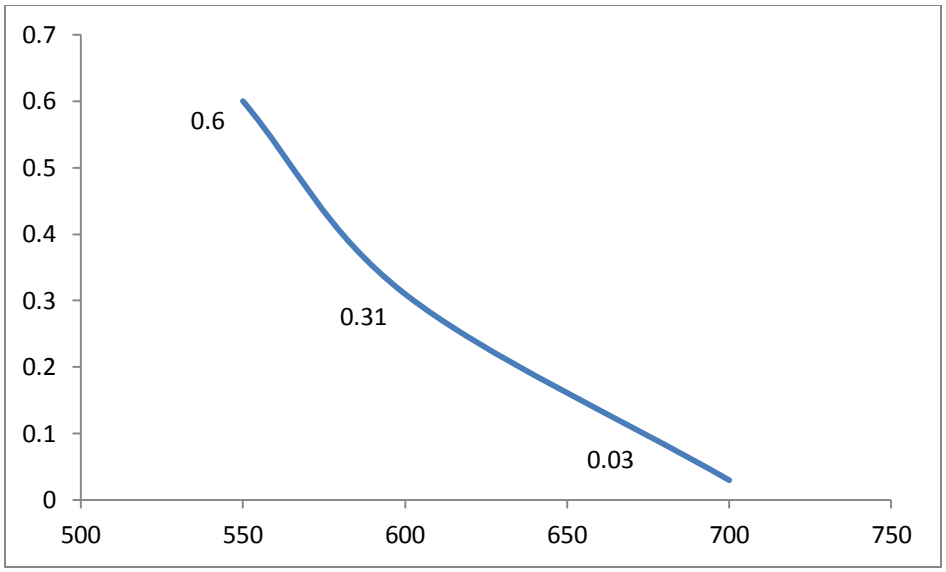


Figure 25: Temperature Vs. I_D/I_G

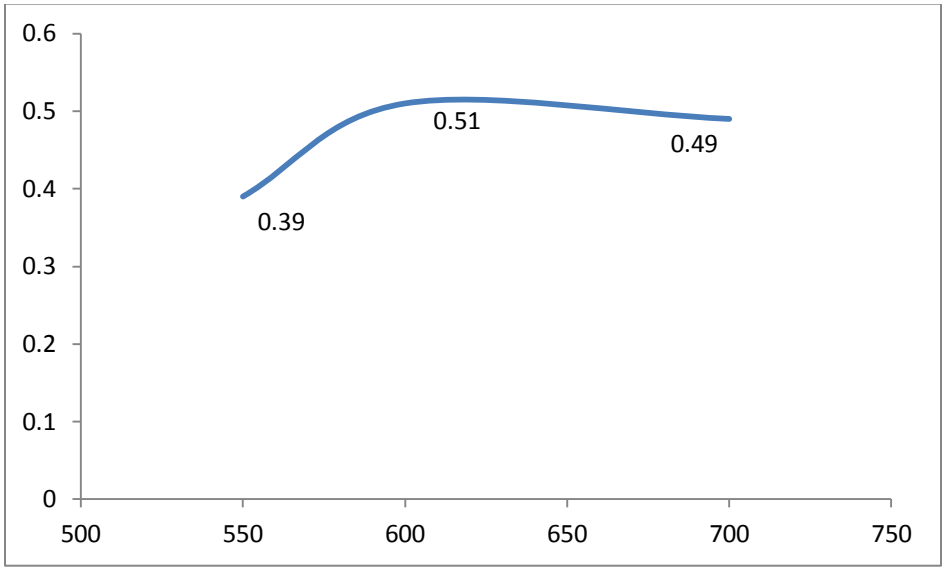


Figure 26: Temperature Vs. I_{2D}/I_G

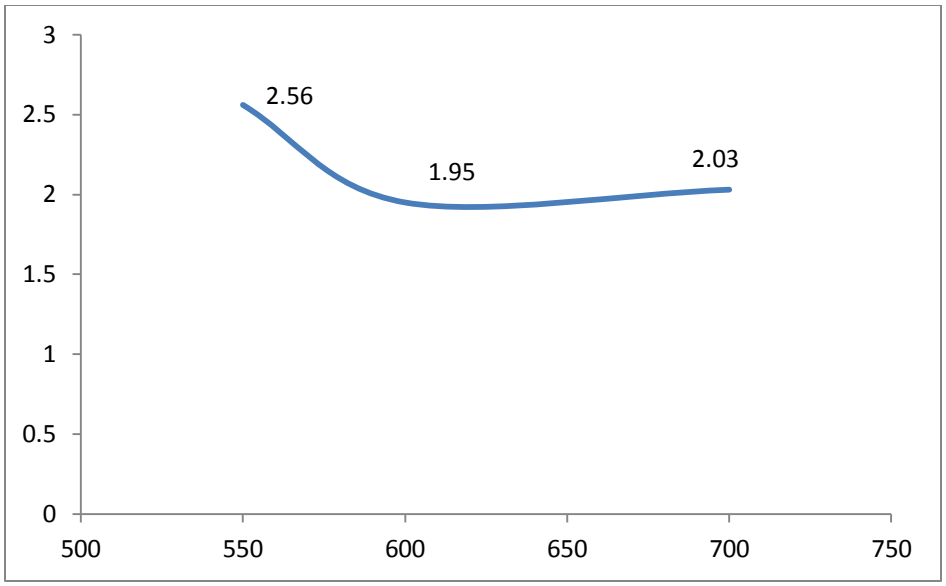


Figure 27: Temperature Vs. I_G/I_{2D}

The above temperature plots indicate that the higher the temperature, the lower the D-peak. This is because the hydrocarbon breaks down easily and interacts better with the metal surface to form graphene.

5.2 Transparency:

Direct graphene synthesis on glass has a big advantage when used as a transparent electrode in organic photovoltaic applications. The efficiency of the electrode is based upon the electrical conductivity, thermal conductivity and optical transparency of the electrode. The sample grown with recipe [C] has an optical transparency measurement of about 60 to 70% and is considerably transparent to the naked eye.

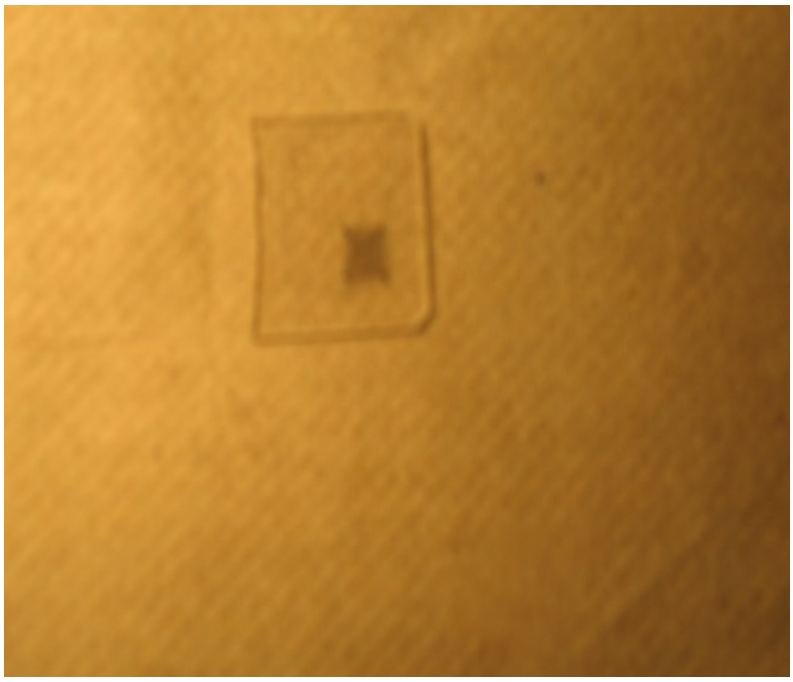


Figure 28: Picture of the sample consisting of graphene on top of glass. The dark square region is the graphene region. Four contacts can be seen at the four corners for the electrical resistivity measurements. The area surrounding the contacts had to be removed through plasma etching as per the procedure.

5.4 Improving the technique:

An important note to make is that both the transparency as well as the electrical conductivity can be made better. Quick cooling will ensure few layer graphene which can have a lower D-peak in the Raman spectra as well as more transparency due to fewer layers present. A considerably low D-peak can ensure an easy flow of carriers and good conductivity due to the reduction of discontinuities and surface resistance. So an improvement to this technique would be to focus on mastering few layer growths or using more temperature

resistant materials like ALON (Aluminum Oxynitride). It has been shown that higher temperature reduces the D-peak and hence will increase the electrical conductivity or making a quick cooling will reduce the number of graphene layers [1].

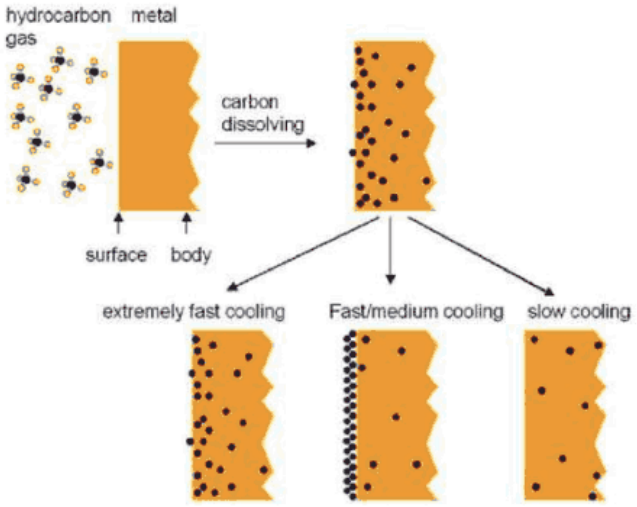


Figure 29: Adapted from [1], Different cooling rates giving different amounts of graphene layers.

This shows that there are still two solid degrees of freedom to manipulate the technique and improve the growth even if the hydrogen etching method is not possible at temperatures that are not high enough. However, if there are materials like ALON that are required for an application, then a very high temperature can be used and hydrogen etching can also be used. This would result in a very transparent, highly conductive and high quality graphene sample ready to be used as a transparent electrode. Even in such a situation, this transfer-free process will still be highly beneficial.

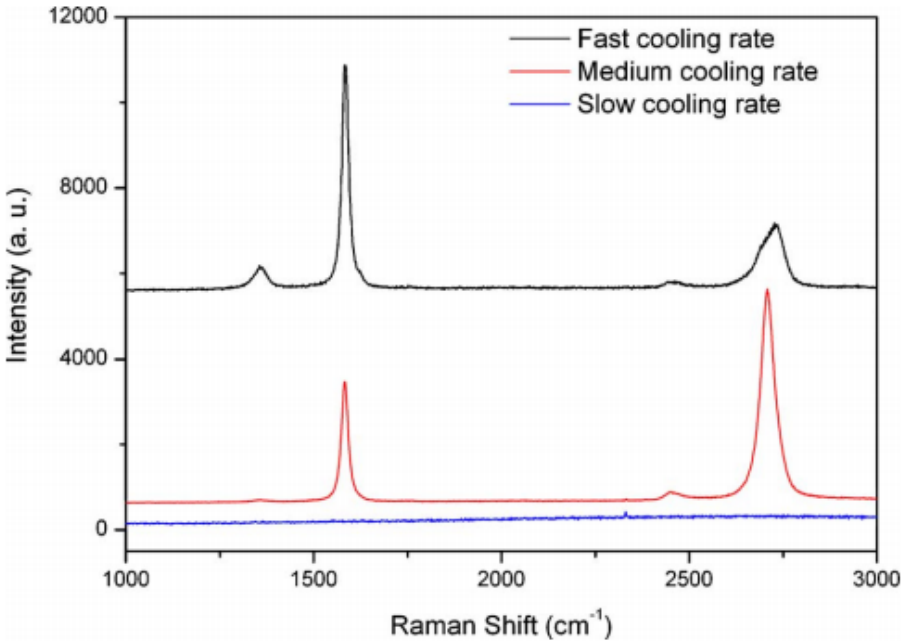


Figure 30: Adapted from [1], Raman spectra indicating that different cooling rates give different amounts of graphene layers.

Another way of improvement would be to reduce the thickness of nickel samples as some groups have shown variations in the number of layers based on the variations in the thickness of nickel. The idea is to reduce the thickness to reduce the amount of carbon interacting and hence reduce the number of layers of graphene. This can improve the transparency.

Reduction in pressure even further using expensive CVD equipment can also improve the quality of samples on glass grown at low temperatures. Therefore, the above mentioned ways of improvement show that this technique has a foreseeable future in industry for scalable production.

Another advantage of high quality graphene used as a transparent electrode would be its high thermal conductivity due to the reduction of discontinuities and surface resistance which favor phonon paths. This can increase the longevity of the device considerably. The reduction in cost due to the straightforward manufacturing process and the possibility of not requiring much of an additional cooling system in photovoltaic cells will also favor scalable production.

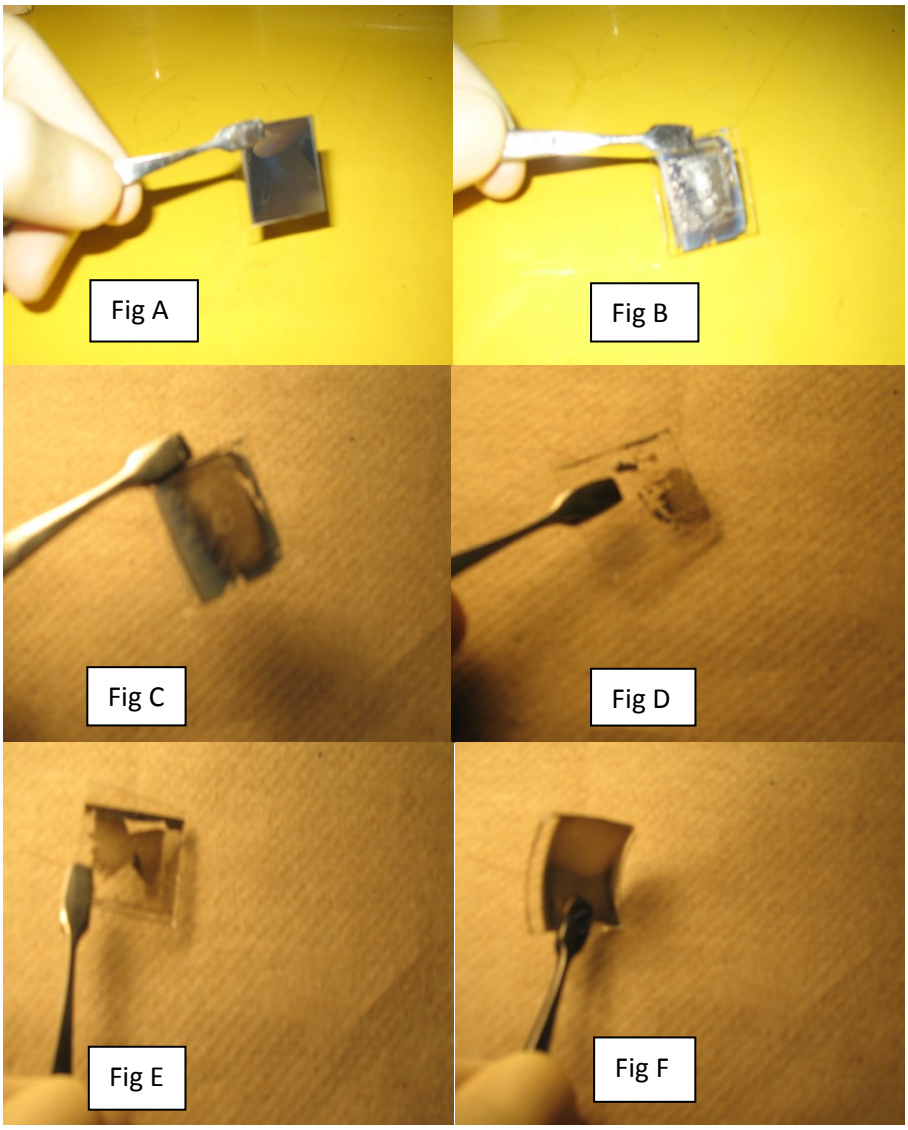


Figure 31: (Fig.A) Graphene grown on nickel before etching, (Fig.B,C,D,E) Destruction of sample due to improper coverage with PMMA during etching or due to lack of optimal drying time in the evaporation chamber, (Fig.F) The bending of the glass shows the intolerance at a temperature of 700°C.

References

[1] Yu, Q., et al. (2008), “Graphene segregated on Ni surfaces and transferred to insulators”, Applied Physics Letters **93**(11): 113103-113103.

[2] Thuvander, M. and H. O. Andrén (2000). "APFIM Studies of Grain and Phase Boundaries: A Review." Materials Characterization **44**(1–2): 87-100.

[3] Ferrari, A. C., et al. (2006). "Raman Spectrum of Graphene and Graphene Layers", Physical Review Letters **97**(18): 187401.

CONCLUSION

We have demonstrated that high quality and continuous graphene layers were able to be synthesized at low temperatures of 600℃, which permits the use of glass directly in the CVD furnace. We then showed a novel technique to etch the remaining catalyst away in a transfer free process. This process can be applied even for high temperature resistant substrates other than glass such as silicon dioxide, ALON etc... So this can be extended to device fabrication and electronics. We also showed from previous works that transparency and electrical conductivity can be improved by simply adjusting few parameters during the growth.

There are two key points that can be inferred from this project. One, the low temperature growth facilitates the use of glass directly in the furnace. Two, regardless of the substrate and temperature used, this transfer free process makes the technique suitable for scalable production in industries for use as a transparent electrode. Therefore, this work will inspire innovative designs using graphene in fields like electronics and optoelectronics.