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Growth of Graphene Film on Copper Foil using Lower Pressure Chemical Vapour Deposition

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Abstract: Graphene is a monolayer of graphite and has hexagonally arranged *sp*^{2} hybridised atoms. It has various properties such as quantum Hall effect at room temperature, the optical properties, the high electron mobility and the best electronic properties. Two different methods used to clean the copper foil. Graphene was grown using Cu catalytic substrate at low pressure (~ 0.06 Torr) and high temperature 980°C using methane and hydrogen gases. Transfer of graphene was done on Si/SiO$_2$ substrate using ammonium persulphate as a copper etchant and PMMA as a resist.

Raman Spectroscopy was used to check the nature of synthesised graphene, which help to determine whether the graphene film synthesised is multilayer, bi-layer or single layer.

Keywords: Graphene , Raman Spectroscopy, PMMA.

1. INTRODUCTION

1.1. Graphene

Carbon is the most fundamental element found on earth. Carbon atoms can be found in different allotropic forms:

1. Graphite is the most common form of carbon, which is made up of the many hexagonal sheets of *sp*^{2} hybridize carbon atoms (graphene) placed on top of each other.
2. Diamond is another form of Carbon, made up of *sp*^{3} hybridizes carbon atoms arranged in tetrahedral geometry. It is the strongest material found on earth.
3. C_{60} or Bucky ball has the same structure of hexagonal sheet of carbon atom but are in spherical shape. It is constitute of 60 carbon atoms, hence named C_{60}.
4. Carbon nanotubes are also made up of hexagonal sheet of carbon but are constructed in cylindrical form giving a tube like structure.
5. Amorphous carbon is the small flakes of carbon bonded in tetrahedral or hexagonal pattern.

Graphene is a 2 – dimensional lattice of hexagonally arranged sp^2 hybridize Carbon atoms. It has been first synthesized in 2004 by **Giem and Novoselov**,[1] since then it became the most exciting area of material science research. Due to its many extraordinary properties, it became the first choice for many electronic and optical applications. The most exciting property of graphene is its high charge carrier mobility which is due to charge carriers in graphene possess a very small effective mass and perform ballistic motion[3]. The other exceptional properties are high conductivity, high transparency and mechanical stability[2]. All these property contribute to its popularity and make it the most desirable candidate to be used in electronic and opto-electronic devices.

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1.2. Properties of Graphene

Graphene is a solitary atomic coating of graphite in which carbon atoms are prearranged into a hexagonal shape. In graphene configuration every atom has four bonds, single sigma bond with each of its three neighbours and one π bond that are oriented out of the plane. Distance between the atoms is about 1.42 Å and atomic thickness is 3.45 Å[4]. Tight binding approximation model is can be used to compute the band configuration of SLG. Because of unique properties, many researches have been going on to develop various graphene based electronic devices.

1.3. Mechanical Strength

Graphene is a hardest material with a tensile power of 130 gigapascal (GPa) as compared to steel (0.4 GPa) and Aramid (0.375 GPa).[7] A Graphene sheet has a Young's modulus or stiffness of 0.5 TPa and spring constants in the region of 1-5 N/m when AFM were conceded out on graphene. Graphene is very light in weight at 0.77 mg/m^2 as compare of 1 m^2 of paper is 1000 times heavier.[8] Graphene also contains the properties of elastic. It can retain its initial size after the strain.

1.4. Electronic Properties

Graphene is a zero band gap semiconductor, because no space between the conduction and valence bands. Both the bands are meeting at the Dirac points. Dirac points are the six corners of the brillouin zone. For low energies, energy vs. movement relation is linear at these six corners. So charge particle has zilch effective mass. These charge particles are known as the Dirac fermion, or graphinos[5]. Electronic mobility of grapheneis very high at the room temperature, with the statement values in surfeit of 15,000 cm^2 V^{-1} s^{-1}[9] and hypothetically probable limits of 200,000 cm^2 V^{-1} s^{-1}.[10] Spreading by the aural phonons of graphene fundamentally limits the room heat mobility to 200,000 cm^2 V^{-1} s^{-1}. Mobility is restricted to 40,000 cm^2 V^{-1} s^{-1} when SiO$_2$ substrate is used. Resistivity of the graphene leaf would be 10^{-6} Ω·cm. This is a smaller amount than the resistivity of silver, the least known at room temperature.

1.5. Optical Properties

Graphene has constant optical conductivity and show the absorption of 2.3% of the visible range (usually for red light). This is because of zero band gaps at the Dirac point. At the room temperature when voltage is applied to the graphene FET than band gap of graphene shifted to 0.25ev. When the magnetic field is applied than optical response of graphene nano ribbons are tunable.

2. LPCVD SYSTEM AND ITS COMPONENT

SSPL DRDO Self Madelow Pressure CVD 2Z75 system is used for graphene growth processes. Hydrogen, methane and nitrogen gases feed through digital mass flow controllers (MFCs) into a furnace. Furnace has 15 cm diameter quartz tube, which is connected to the vacuum pump by the iso-cross. A digital pressure gauge measures the pressure on both side of the furnace. Figure 1 represents low pressure chemical vapor deposition system.

The main objective of this project is to grow high quality graphene and then to transfer it on desired surface for further application. Initial experiments were done to optimize the growth parameters.The basic components of a LPCVD system are:-

2.1. Furnace

The furnace is made of a quartz tube, 125 cm in length. It is divided into two parts- Zone 1 and Zone 2. Zone 1 can reach a maximum of 850°C, while zone 2 settings can be adjusted to reach temperatures around 1000°C. Figure 2 represents the LPCVD Control Panel.

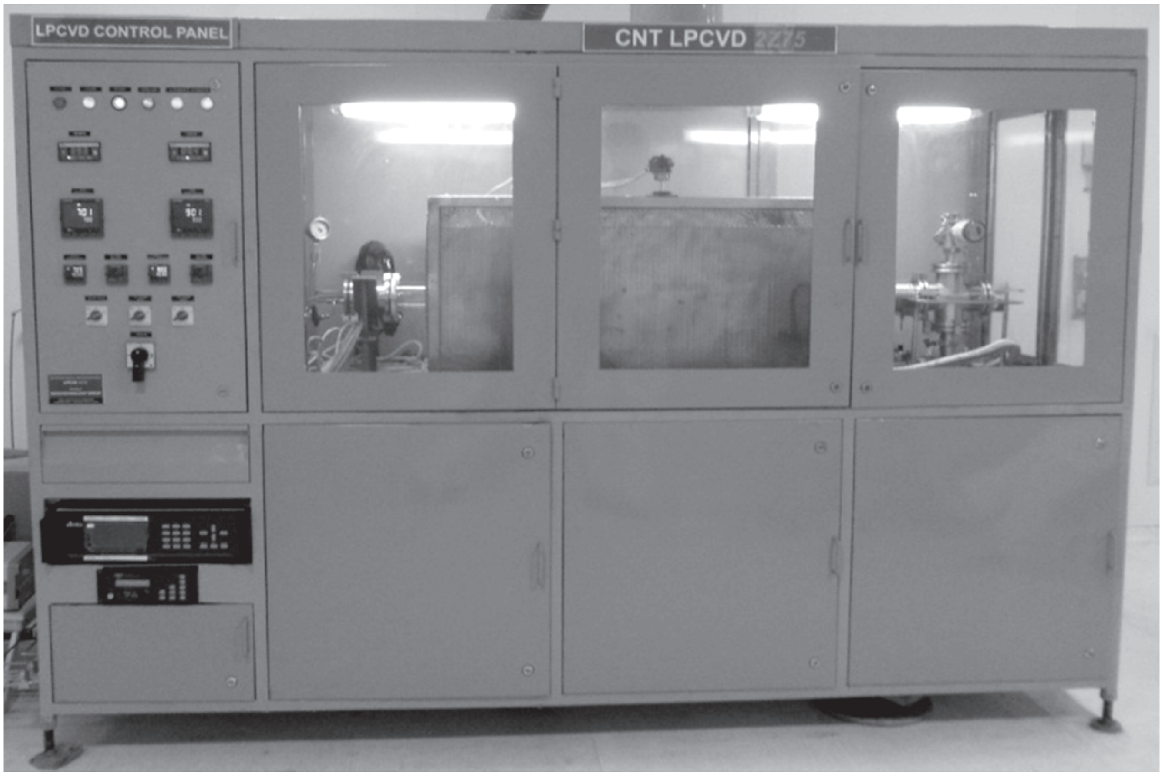

Figure 1: Low pressure chemical vapor deposition system

Figure 2: LPCVD Control Panel

2.2. Sample Holder

The sample holder was made of quartz tube with a substrate holder at one end. It was 110cm in length of which 104 cm was inserted in the Furnace and 6 cm remained outside which is connected to quartz coupling connector (QCC).

2.3. Temperature Controller

The value of the temperatures in zone 1 and 2 are set using Eurotherm 2404 module temperature controllers. Each zone has a main controller and a safety controller. The main controller fixes the temperature of the corresponding zone. The safety controller checks whether the temperature is not overshooting, if it goes beyond a certain set value it will shut down the furnace.

2.4. Gas Flow Controller

The flow of gases is manipulated by the use of Mass Flow Controllers (MFC). They convert the mass flow rate to volume flow rate and hence allow us to use amount of gases accurately. Following were the ranges of MFCs used:

2.5. Vacuum Pump

This pump sucks the gases flow through the furnace tube thus creating a very low pressure atmosphere in the CVD system. The lowest pressure attainable via the pump is 0.04 Torr. Figure 3 represents the vacuum pump.

Figure 3: Vacuum Pump

2.6. Digital Ultrasonic Cleaner

Ultrasonic is the application of mechanical sound waves to the cleaning process. This type of cleaning has proven to be the most effortless, quick and efficient method known today. Ultrasound utilizes frequencies from 18 khz (18,000 cycles per sound). High frequency electrical power is transformed into ultrasound waves by means of ultrasonic transducers. We use loba life digital sonicator. The specifications are 170w, 230v ac, 50 Hz. Itis used for cleaning the substrate.

2.7. Characterization System

Today different characterization techniques have been developed to determine the structure of the graphene films. Each technique gives a different perspective of the structure and performance of the film. Scanning electron microscopy (SEM) can pick out characteristic film defects on the micron scale. Transport measurements quantify the charge mobility of the film. Raman spectroscopy gives information about SLG, BLG or FLG by estimate the graphene layer thickness.

2.8. Optical Microscope

The optical microscope generates a micrograph when light is focused and images captured by normal light sensitive cameras. Olympus Optical Microscope Mx-61 is used for here. The eyepiece is to bring the image into focus. It looks like cylindrical form which contains two lenses. In the optical microscope when light fall on the sample than this light collect by one or more objective lenses. For higher resolution water immersion objectives is used.

Optical microscopy used to characterize exfoliated graphene samples. The exact number of layers is tricky to find out precisely by this method, but single layer differences in thickness between adjacent flakes can be resolved easily.

3. RAMAN SPECTROSCOPY

The basic principle of Raman spectroscopy is that it is based on inelastic dissemination of monochromatic light, normally by a laser source. When the monochromatic light fall on the sample than photon frequency change due to the Inelastic scattering. Sample absorbed photons of the laser light and then reemitted. As compare to the original monochromatic frequency reemitted photons frequency is changed, which is called the Raman Effect. This change provides the details about vibrational, rotational and other low frequency transitions in molecules. Here labram hr jobin yvon model 800se horiba scienticfic raman spectroscopy is used. Table 1 briefly explains the raman spectrography.

Table 1
Raman Spectroscopy

Band	*Wavenumber* (cm^{-1})
D	1350
G	1582
G'	2450
2D	2685

Raman spectrum of graphite is consisting of only two main bands and a few more very small bands. The Raman spectrum of graphene is very similar to graphite because graphite is made up of multilayer graphene. The two main bands in the graphite spectrum are known as the G-band at ~1582 cm^{-1} and the 2D band at ~2685 cm^{-1}. A third band known as the D-band at ~1350 cm^{-1} is very weak in graphite. The G-band is the most important mode in graphene and graphite. It represents the planar configuration sp^2 bonded carbon that constitutes graphene. The band is resonant, which means that it is much more intense than we would expect it to be otherwise. The band position is pretty much independent of excitation laser frequency. The G band position shifts to lower energy when the layer thickness increases. The D-band is known as the chaos band or the deficiency band. It represents a ring breathing mode from sp^2 carbon rings.Figure 4 shows the Raman Spectra of Graphite and exfoliated graphene under 514 nm excitation. The difference in the shape and position of the 2D peak is reported to identify the number of layers, though these two sources show different shapes. The 2D-band is the second order of the D-band, also referred to as an overtone of the D-band. It is the result of a two phonon lattice vibrational process, but unlike the D-band, it does not need to be activated by proximity to a defect. As a result the 2D-band is always a strong band in graphene even when no D-band is present, and it does not represent defects. This band is also used when trying to determine graphene layer thickness. 2D band exhibit strong dispersive behaviour so the position and shape of the band can be significantly different with various excitation laser frequencies. Table 2 briefly gives the data's of the ratio of I_{2D} to I_G. The graphene growth mechanism consist various process, which are cleaning, pre-annealing, growth and at last cooling.

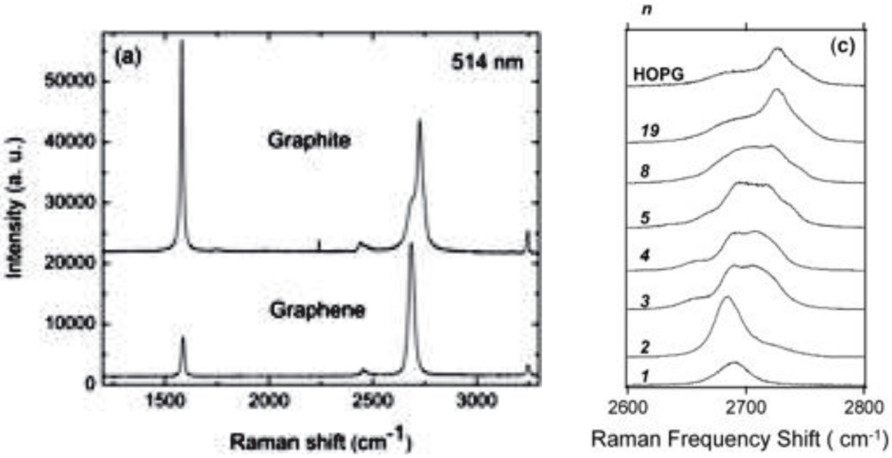

Figure 4: Raman Spectra of Graphite

Table 2
Ratio of I_{2d} to I_g

I_{2D}/I_G	*Structure of Graphene*
< 1	Few layer
Between 1 to 2	Bilayer
> 2	Single layer

3.1. Cleaning of Sample

For the synthesis of high quality of Graphene, 25 μm thick, 99.8% or 99.999% pure copper foil from Alfa Aesar is used. At the high temperature amorphous carbon is deposited on the copper foil. The reason behind this is Cu foil may contain thin layer of organic impurities; this impurities can be removed by the cleaning process.

Firstly Cu foil is pressed between two clean quartz slides to keep it as straight as possible. For cleaning, Acetone is used mainly to remove organic impurities but it also leaves its own residues due to its very fast evaporation rate so isopropyl alcohol (IPA) is used as solvent to remove left over acetone. Finally Cu foil is placed in De-ionized (DI) water to remove remaining organic solvents. After Cu foil dry with Nitrogen. Figure 5 shows the Cleaning of the Cu foil and then ultrasonicate.

Figure 5: Cleaning of the Cu foils and then ultrasonicate

3.2. Pre-Annealing of the Sample and Growth Process

Copper foil contains copper oxide layers, which is undesirable for high quality of graphene synthesis. To remove oxide layer acetic acid may be used but acetic acid leaves the surface too rough which is also not desirable. Another method for remove the oxide layer is pre-annealing of copper foil in the presence of H_2 at high temperature (700°C). Pre-annealing process has another advantage it can increase the grain size of polycrystalline copper foil.

Copper foil has much smaller grain size with large number of grain boundaries. Graphene tends to grow preferentially on grain boundaries first as compared to flat copper surface, which ultimately leads to multilayer graphene on those regions. Pre-annealing is increase the copper grain size, which reduces the effect of grain boundaries on graphene growth. Pre-annealing was performed Low Pressure CVD system in SSPL DRDO. First set the annealing temperature for both zone and flow the H_2 gas. After reaching the annealing temperature, flow rate of gases were left unchanged and annealing was performed for 2 hours. After the pre-annealing process, temperature was ramped up and furnace was allowed to heat for growth of graphene under H_2 and CH_4 ambient.

After pre-annealing process carbon containing gas flow for the synthesis of graphene. In this stage, methane is used as the carbon source or precursor while H_2 was used as carrier gas. Flow rate of precursor gas and carrier gas can change according to quality of graphene. Gases flow for the particular growth time means growth time also a important parameter. After the flowing of the gases methane is deposited onto the copper surface. Growth mechanism mentioned in previous chapter. In this project growth time vary from 30 min to 1 hr. and see the effect of growth time on the graphene synthesis.

3.3. Cooling of the Sample

After the growth process precursor gas was closed. At the precursor gas closing time furnace temperature was very high approximately 850^0C to 950^0C. For unloading the sample furnace temperature brings back to room temperature. The thermal expansion coefficients of graphene and copper are different so the cooling process shows the important role. Due to different thermal expansion coefficient Wrinkles introduce on the graphene surface which can be change the properties of the growth film. So fast cooling is required for good quality of graphene. Another reason is that, received copper foil surface is not smooth and contains step edges which represent surface irregularities. Since graphene growth on copper foil is surface catalysis process, graphene preferentially nucleates on these step edges because such irregularities on the atomic scale contain dangling bonds which present lower energy barrier for attachment to the ad-atoms that govern graphene growth. The result is that for the same growth time stepped regions contain few layer graphene compared to smooth copper surface. Though annealing of copper at higher temperatures mitigate the effect of such surface irregularities.

3.4. Transfer Process

First, polymer film was deposited on the Cu foil to serve as mechanical support for graphene film during subsequent transfer process. Poly methyl metha acrylate (PMMA) was used here as a photoresist (PR) which can coat micro meter thick films in single coat. The advantage of photoresist is that it can be easily removed in acetone.

Cu foil placed in the **DELTA 6 RC (SUSS MICROTEC)** spin coater for depositing PMMA film on the Cu foiland PMMA was poured on the foil. Spin coater spreading the PMMA for 2500 rpm for 90 sec. Then sample is bakedat 170° C temp for15 min. Than Cu foil was placed in copper etchant solution for etching the Cu surface. There are so many solution present for etching the Cu foil like ferric chloride ($FeCl_3$), ammonium persulfate ($(NH_4)_2S_2O_8$). Here we are using Ammonium per sulfate (molecular weight = 228 gram/mole) as a Cu etchant. First make 0.5 M solution of ammonium persulfate (0.5 mole* 228 gram/mole in 1000 ml). Typically for 25 μm thick foil, copper etching took approximately 3 hours. When the copper etching was complete, piece of 300nm SiO_2/Si was taken and clean with IPA and dry with N_2 gas. Graphene membrane was scooped out from ($(NH_4)_2S_2O_8$) onto SiO_2/Si and transferred to DI water bath (3 time for every 20 min to remove $(NH_4)_2S_2O_8$ residue). After DI dip transfer graphene dried with Nitrogen. During this step, care may be taken that since residual of water may be present on SiO_2/Si substrate. So substrate was then placed on hot plate preset at 170° C for 15 minutes. This step was done to evaporate thin layer of water that may be present on SiO_2/Si substrate. This process improves the adhesion of graphene to the SiO_2/Si substrate. Figure illustrates the flow chart of transfer of graphene onSiO_2/Si substrate.

After this step, to remove the PMMA film SiO_2/Si substrate with attached graphene was placed in acetone solution. Then the substrate was placed in IPA for 10 minutes, to remove left over acetone residue. Finally substrate was placed in DI rinse for 10 minutes to remove left over organics. Subsequently, the substrate was dried with Nitrogen and the sample was ready for characterization

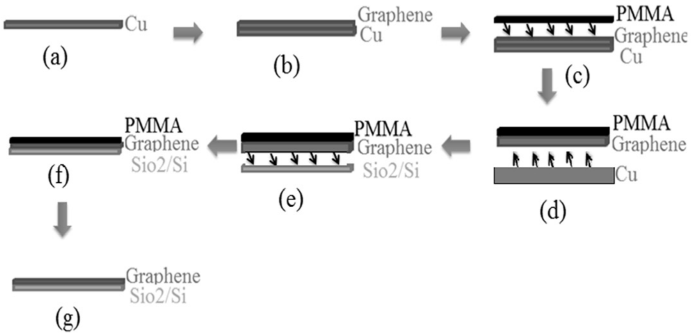

Figure 6: Flow chart of transfer of graphene onSiO_2/Si substrate

4. RESULT AND DISCUSSION

40 growths have been run and selected a few examples and discuss the results of optimization. It is found that flows of 1000 sccm hydrogen and 20 to 100 sccm methane reproducibly grow high quality graphene films on the Cu given proper purging procedures. Then transfer this graphene on the SiO_2 substrate. Transfer process show below:

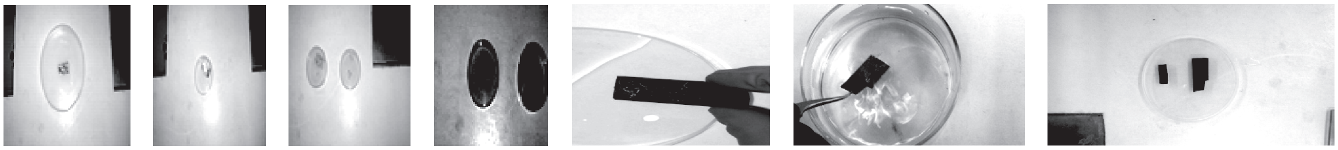

Figure 7

Figure 7 shows the transfer process. After the transfer of graphene on silicon dioxide substrate, the sample were characterized by Raman spectrometer and the spectrum of all the samples shows the presence of graphene on it as they contain a D band, G band and a 2D band. This signifies the successful transfer of graphene on the silicon dioxide substrate. Raman spectra were acquired on graphene on copper without the transfer process. All point scans were obtained with 100x microscope objective that corresponds to 0.6 μm spot sizes. Each point scan was an average of 5 spectra taken at random locations across the sample and individual spectrum was an average of 4 exposures each of duration 15seconds. Laser power for each point scan was 2.5 mW.

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