



**CHALMERS**

**Graphene grown by chemical vapor deposition on evaporated copper thin films**

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**Graphene grown by chemical vapor deposition on evaporated copper thin films**

**Thesis for the degree of Master of Science**

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**Diploma work performed at:**

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## Abstract

Graphene is a thin atomic layer of carbon atoms which has a hexagonal lattice structure. Due to its exceptional properties such as high electrical conductivity, high carrier mobility, high thermal conductivity, high optical transparency and super hydrophobicity, graphene is expected to play an important role in future nanoscience and nanotechnology. Chemical vapor deposition (CVD) is a novel technique proposed recently to synthesis large area high quality graphene, which was not possible by the conventional mechanical exfoliation method of graphite. However, though a lot of progresses have been made using Cu foil as catalyst in CVD, this thesis will focus mainly on evaporated Cu thin film grown graphene, because for industrial application it is more convenient, which is largely unexploited in literature. Cu was opt here because the solubility of C in Cu is extremely small, making it easier to achieve uniformly monolayer graphene, which is very difficult otherwise, e.g. using Ni as the catalyst. Thus, investigation of graphene's quality on top of Cu thin film by tuning the thickness of Cu also alteration of other parameters such as temperature, hydrogen concentration to optimize the graphene growth condition and finally fabricating suspended graphene devices are the goal of this project. Suspended graphene draw attention because in suspended graphene devices carriers will have relatively high mobility with less scattering which is very promising for different applications. Most importantly, suspended graphene can vibrate, whose resonance frequency is sensitive to the mass of absorbed particles, making it promising for future ultrasensitive mass sensors. In this work, after CVD synthesis, transfer of graphene onto foreign Si substrates with 300 nm SiO<sub>2</sub> was used to inspect the graphene. We stress that this complex transfer technique is not easy to be industrialized, and is only used here to estimate the quality of graphene because the graphene is otherwise invisible on Cu. In the final devices, this transfer step is unnecessary, as the graphene can be suspended simply by locally removing the Cu underneath the graphene channel, rendering a fully semiconductor industry compatible process. The graphene on SiO<sub>2</sub>/Si samples were briefly characterized by scanning electron microscopy, conductance measurements and Raman spectroscopy. It was found that using 600 nm thick Cu catalyst with annealing in nominal 750°C for 5 minutes continued by 5 minutes growth in 20 sccm H<sub>2</sub>, 30 sccm pre-diluted methane(5% in argon) and 1000 sccm argon gas flow was the optimal CVD condition. Subsequently, suspended graphene channel devices were fabricated by two step lithography, together with techniques such as wet etching, lift off and critical point drying, etc. Nevertheless, despite some devices appear very successful in microscope, they do not show the expected good enough electrical performances, even though the Raman spectroscopy indicates decent quality graphene. The reason is ascribed to the polycrystalline nature of the graphene, which means the effect from the grain boundaries need to be considered in future studies. Under the background that arrays of suspended graphene devices have never been reported using a scalable and transfer-free technique, and even the CVD using evaporated Cu thin film catalyst has not been thoroughly investigated in literature, our proof-of-principle results indicates a promising future of this research direction, at least good enough for continued improvements.

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# 1. INTRODUCTION

## 1.1 Motivation

Graphene is a thin atomic layer of carbon atoms which has a hexagonal lattice structure shown in figure 1.1 <sup>[1]</sup>. It shows very good electrical, optical and mechanical properties. Graphene is very stable at room temperature. Comparing with many other materials graphene has high current density, ballistic transport, chemical inertness, high thermal conductivity, optical transmittance and super hydrophobicity <sup>[2]</sup>. Intrinsic graphene is characterized as a semi-metal or zero-gap semiconductor and its exceptional electronic properties for an atomic monolayer, with a distressingly low absorption ratio of 2.3% of white light <sup>[3]</sup>. Electrical characterization has shown an amazingly high electron mobility at room temperature, with experimentally reported values in excess of  $200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  <sup>[3]</sup>. The corresponding resistivity of the graphene sheet would be  $10^{-6} \Omega \cdot \text{cm}$ , less than the resistivity of silver, one of the lowest resistivity substances known at room temperature <sup>[3]</sup>. Graphene is believed to play vital role in future nanoelectronics such as ballistic transistors, field emitter, components of integrated circuits, transparent conducting electrodes and sensors. The high electrical conductivity and high optical transparency promote graphene as a candidate for transparent conducting electrodes, required for applications in touch-screens, liquid crystal displays, organic photovoltaic cells and organic light-emitting diodes (OLEDs) <sup>[3]</sup>.

So far, from mechanical exfoliation of highly ordered pyrolytic graphite (HOPG), graphene with best electronic properties has been synthesized but with lateral dimensions are at most tens of micrometers limiting the fabrication of consistent, wafer scale graphene structures <sup>[4]</sup>. Other fabrication methods are also developed recently.

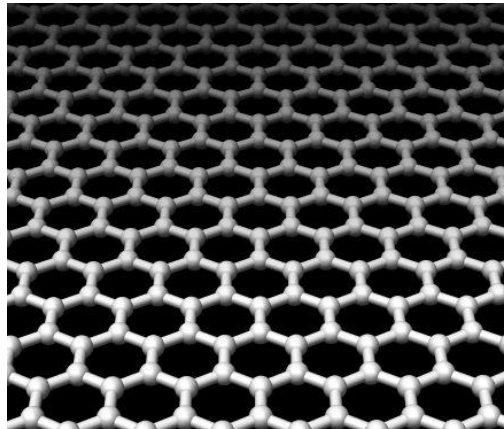


Figure 1.1. Graphene, honeycomb-like lattice structure <sup>[1]</sup>.

For example, Konstantin et al. produced graphene from high temperature annealing of single crystal SiC <sup>[5]</sup> and Alfonso et al. from chemical vapor deposition (CVD) on metal substrates, all were the techniques employed for demonstrating relatively good quality graphene transistors <sup>[6]</sup>. High temperature decomposition of SiC is a process where Si is evaporated leaving behind free carbon atoms that subsequently form graphene layers at the surface. However, this technique is expensive and is not appropriate for graphene transfer onto other

substrates <sup>[7]</sup>. Comparing with other techniques CVD is one of the most promising, inexpensive and readily accessible way for fabricating high quality and large area graphene onto alteration metal substrates such as Cu or Ni. Carbon dissolves in Ni at high temperature and then precipitates forming graphene before and during the cool down. The method is sensitive to process timing that is not optimal for getting a monolayer of graphene in every sample. More controllable graphene has been grown on Cu foils in CVD. Graphene on copper is in principle straightforward, involving the decomposition of methane gas over a copper substrate typically held at 1000 °C <sup>[8]</sup>. The mechanism is based on surface chemistry because of the low solubility of C in Cu and therefore the growth is self-limited to a single layer of graphene. The combination of very low carbon solubility in Cu, common to noble metals that have closed d shells and strong free-electron-like surface states, along with its catalytic activity towards hydrocarbon gases render Cu as a unique catalyst. Recently, 30-inch graphene films for making transparent electrodes have been realized by CVD <sup>[9]</sup>. However, the main challenge is not only to grow high quality large area graphene layer but also a reliable and scalable transfer onto other substrates. We want to get rid of transfer finally because transfer process is very complicated and it is not a reproducible process. Transferred graphene has cracks, wrinkles also the quality of graphene varies from sample to sample.

One method to get rid of the complicated graphene transfer process is the direct deposition of graphene onto insulating substrates. However, the graphene is typically of low quality. Here in this report, we chose to use Cu thin film for graphene deposition because we want to get rid of transfer process eventually by locally removing the copper to have suspended graphene devices. Furthermore, the substrate is flat and rigid compared with Cu foils, which is compatible with existing planar Si technology.

We hope that suspended graphene will have better quality and higher electron mobility because graphene will be suspended so electrons will have higher mean free path to travel with less scattering. Graphene will not be transferred but copper will be etched locally, it will be discussed more in the suspended graphene section. Suspended graphene could be used as a mass sensor as well because graphene which is one atom layer thick has very small mass and it will be very sensitive in sensing molecules <sup>[10]</sup>. Comparing to other materials of the same scale, graphene is more mechanically stable, strong and flexible <sup>[10]</sup>. One experiment was done by graphene resonator manufactured and mechanical exfoliation technique was used and it was found that graphene has mass sensitivity of 2zg with a detection bandwidth of 3 Hz which is very promising and even better than the result achieved for carbon nanotubes at room temperature <sup>[10]</sup>. It is believed that the sensors made from graphene will be extremely sensitive than any other sensors. In our case, graphene which is floating will be very sensitive to the molecules. It is expected to have high electron mobility and will have more sensitive response to the gate. Moreover, suspended graphene will be reproducible and the quality could be kept same for all the samples.

Very few researchers are trying to grow large area graphene on Cu thin films due to process difficulties. The main reason behind the difficulty is Cu thin films have small domains which are quite similar to size of the domains of graphene which leads to the poor electrical and

mechanical properties <sup>[11]</sup>. Another difficulty is due to the difference in thermal expansion between substrate and Cu which causes strain eventually leading to damage of Cu films such as holes, delaminating, melting, etc. Here, we are trying to improve the quality of graphene layer grown on Cu thin films by CVD growth process making it defects/cracks/wrinkles free so that it can be used for electronic device applications. All the parameters on the growth process have to be studied properly. By optimizing the process parameters, within the limited project time period, we will try to develop a scalable technique to fabricate arrays of suspended graphene devices.

## **1.2 Factors Affecting Quality of Graphene in CVD**

In polycrystalline materials, properties are often dominated by the size of grains and also by the atomic structure of the grain boundaries <sup>[12]</sup>. These effects are more obvious in two dimensional material graphene. Recent work has shown that CVD graphene membranes are composed of multiple grains stitched together by lines of atomic defects <sup>[12]</sup>. It was experimentally found that these grain boundaries severely weaken the mechanical strength of graphene membranes but do not as drastically alter their electrical properties <sup>[12]</sup>. Additionally, during growth and transfer processes, strains induced causing out-of-plane rippling in free standing membranes. Increase in graphene domain size decreases density of such grain boundary defects. Graphene films with large domains have higher mobility than those with small domains predominantly due to a decrease in defects <sup>[13]</sup>.

The thickness of Cu films also plays major role in forming good quality graphene. Very thick film causes thermal straining problem during CVD process and hence deteriorate the quality of graphene. Very thin films have lots of defects such as holes, wrinkles generated during CVD process which ultimately propagate to the graphene. Hence, there is certain window of thickness from 500 nm – 800 nm between which we can get better quality graphene provided that it is tuned to other parameters.

High temperature and low methane flow rate and partial pressure are preferred to generate a low density of graphene nuclei leading to high carrier mobility. On the other hand, high methane flow rate or partial pressure is preferred for a better continuity in graphene films. Another important point which needs to take into account is that graphene are produced in our cold-wall low-pressure CVD where the temperature of substrate differs significantly from the susceptor temperature. It is known that, during processing, the wafer temperature varies widely with pressure and gas composition, and is also dependent on susceptor and/or wafer coatings. The temperature difference between susceptor and wafer in the cold-wall LPCVD is minimal for a) high emissivity of susceptor and wafer back side; b) low emissivity of wafer front side; c) high total pressure; and d) low emissivity of the reactor wall.

This paper is divided in to three parts which are transferred graphene, suspended graphene and bubbling transfer of graphene. The main goal was suspended graphene without transfer but in order to do that it was very important to improve the quality of graphene. Traditional transferred methods were used to investigate graphene quality.

## 2. EXPERIMENTAL METHODS

### 2.1 Resistive Thermal Evaporation

Resistive thermal evaporation is a deposition technique. Electrical energy is used to create the sufficient temperature to heat a crucible up to the point where deposition material starts to evaporate. High level of vacuum environment is necessary to perform this process. Materials with any specified thickness can be deposited.

### 2.2 Electron Beam Evaporation

In electron beam evaporation desired material is heated by a high-intensity beam of electron. Focused electron beam melts the region of the deposited material until it starts to evaporate. Deposited material starts to evaporate and then it covers the sample. Kinetic energy of the electrons is transformed as heat while they hit the target material.

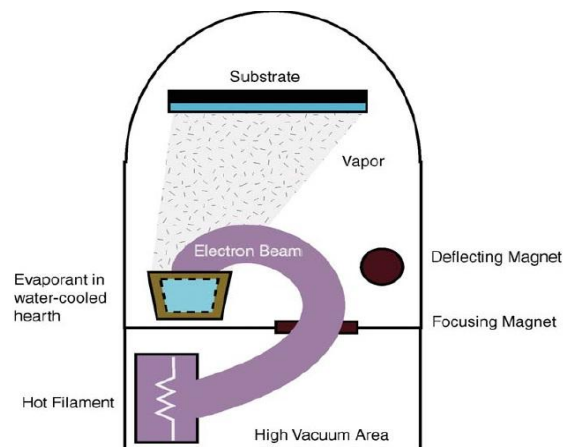


Figure 2.1. Hot filament emits electron. Focusing magnet bent the electron flow towards the sample. Sample starts to evaporate and condense on the surface of the substrate <sup>[14]</sup>.

### 2.3 Scanning Electron Microscopy

In SEM a focused high energy electrons are used to form an image. Image is attained by detecting the backscattered or secondary electrons from the surface of the sample.

Essential components of all SEM include Electron Gun, Electron Lenses, Sample stage, detectors for all signals of interest, display.

### 2.4 Raman Spectroscopy

In order to characterize samples or a system widely Raman spectroscopy technique is used. By using Raman spectroscopy it is possible to investigate vibrational, rotational and other low-frequency modes of a system or sample. The sample will be exposed under laser light and

light will interact with molecular vibrations, phonons or additional excitations in the system [15].

## 2.5 Photolithography and Lift off Process

Photolithography is a process by which desired samples get shaped or patterned. Samples need to be spin coated and baked before exposing to UV light either by positive resists or negative resists shown in figure 2.2. The main difference between these two resist is exposed area gets soluble in UV light whereas unexposed area gets soluble for using negative resist.

Here, photolithography is done first to get desired pattern before depositing metal layers. Then, metal layer is deposited by evaporation. After that, the photoresist is removed along with unwanted metal layers which are at the top of it using acetone shown in figure 2.2. In our experiment we cannot use ultrasonic agitation because of very fragile structure of graphene membrane.

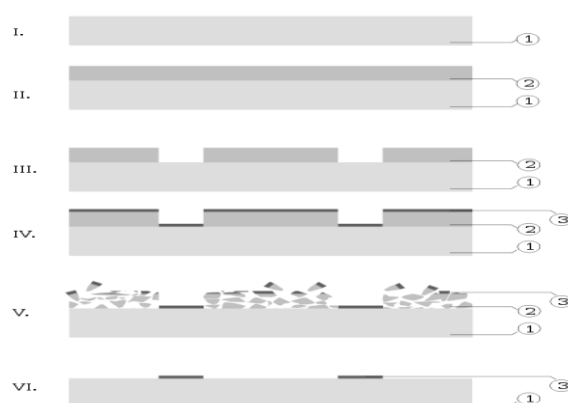


Figure 2.2. Lift off process steps (I. Substrate preparation, II. Sacrificial layer deposition, III. Patterning the sacrificial layer, IV. Target material is deposited, V. Washing both the sacrificial layer and target material, VI. Final patterned layers. (1. Substrate, 2.Sacrificial layer, 3.Target matter) [16].

## 2.6 CVD Process

Chemical vapor deposition involves chemical reaction. In this process molecules are heated and transformed to a gas form which is called precursor. A substrate is placed into the chamber to be coated. These gas molecules react while they come closer to the heated substrate and decompose into a solid material in the form of thin film or powder on the surface of the substrate. Volatile by-products can also be produced but they are removed by gas flow through the reaction chamber. CVD coating are typically fine grained and highly pure.

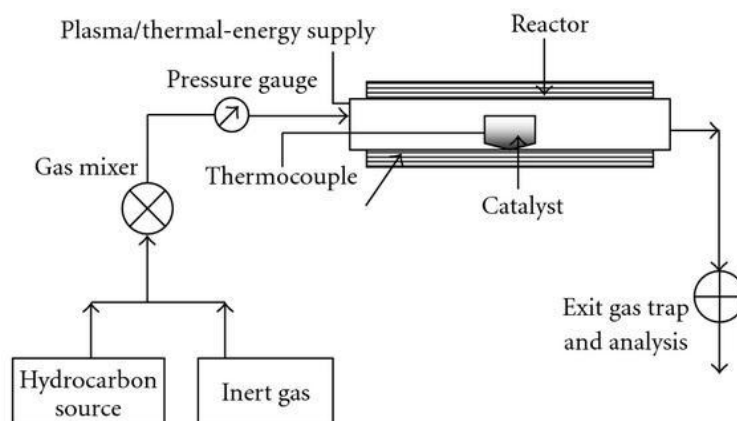


Figure 2.3. Schematic diagram of CVD process<sup>[17]</sup>.

There are two different kinds of CVD reactors like as hot wall and cold wall reactors. In hot wall reactor the temperature is relatively uniform everywhere. Reactor walls never get heated in cold wall system but in hot wall system reactor walls are also get heated and some materials are deposited on the wall. However, cold wall system is cleaner because less product deposits on the wall. In this experiment graphene was grown by CVD on Cu thin film mostly by cold wall system. Total process was involved into two steps, which are both catalyzed by Cu.

1. Decomposition of  $\text{CH}_4$
2. Graphitization.

## 2.7 Decomposition of $\text{CH}_4$

Methane was decomposed and the temperature was around  $1000^\circ\text{C}$ . Decomposition of hydrocarbon is a slow process but with the help of Cu it was done within few minutes. Copper helped to accelerate the reaction. In the chemical reaction  $\text{CH}_4 = \text{C} + 2\text{H}_2$ , carbon atoms are generated and when it hits Cu substrate it formed hexagonal shape which is graphene.

## 2.8 Graphitization

Copper can accelerate the graphitization but only allows the carbon atoms to have monolayer on the top of it. Carbon solubility in copper is very small. As a result when carbon atoms hit the copper surface they formed hexagonal shape which is graphene and when the surface area of copper is completely covered, reaction stops. In this experiment it was also encountered that the domain size of graphene roughly follows copper domain size. Despite these basic arguments above, however, it should be pointed out that in reality multilayer graphene flakes can still be detected occasionally due to the complicated kinetic procedures in the CVD growth.

## 2.9 Characterization

During investigations of the samples produced in this work, scanning electron microscopy (SEM) was used to study the surface morphology of the samples. In this experiment SEM characterization technique was used because it is a quick and convenient technique.

## 3. CVD OF GRAPHENE

### 3.1 Transfer Method

The transfer of the graphene to another substrate was done in several steps, see figure 3.1-3.4.

#### Step 1

Copolymer MMA/MAA or polymer PMMA was spin coated on top of graphene to mechanically support the graphene after the Cu is etched away.

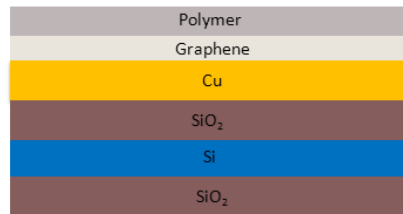


Figure 3.1. Polymer coating.

#### Step 2

Edges were scratched carefully to allow etchant to interact with the Cu and hence etch it away. Diluted HCl /HCl +HF in water with 3 drops of H<sub>2</sub>O<sub>2</sub> were added later to accelerate the reaction, this total volume was used as etchant.

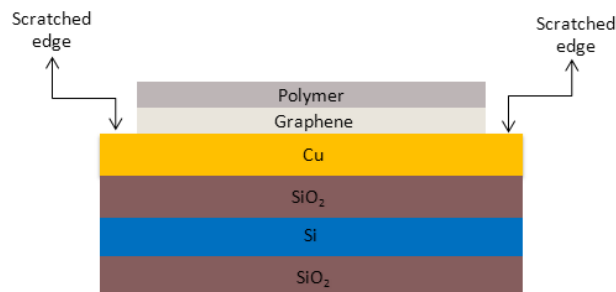


Figure 3.2. Scratched edges.

### Step 3:

The sample was kept in the etchant for a night /3 hours until Cu is etched away. An adhesive tape was also attached to the polymer beforehand because when Cu will be etched graphene will be floating.

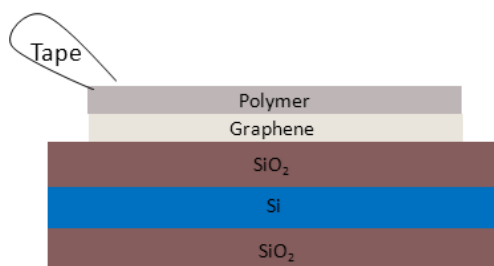


Figure 3.3. Cu is etched and an adhesive tape is attached.

### Step 4

Once the Cu is completely removed, graphene was transferred resist by aligning a substrate beneath them and then the water was removed slowly. The substrate used is oxidized silicon with 300 nm of oxide; thickness is chosen to give optimum optical contrast.

Graphene with polymer was placed carefully on the top of another substrate. Acetone, IPA (isopropyl alcohol) were use sequentially to remove polymer layer and blow dry in N<sub>2</sub>.

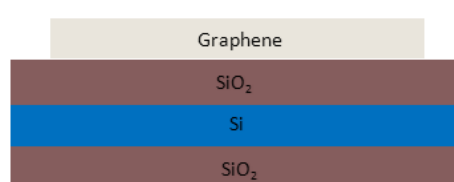


Figure 3.4. Transferred graphene.

### 3.2 Role of Hydrogen on CVD Graphene

Hydrogen gas plays double role during the graphene growth. Without additional co-catalyst  $H_2$  it is not easy to have any graphene growth. On the other hand if too much  $H_2$  is used then the quality of graphene becomes poor because

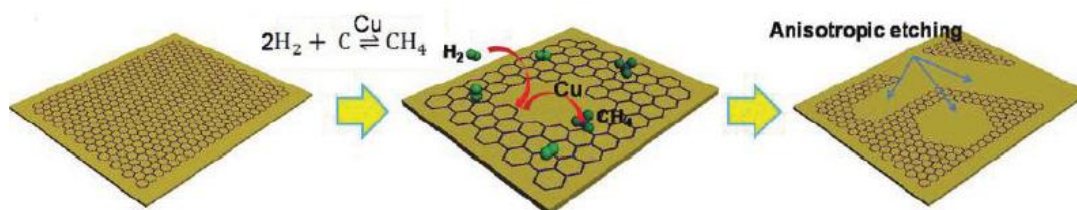


Figure 3.5. Schematic diagram of Cu etching mechanism <sup>[18]</sup>.

$H_2$  etches away the weaker carbon bond from graphene and produces methane and limits the graphene growth. In figure 3.5 we can see  $H_2$  reacts with carbon with help of the catalyst Cu and produces methane. Without the presence of Cu catalyst no graphene etching has been observed <sup>[18]</sup>. This etching is highly temperature dependent <sup>[18]</sup>. It means extra amount of  $H_2$  flow is bad for graphene growth. However, without additional co-catalyst  $H_2$  it is very difficult to have any graphene growth which indicates that we need appropriate amount of  $H_2$  to have good quality of graphene.

Summarily, during CVD graphene growth  $H_2$  acts both as a reactant and product. Increasing  $H_2$  will drive the reaction backwards. But also one important thing is  $H_2$  is a co-catalyst so we need some  $H_2$  to get the reaction to start. Therefore there will be an optimal amount of  $H_2$  where we can maximize the graphene outcome.

### 3.3 Result and Discussions for Transferred Graphene

One of the main goals of this project was making graphene suspended in order to do that better quality of graphene was very important. To improve the quality of graphene and to optimize the growth condition old transferred method was used. We have tried different growth condition such as with  $H_2$  and without  $H_2$  during the growth to optimize the growth.

The best growth method or recipe with  $H_2$  during the growth for which better quality of graphene with less cracks and wrinkles has been achieved will be discussed now. Best quality of graphene achieved without  $H_2$  will be discussed in section 3.5. The graphene was grown by low pressure CVD Black Magic system. Cu thin films were deposited on 400 nm oxidized Si by evaporation. The choice of Cu's thickness is very critical; if the films are too thin (e.g. 100 nm), Cu can be partially evaporated and hence leaves somewhat holey structure <sup>[19]</sup>. In contrary, if the films are too thick (e.g. 1000 nm) large strain can be accumulated on the structure due to different thermal expansion of films with the substrate that may lead to cracks and/or film delamination. Different thickness of Cu thin film was tested also with Ni but the best quality of graphene achieved for 600 nm Cu thin film.

### 3.4 Graphene Growth with H<sub>2</sub>

Generally, the procedure followed the work prior to this project done by Sun, et al <sup>[7]</sup>. The graphene was grown by low pressure CVD Black Magic System. Cu thin films were deposited on SiO<sub>2</sub>/Si substrate by evaporation. For relatively thin films (<500 nm) thermal evaporation system was used, while for thicker films (>500 nm) e-beam evaporation was preferred due to higher deposition rate.

Firstly, samples were soaked in acetic acid, acetone, and isopropanol, respectively, to clean possible contaminations and native oxides. During the CVD for the graphene growth, the sample was put on top of the heater [see figure 3.6]. Selecting the right temperature was difficult because we used cold wall CVD and the temperature measured by thermocouple was not the real temperature. Copper reflects heat back to the substrate and therefore the real temperature of the sample was much higher than desired. Also, if thermocouple is placed on top of the sample it is not reproducible to measure the real temperature either because each time the sample has different contact (hence temperature) to the underlying heater due to different force applied by the thermocouple to the sample. Furthermore, it was noticed Cu is melting around the nominal temperature 800°C in this cold wall system but when same samples were being tested in a separate hot wall system it was possible to reach 1000°C without having any damages. So it was verified that the temperature measuring by the thermocouple is a nominal temperature and we varied temperature manually by observing the samples condition i.e. Cu grain size. However, one of the best recipe to grow graphene was the one done in the last trial, they are: 600 nm Cu annealed in nominal temperature 750°C for five minutes continued by 10 minutes growth in 20 sccm H<sub>2</sub>, 500 sccm pre-diluted methane (5% in argon), and 1000 sccm argon.

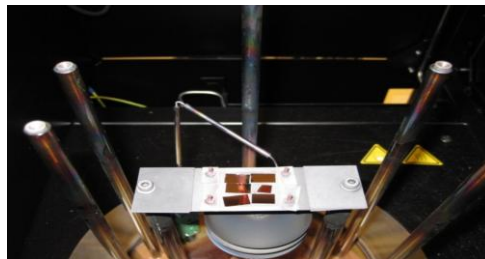


Figure 3.6. Substrate inside CVD chamber.

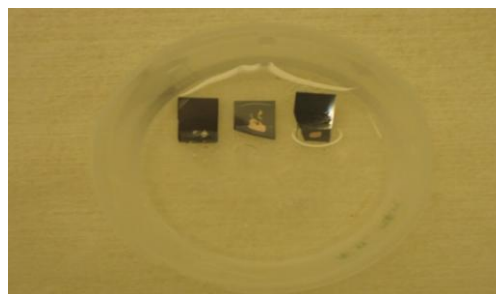


Figure 3.7. Graphene on substrate during transfer.

The transfer of the graphene to the other substrate was done by wet chemical etching. Polymer PMMA was spin coated on the substrate to mechanically support the graphene after the Cu was etched away shown in figure 3.1. Spin coating was done at 2000 rpm for one minute. Post-baking of 160°C for five minutes was also required to increase the adhesion of the polymer and removing the remaining solvent in the copolymer. After that, edges of the substrate were carefully scratched to allow etchant to interact with the Cu, and hence etched it away. Etchant used was diluted HF and HCl (HF:HCl:H<sub>2</sub>O=1:1:6). Three drops H<sub>2</sub>O<sub>2</sub> were also added.

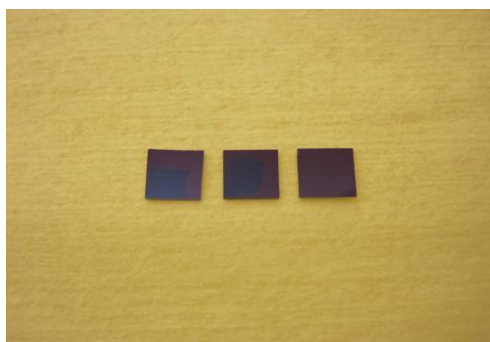


Figure 3.8. Graphene on substrate after transfer.

Once the Cu is completely removed the graphene was transferred to silicon substrates with 300 nm of oxide; thickness was chosen to give optimum optical contrast<sup>[20]</sup>. Surface tension occurred during removal of water promoted the adhesion of graphene-resist layer to the substrate or standard transmission electron microscopy (TEM) Cu grid with amorphous carbon network. TEM grids without holey carbon has poor adhesion to the graphene and often results in transfer failure. Both then were dried at room temperature. Post-bake at 160°C for five minutes was done to completely dry the substrates. Removal of resist was finally done by soaking the substrates in acetone. Post annealing at 450°C for 10 minutes in H<sub>2</sub> and argon atmosphere was also necessary to completely remove polymer.

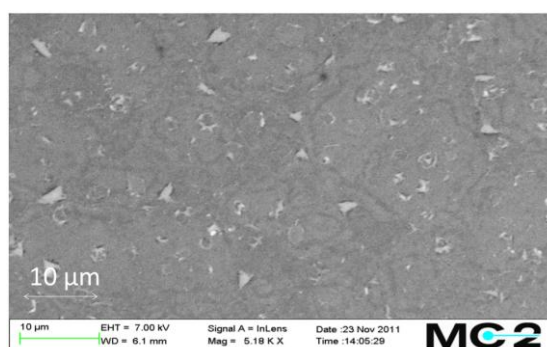


Figure 3.9. Graphene transferred to SiO<sub>2</sub>/Si, etching solution as HF and then HCl later, PMMA as resist used and dissolved with acetone.

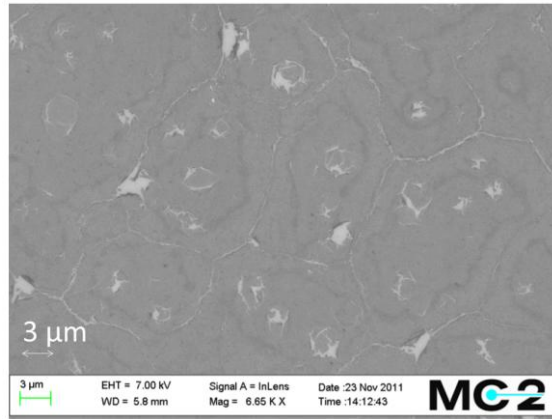


Figure 3.10. Graphene transferred to  $\text{SiO}_2/\text{Si}$ , etching solution as HF and then HCl later, PMMA as resist.

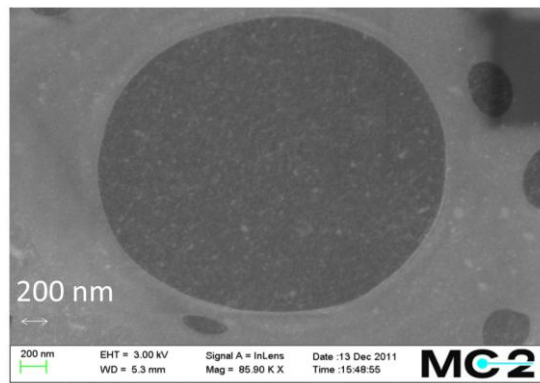


Figure 3.11. Graphene transferred on Cu TEM grid, covering a relatively large hole in amorphous carbon network.

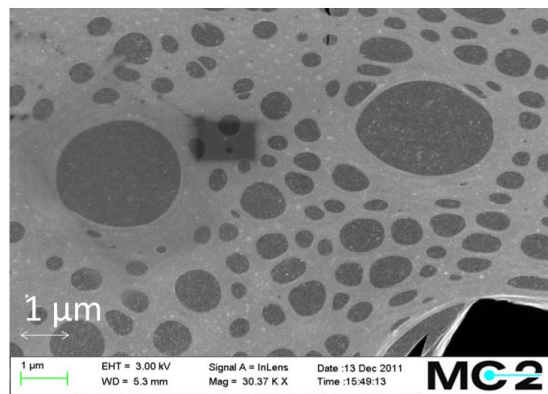


Figure 3.12. Graphene transferred on Cu TEM grid.

Figure 3.9, 3.10, 3.11 and 3.12 show the graphene grown using this recipe. It exhibits good quality of graphene covering relatively large area. It can be suspended in the TEM grid without cracks. By a quick measurement using multimeter, the resistance was found to be around  $30 \text{ k}\Omega$  which also proves the quality of graphene is relatively good.

After some more trials we optimized the grow condition even better. It was found 600 nm thick Cu with annealing in 750°C for 5 minutes continued by 5 minutes growth 20 sccm H<sub>2</sub>, 30 sccm pre-diluted methane in argon and 1000 sccm argon. Here the main difference from the previous recipe is the pre-diluted CH<sub>4</sub> flow is reduced from 500 sccm to 30 sccm. We tried lower concentration of CH<sub>4</sub> (20 sccm H<sub>2</sub>, 1000 sccm Ar and 30 sccm 5% CH<sub>4</sub> in Ar) in order to improve the quality of graphene. The reason behind such idea was lower concentration slows the growth along with low nucleation density which improves the quality along with larger domain size. Indeed high concentration increases the nucleation density which lead more domains in fact we want less domains. For graphene transfer, again, we use PMMA as resists and HF and HCl as the etchant and acetone treatment can optimize the transfer condition along with the post annealing at 450°C for 10 minutes in H<sub>2</sub> and argon atmosphere. Characterization was done by Raman spectroscopy for the sample produced under this condition. Figure 3.13 shows negligible D peak which indicates less defects and from 2D peak (Full width at half maximum (FWHM) is  $\sim 33\text{cm}^{-1}$ , see figure 3.14) it is clear that we have monolayer of graphene.

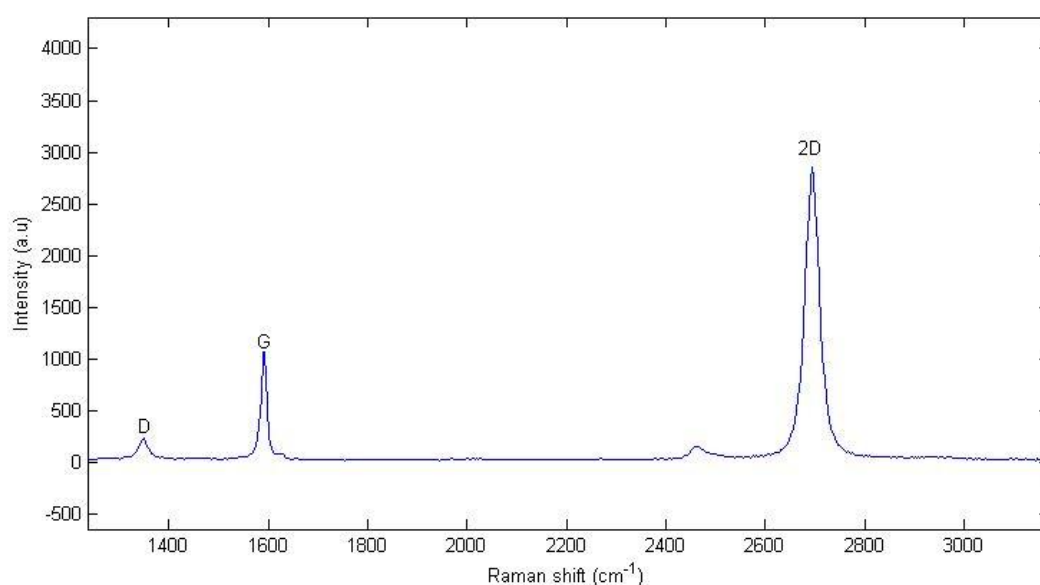


Figure 3.13. Raman spectroscopy with 514 nm laser. Transferred graphene on 300 nm SiO<sub>2</sub>/Si substrate.

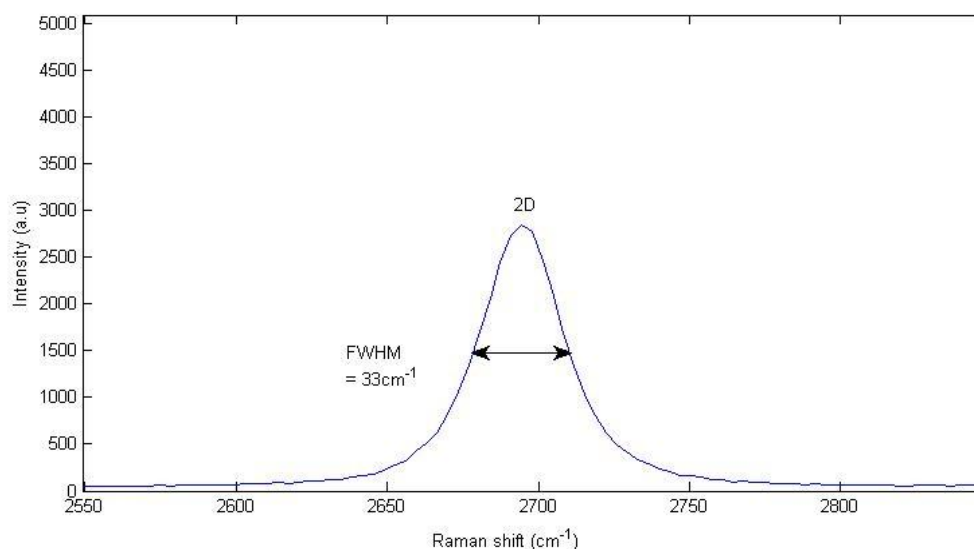


Figure 3.14. Raman spectroscopy with 514 nm laser. FWHM of 2D peak.

### 3.5 Graphene Growth without H<sub>2</sub>

Li Tao et al. recently argued that during the graphene synthesis on evaporated Cu thin film, H<sub>2</sub> flow should be removed during the growth, because the dominant (111) crystallites in the Cu thin film is known to absorb enough H<sub>2</sub> during the annealing process prior to the actual graphene deposition <sup>[21]</sup>. With this method, they claimed that the graphene quality can be greatly improved. Using this idea we went for another graphene growth without H<sub>2</sub> both for high (0 sccm H<sub>2</sub>, 1000 sccm Ar and 500 sccm 5% CH<sub>4</sub> in Ar) and low (0 sccm H<sub>2</sub>, 1000 sccm Ar and 30 sccm 5% CH<sub>4</sub> in Ar) methane flow during the growth and followed the same procedure described in section 3.1 and 3.4. We have investigated our sample by Raman spectroscopy. However, we found that this idea did not work in our case. From figure 3.15 we have noticed the absence of high quality graphene. High D peak indicates a lot of defects and 2D peak is very small which means we have low quality graphitic material instead of having high quality graphene.

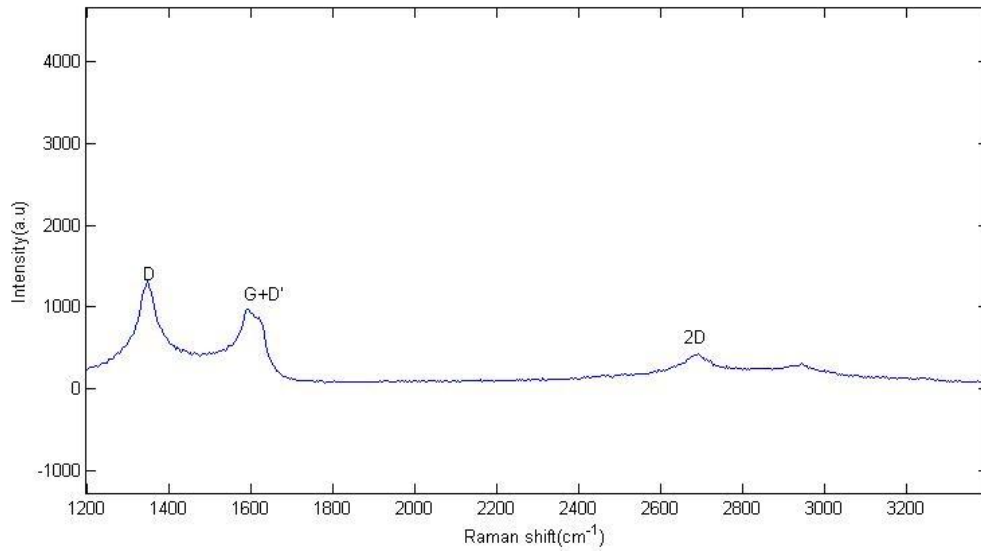


Figure 3.15. Raman spectroscopy with 514 nm laser. Transferred graphene on 300 nm SiO<sub>2</sub>/Si substrate. No H<sub>2</sub> during the growth but high (500 sccm) methane flow.

Low flow (30 sccm) of methane also gave bad result, although slightly better than the high flow case as evidenced by the somewhat enhanced 2D peak. Figure 3.16 shows Raman spectroscopy of graphene on 300 nm SiO<sub>2</sub>/Si substrate. High D peak indicates a lot of defects. Based on these experiments, it is clearly visible the quality of graphene did not improve as suggested by Li Tao et al.<sup>[21]</sup> maybe because we used different setup.

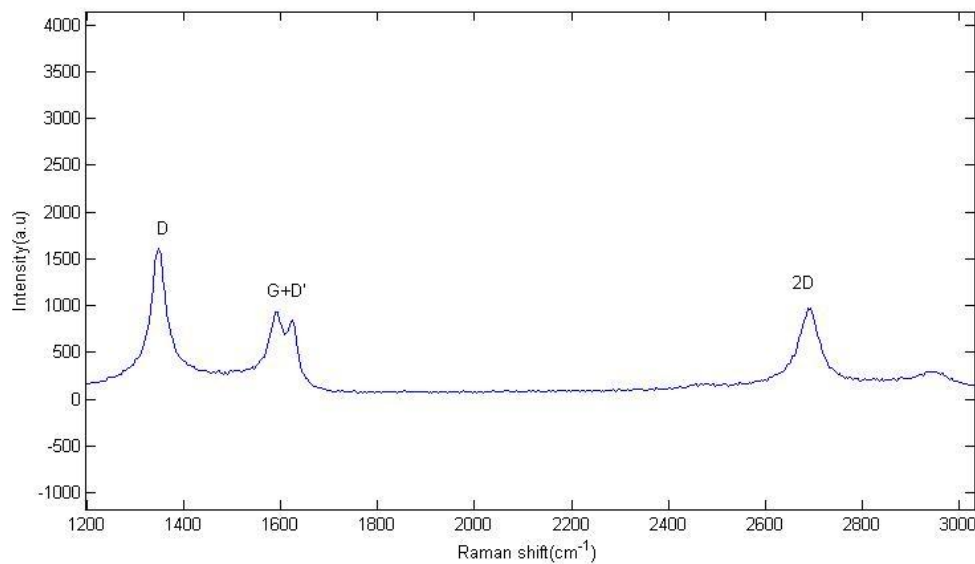


Figure 3.16. Raman spectroscopy with 514 nm laser. Transferred graphene on 300 nm SiO<sub>2</sub>/Si substrate. No H<sub>2</sub> during the growth but low (30 sccm) methane flow.

## 4. SUSPENDED GRAPHENE DEVICE FABRICATION

### Step 1

Using evaporation technique, 600 nm Cu was deposited on 400 nm SiO<sub>2</sub>/Si substrate.



Figure 4.1. 600 nm Cu layers on the top of SiO<sub>2</sub>/Si substrate.

### Step 2

CVD Graphene on the top of Cu substrate.



Figure 4.2. Graphene growth using CVD.

### Step 3

After the lithography and patterning the resist gold was deposited by evaporation.

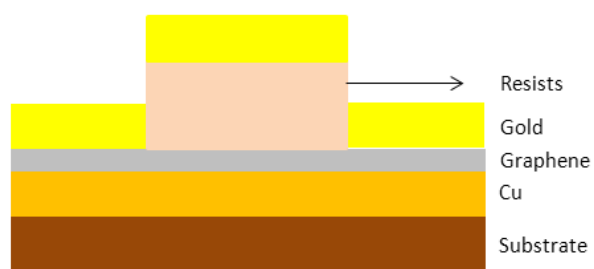


Figure 4.3. 100 nm Au layer on top of Graphene.

#### Step 4

Hot acetone was used to lift off gold layer.



Figure 4.4. Gold layer lift off using acetone.

#### Step 5

Patterning graphene using oxygen plasma and Cu etching using  $\text{FeCl}_3$ .



Figure 4.5. Suspended graphene.

### 4.1 Suspended Graphene

Substrate used for suspended graphene growth was 400 nm oxidized  $\text{SiO}_2/\text{Si}$  and 600 nm Cu was deposited on the top of it by evaporation. Then sequentially samples were soaked in acetic acid, acetone and isopropanol respectively, to clean possible contaminations and native oxides. Cold wall CVD process was used to grow graphene. But before the growth we did annealing in  $750^\circ\text{C}$  for 5 minutes with 20 sccm  $\text{H}_2$  flow. During the growth we used (20 sccm  $\text{H}_2$ , 1000 sccm Ar and 30 sccm 5%  $\text{CH}_4$  in Ar). After the growth samples were spin coated with negative resist ma-N1410 and baked at  $100^\circ\text{C}$  for 1 minute. Mask aligner was used to provide a pattern. Samples were being exposed in UV-lithography after that 100 nm gold was deposited by evaporation. We used bigger mask aligner in first UV-lithography shown in figure 4.6. In figure 4.6 dark portion means there is no gold remained after the exposure. The name of the resists, developer, developing time and exposure time listed in table 1.

|                    | First attempt | Second attempt |
|--------------------|---------------|----------------|
| Name of the Resist | ma-N1410      | S 1813         |
| Spin-rate[rpm]     | 3000          | 8000           |
| Developer          | ma-D 533s     | MF-319         |
| Developing time[s] | 50            | 40             |
| Exposer time[s]    | 5             | 4              |

Table 1. Listed parameters used for UV-lithography and to pattern resist for gold lift-off process.

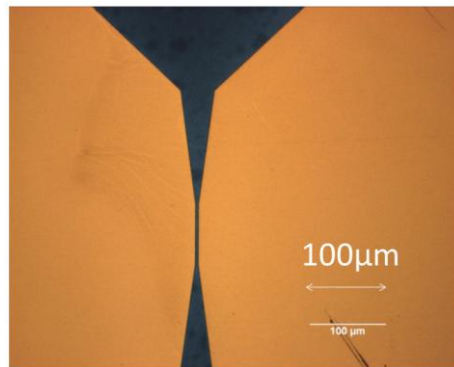


Figure 4.6. The mask was used in our first lift off process. The dark portion will have no gold after liftoff process.

Samples were heated in acetone to 50°C carefully so that graphene layer will not be damaged during lift off gold layer. We went for second UV-lithography with a different contact mask aligner shown in figure 4.7.

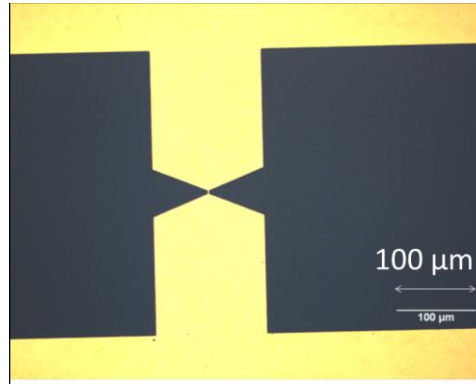


Figure 4.7. This mask was used during second UV-lithography along with the positive resist. Cr is clearly visible and after liftoff process the dark portion will have gold because we used positive resist.

We used positive resist S 1813, 8000 rpm and 1 minute for spin coating and exposed it for 4 s. After exposing developer MF-319 for 40 s was used then samples were blow dried. In order to remove the redundant graphene, samples were etched by oxygen plasma with 50W for 20s. To protect graphene from oxygen plasma etching another different mask was used shown in figure 4.8.

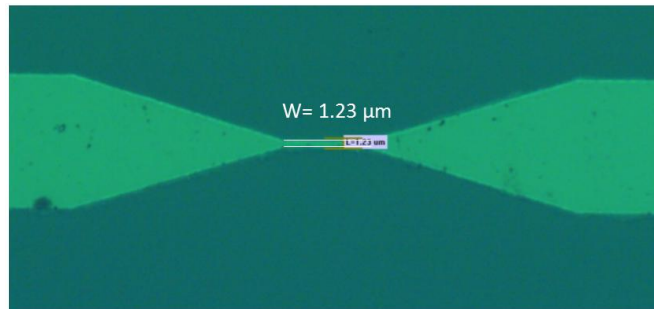


Figure 4.8. This mask was used to protect graphene from oxygen plasma.

After plasma etching samples were put in acetone and heated for couple of minutes in order to remove the remaining resist. Wet etchant 45%  $\text{FeCl}_3$  was used to etch Cu. To avoid unwanted (those portion we want the presence of Cu) under etching problem samples were put in to  $\text{FeCl}_3$  for 1s only because  $\text{FeCl}_3$  is a strong etchant. We wanted to avoid our suspended graphene get collapsed by the surface tension. For this reason, we used critical point dryer method to dry the samples.

## 4.2 Result and Discussion for Suspended Graphene

The idea discussed in section 4 and 4.1 did not work out practically. Unfortunately we did not see any suspended graphene while we observed our samples in SEM, see figure 4.9.

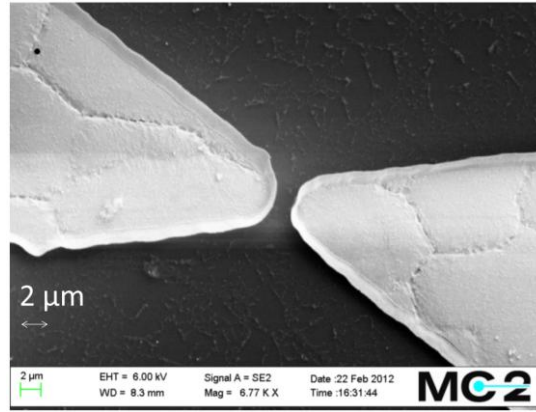


Figure 4.9. No suspended graphene observed in SEM.

During investigation it was observed that using a lift off procedure and UV-lithography we could indeed produce small enough features when using a larger lift-off area. Our second gold lift off process was successful figure 4.10 while we used the mask, shown in figure 4.7. Since the lithography basically works, one of the main reason behind this we believe is that the quality of graphene we produced was not enough or graphene has been damaged during fabrication process.

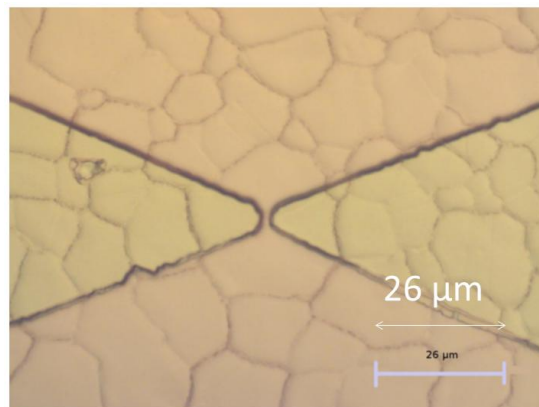


Figure 4.10. Image of a successful lift off, gold features on Cu film.

It is worth nothing that our first lift off attempt was unsuccessful and no separation between features was achieved because it is more difficult to perform lift off process in order to remove a small area, see figure 4.6 and 4.7.

Using more advanced lithographic technology, i.e. electron beam lithography, it was indeed possible to fabricate suspended graphene. Previously Niclas Lindvall, from the Quantum Device Physics Laboratory at Chalmers University of Technology, has successfully fabricated some suspended graphene devices, see figure 4.11 <sup>[22]</sup>.

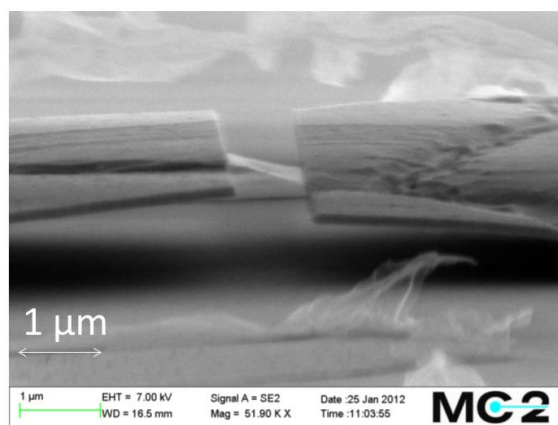


Figure 4.11. Successful suspended device fabricated by Niclas Lindvall <sup>[22]</sup>.

Obviously, E-beam lithography has much higher resolution where in our case UV-lithography is limited up to 1~2  $\mu\text{m}$ . Besides, some problem was encountered such as extensive under etching of copper which lead to many faulty devices. Instead of  $\text{FeCl}_3$ , HCl based solution was used for 20 s here. It proves that we are thinking in a right way but in order to optimize this process we have to play with some parameters. At this stage, it is still not clear whether the higher success rate from Niclas Lindvall's experiment is from the choice of wet etching solution of Cu, or from the choice of lithographic method (UV vs. E-beam). If, however, it is indeed due to the higher resolution from E-beam lithography, then it is reasonable to speculate the major technical bottle neck in this project is the quality of the Cu thin film grown graphene. With E-beam lithography, the feature size is much smaller and there is a large chance that the active region of the suspended graphene device is right within one domain and contain less defects compared with the much larger devices prepared by UV lithography. Nevertheless, presently, even with the devices fabricated by E-beam lithography, the graphene is electrically rather resistive (typically several hundred  $\text{k}\Omega$  or even  $\text{M}\Omega$ , two terminal measurement). This seems to support our assumption that the graphene quality is still inferior to what we expected, despite the reasonable Raman spectrum (e.g. in figure 3.13). Certainly, the domain size of the graphene needs further improvement to make the suspended graphene devices suitable for the application of mass sensors. This factor, we believe, is more important than the device lithographic fabrication process itself. Indeed, recently it has been pointed out that the domain size of the graphene (hence the domain size of the Cu catalyst <sup>[11]</sup>) is the limiting factor for the quality of graphene <sup>[23]</sup>.

### 4.3 Bubbling Transfer of Graphene

We have investigated completely different way of fabricating and transferring graphene called bubbling transfer of Pt grown graphene. It is not our main task in fact it is not possible to have any transfer-free suspended graphene by this method but this method we believe is interesting and promising for producing decent quality graphene for other application purpose.

Recently a paper published in Nature Communications by Libo et al <sup>[24]</sup> and they suggested a reproducible high quality of graphene produced in Pt foil. We followed their method to improve the quality of graphene. We had Pt samples of 125 $\mu\text{m}$  thick. Then sequentially

samples were soaked in acetic acid, acetone, and isopropanol, respectively, to clean possible contaminations and native oxides. Pt annealed in nominal temperature [section 1.1] of 930°C for ten minutes continued by seven minutes growth in 700 sccm H<sub>2</sub>, 80 sccm diluted methane in argon, and 1000 sccm argon. The ratio between methane and hydrogen was around 4:700. We tried to mimic their growth condition as much as possible but still it is not possible to be identical because we used LP-CVD to grow graphene where they used AP-CVD. After the growth Pt was spin coated (2000 rpm for 1 minute) by PMMA and backed for 5 minutes at 160°C. Later, edges were carefully scratched to allow hydrogen to separate PMMA with graphene. In order to separate graphene with PMMA from Pt, water electrolysis process was used. A mixer (to transport ions and increase the conductivity of water) of NaOH: H<sub>2</sub>O = 160: 1000 (weight ratio, NaOH is in powder form) was used as our aqueous solution (1M NaOH) with a current supply of 1A for around five minutes. Pt was treated as anode and Pt/graphene/PMMA was used as cathode, as shown in figure 4.12. At the cathode reduction reaction took place to produce H<sub>2</sub>. It was noticed that within a few minutes PMMA/graphene was detached from Pt substrate due to large number of H<sub>2</sub> bubbles at the interface between the graphene and Pt substrate.

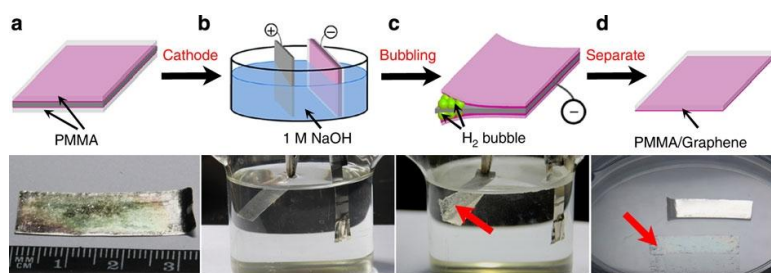


Figure 4.12. Bubbling transfer process of Graphene grown in Pt substrate. This image is taken from Ref. <sup>[24]</sup>, which is similar to our experiment. (a) Pt foil with PMMA. (b) Pt with PMMA graphene was used as a cathode in 1M NaOH aqueous solution. (c) H<sub>2</sub> bubbles produced at the cathode gradually separating Pt with PMMA graphene. (d) Complete separation of PMMA graphene from Pt.

After separating PMMA with graphene it was then transferred to SiO<sub>2</sub>/Si substrate and baked for 5 minutes at 160°C temperature for better adhesion. We used acetone and heated our sample at 50°C for 10 minutes. Though, it was not possible to remove the polymer completely. We used 1165 instead and put the sample over night to remove polymer more thoroughly, see figure 4.13.

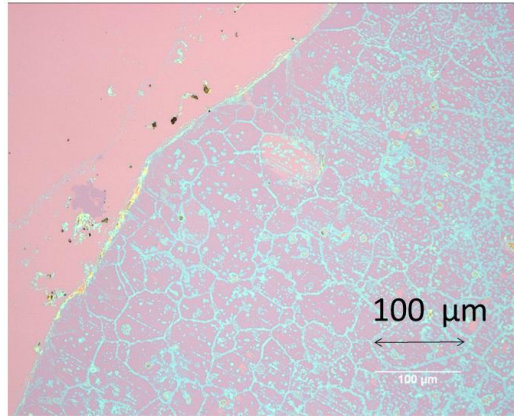


Figure 4.13. Graphene with PMMA on SiO<sub>2</sub>/Si substrate.

But unfortunately some residues were still there. The reason was most likely due to unwanted precipitates from metal hydroxide produced by the –OH groups in NaOH.

Samples were characterized by Raman and after characterization we did not see any high quality graphene, as shown in figure 4.14. Reason was not clearly understood but we believe H<sub>2</sub> flow was very high which has damaged the graphene. Furthermore, this process needs to be optimized by tuning some parameter such as temperature and the H<sub>2</sub> flow.

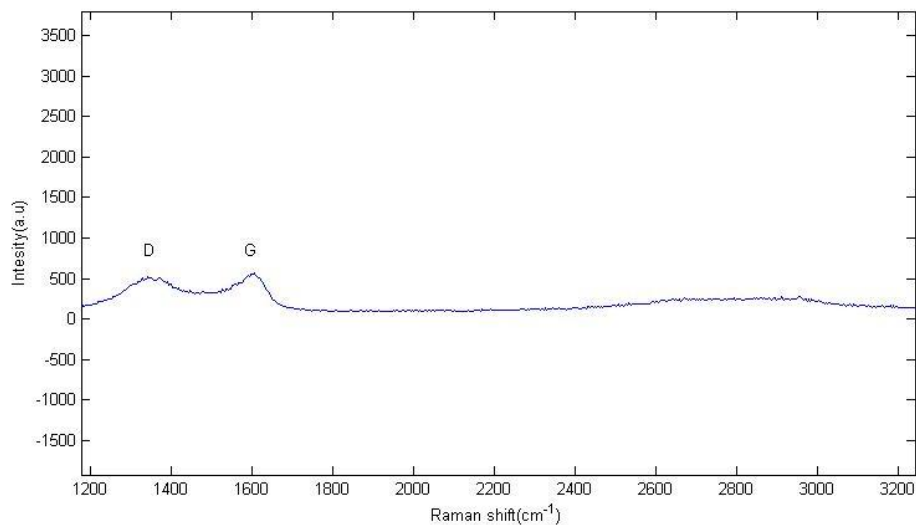


Figure 4.14. Raman spectroscopy with 514 nm laser. Graphene grown on Pt foil then transferred on 300 nm SiO<sub>2</sub>/Si substrate using bubbling transfer.

## 5 FUTURE WORK

Further study and research should be done to improve the graphene quality which is the key issue for fabricating suspended graphene devices. Also, different amount of hydrogen gas concentration can be tested to improve the growth condition. E-beam lithography also can be used for fabricating devices. Moreover, different characterization techniques can be introduced such as detailed electrical measurement to test the electronic properties of

graphene. If it is possible to fabricate suspended graphene with high mobility, we can implement this idea to make gas sensors. Bubbling transfer of graphene method <sup>[24]</sup> is quite encouraging and reproducible which can be improved by tuning some parameters and also we can try to use this method both for graphene on Cu foils and Cu thin film.

## 6 CONCLUSIONS

After several trials and alteration the parameters, we optimized the transfer process. It was found that, 600 nm thick Cu with annealing in 750°C for 5 minutes continued by 5 minutes growth with 20 sccm H<sub>2</sub>, 30 sccm diluted methane in argon and 1000 sccm argon is the best recipe so far. Furthermore, PMMA as resists and HF and HCl as the etchant and acetone treatment can optimize the transfer condition along with the post annealing at 450°C for 10 minutes in H<sub>2</sub> and argon atmosphere.

We believe one of the main reasons for the low success rate for suspended graphene devices was still poor graphene quality. However, we tried graphene growth without H<sub>2</sub> both for high and low methane flow to improve the quality suggested by Li Tao et al <sup>[21]</sup> to improve the quality, because better quality of graphene can lead us towards fabricating successful suspended graphene devices. But the quality of graphene was not good enough in our case, meaning that removing H<sub>2</sub> flow in the growth is not the best solution.

Recently a new way of graphene fabrication has been introduced by Libo et al <sup>[24]</sup>. This new technique was not related to this suspended graphene project but this technique is quite interesting and encouraging. We also tried bubbling transfer of graphene suggested by Libo et al <sup>[24]</sup> to improve the graphene quality. We encountered some problems like as removing the PMMA completely. However, our experiments did prove that the bubbling transfer has a promising future, due to its easy operation and quick speed.

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