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GRAPHENE GROWTH ON COPPER BY CHEMICAL VAPOR DEPOSITION

Myat Shwe Wah[1], Win Tha Htwe[2] and Soe Myint Maung[3]

Abstract

Synthesis methods are needed for its growth on wafer scale to bring graphene to the production level. One of the more promising production techniques to synthesize large area graphene is chemical vapor deposition (CVD) onto transition copper substrates. Recently copper has gained popularity as an important substrate material for graphene growth due to its lower carbon solubility, which allows better control over number of graphene layers. CVD growth has been performed at temperatures ranging from 1000°C to 1050°C using methane as the carbon source with diluted in a suitable mixture of argon (Ar) and hydrogen (H_2). It was found that apart from growth parameters surface texture plays a very important role in graphene growth. The growth mechanism of graphene on copper is surface related and surface morphology was determined by Scanning Electron Microscopy (SEM) and Raman spectroscopy was used to distinguish number of layers on gaphene deposition on copper foil.

Keywords: Graphene, Chemical Vapor Deposition (CVD), Scanning Electron Microscopy (SEM) and Raman Spectroscopy

Introduction

Graphene is one of those materials which are topic of current research interest due to its excellent properties e.g. one atom thick, mobility of the order of 200000 cm^2/Vs, ability to with stand current density of 10^8 A/cm^2, transmittance of about 97% of visible light and high thermal conductivity of the order of 5×10^3 W/mK [Lerf, A., et al.]. It was long believed that two-dimensional materials (2D) were unstable thermodynamically and they only serve as building blocks of complex three dimensional (3D) structures [Gein, A. K., et al.]. Graphene is the name given to arrangement of carbon atoms on hexagonal honeycomb lattice that is exactly one atom thick [Niyogi, S., et al.]. It is this arrangement and symmetry of carbon atoms that gives unique properties to graphene [Nakajima, T., et al.]. Graphene was first obtained in the form of small flakes of the order of several microns through mechanical exfoliation of graphite using scotch tape production scale, fabrication method is needed that can synthesize wafer scale graphene.

Though this method gives the highest quality graphene but to bring graphene to the Chemical vapor deposition (CVD) is one technique that has the ability to synthesize wafer scale graphene [Nima R., et al.]. Two techniques such as Atmospheric Pressure CVD (APCVD) and Low Pressure CVD (LPCVD) are available and LPCVD is implemented in this investigation. The method mainly involves the adsorption, decomposition and segregation of carbon containing precursor on the transition metal surface at elevated temperature either at low or atmospheric pressure which results in graphene synthesis. The aim of this project is to synthesize monolayer graphene through CVD method. In this study, copper had been used as the substrate material for graphene synthesis due to its small carbon solubility at elevated temperatures which allows better control over the number of graphene layers. The deposited graphene on silicons were investigated by Scanning Electron Microscopy (SEM). Raman spectroscopy was used to distinguish number of layers on gaphene deposition on copper foil.

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1 Associate Professor, Head of Department of Physics, University of Computer Studies , Kyaing Tong, Myanmar
2. Professor, Science and Math Department, Spoon River College, Canton, IL 61520, USA
3. Brigadier General, Defense Academic Service Science and Technical Research Centre, Pyin Oo Lwin

Materials and Methods

Commercially available copper foils have been used for the graphene synthesis for overall cost reduction in fabrication process. However, these foils have some face roughness and strongly inhomogeneous corrugated surface due to pressure in nano level due to cold rolling process during manufacturing and this surface unevenness cause to produce graphene thickness variation on copper [Niyogi, S., et al.]. Since graphene growth on copper is surface limited, so smoothness of copper surface plays very important role in getting monolayer coverage across the entire surface of the substrate. Figure shows SEM image of as grown graphene on copper. From electronic applications point of view, field effect mobility, transmittance and sheet resistance are the important parameters. For CVD grown graphene shows field effect mobilities of the order of $3000 cm^2/Vs$, optical transmittance of the order of 90% and sheet resistance of the order 280 Ω/sq. It must be mentioned that graphene obtained by CVD is inferior to graphene obtained by mechanical exfoliation in terms of above mentioned parameters.

One reason is that graphene obtained by CVD is in the form of continuous sheet which is inherently polycrystalline because graphene domains of different orientations merge together to from graphene sheet and because of the presence of grain boundaries, the overall film shows poor electrical properties. So efforts have begun in this direction to obtain single crystal isolated graphene domains with improved electrical properties.

Chemical Vapor Deposition Method

The essence of this technique is that precursors in the vapor phase adsorb and react at the substrate surface at elevated temperatures under low pressure (of the order of millitorr) or atmospheric pressure that results in the deposition of thin film as a result of chemical reaction. In case of graphene synthesis, precursors are usually carbon containing gas e.g. methane or vapors of any liquid carbon source e.g. alcohols that react on the transition metal surface under the ambient environment (e.g. Ar to avoid deposition of amorphous carbon). Graphene obtained recently is the result of refinement of previous methods to get controllable deposition. The solubility of carbon in transition metal along with CVD conditions play an important role in determining growth mechanism and ultimately controls the number of graphene layers. Recent promising results of graphene growth on copper shows that it may serve as alternate route towards scalable growth of graphene with higher monolayer coverage.

Solvent cleaning

The starting substrate is 25μm thick, 99.999% pure copper foil from Amarica. The as-received copper foil may contain thin layer of grease or organic impurities that may result in the deposition of amorphous carbon at high temperatures, so solvent cleaning step is performed to remove them. The recipe for solvent cleaning step is summarized in Table 1. Acetone is used mainly to remove organic impurities but it also leaves its own residues due to its very fast evaporation rate so methanol is used as solvent to remove left over acetone. Finally foil is placed in De-ionized (DI) water bath to remove remaining organic solvents. After Nitrogen dry step, foil is pressed between two clean quartz slides to keep it as straight as possible. During ozone clean, foil is placed on clean quartz slide that is also used during thermal annealing step.

Table 1 Solvent cleaning recipe

Acetone	Methanol	De-ionized Water (DI) dip	Nitrogen dry	Ozone Clean
5 minutes	5 minutes	5 minutes	Gently until foil is dry	2 minutes

Thermal annealing

As received copper foil contains thin layer of native copper oxide, which is highly undesirable for graphene growth. Acetic acid may be used to remove native oxide layer but it leaves the surface too rough which is also not desirable. Thermal annealing of annealing of copper foil is performed in Ar and H_2 at 900°C. The purpose of thermal annealing is two-fold: first, to remove native copper oxide layer by H_2 reduction and second, to increase the grain size of polycrystalline copper foil. As received 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. Thermal annealing increase copper grain size which reduce the effect of grain boundaries on grapheme growth.

Thermal annealing was performed in our home made CVD system. It essentially consists of Lindberg blue M furnace with 1 in. diameter quartz tube. The tube can be fed by Ar, H_2 and CH_4. The flow rate of CH_4 and H_2 is maintained by single regulated flow meter while Ar flow rate is measured by unregulated flow meter. Typical thermal annealing recipe is summarized in Table 2. Copper foil on quartz slide was loaded into the quartz tube and the temperature was ramped up to 900°C under H_2 (36 sccm*) and Ar (280 sccm) ambient. H_2 was used during the ramp up step to avoid oxidation of copper at elevated temperatures. After reaching the annealing temperature, flow rate of gases were left unchanged and annealing was performed for 2 hours. After the annealing step, temperature was ramped down and furnace was allowed to cool down naturally under H_2 (36 sccm) and Ar (280 sccm) ambient. Copper foil was unloaded from the quartz tube at room temperature.

Table 2 Thermal annealing recipe

Step Number	Processing Step	Temperature	Processing gas	Duration (minutes)
1	Ramp up	1000°C	Ar (280 sccm) and H_2 (36 sccm)	20
2	Annealing	1000°C	Ar (280 sccm) and H_2 (36 sccm)	120
3	Ramp down	Room temperature	Ar (280 sccm) and H_2 (36 sccm)	Natural cool down

Synthesis of Graphene by Chemical Vapor Deposition Method (CVD)

Two different types of Cu catalyst deposition were tested for catalyst depositions with E-bean Evaporation system. A mixture of Hydrogen (H_2 99.9995%) and methane (CH_4 99.9995%) was used as a precursor gas for Graphene growth. The CVD reactor is tubular quartz hot-wall, resistivity heated furnace, containing 140 nm inner diameter quartz tubes. In the deposition system, (Ar, 99.999%) was used as carrier gas, H_2(99.999%) was used for soaking and , the substrates were positioned in the CVD furnace as shown in Figure1.The reactor temperature was increased under an argon flow (using 1000 sccm).

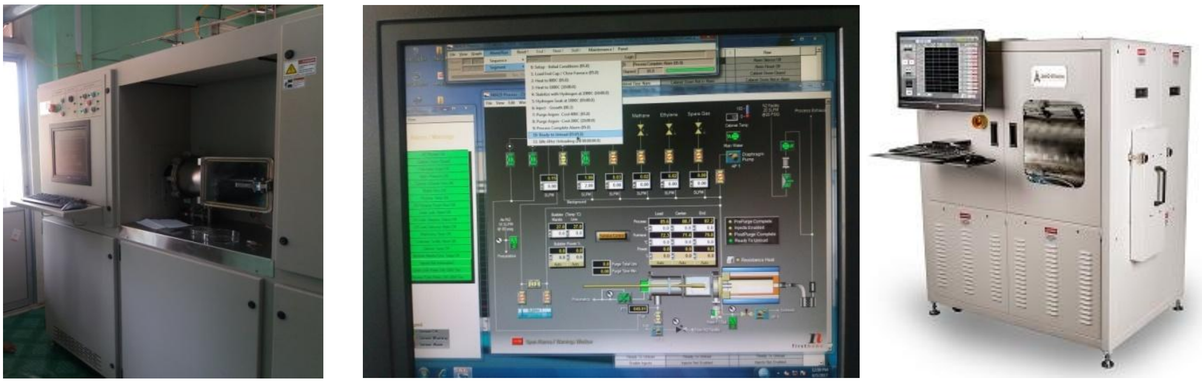


Figure 1 Photo of chemical vapor deposition machine LPCVD AMOD 006 series system manufactured by Angstrom Engineering

Graphene growth on copper

Graphene on copper is in principle straightforward, involving the decomposition of methane gas over a copper substrate typically held at 1000 °C. Growth of predominantly monolayer graphene on copper foil has recently been reported using hexane at 950 °C to explore the possibility of using liquids precursors that could facilitate the doping of graphene during synthesis by using nitrogen and boron containing organic solvents. The specific growth parameters that have been utilized for achieving the best graphene films on Cu. Most of the depositions have been performed on copper foils with thicknesses ranging from 25–50 nm. Recently grapheme deposition on e-beam and thermally evaporated copper thin films has developed and widely used in grapheme film deposition on other substrates.

Results and Discussion

Three objectives of this research is development fabrication of single and many layers graphene grouth on copper foil, secondly, graphene characterization is required to carried out in two-ways: first to identify number of layers in a given sample and second to determine the quality of grown film in terms of defects. Third and ultimate objective is to be able to manufacture the most reliable and highly sensitive biosensors, high efficient solar cells, and rapidly charged high energy density super capacitors in very near future.

The surface morphologies by SEM observation have been characterized using JEOL Scanning Electron Microscope model JSM – 5610 LV. Graphene growth on copper has been successfully prepared by chemical vapor deposition method (CVD) and the shape and size are not well uniformed as shown in Figure 2. Notice that Graphene layer on copper is not homogeneous. The reason could be copper substrate sample preparation, cleaning and handing. Temperature control and gas flow rate may need to be optimized. Copper substrate quality and purification still need to be careful about optimizing the process on CVD method. Photo of copper substrate after graphene growth using chemical vapor deposition was shown in Figure 3.

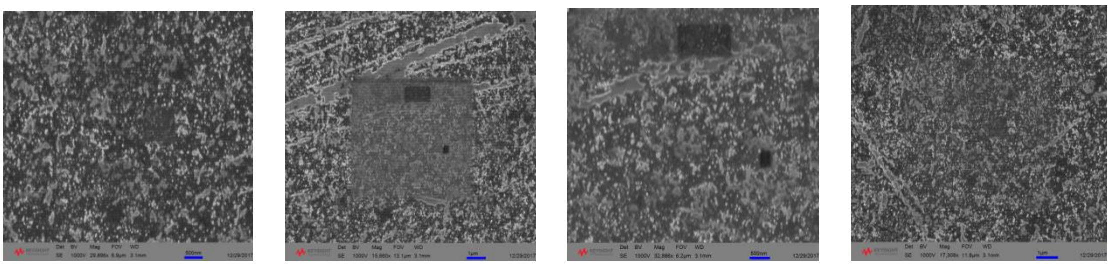


Figure 2 The SEM images of copper substrates after graphene growth on copper

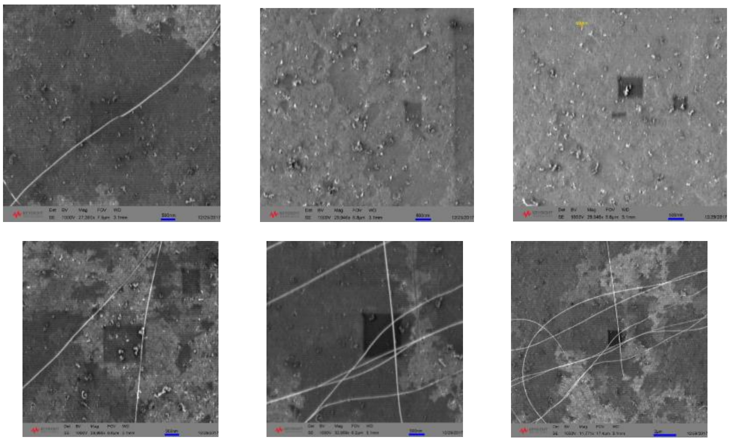
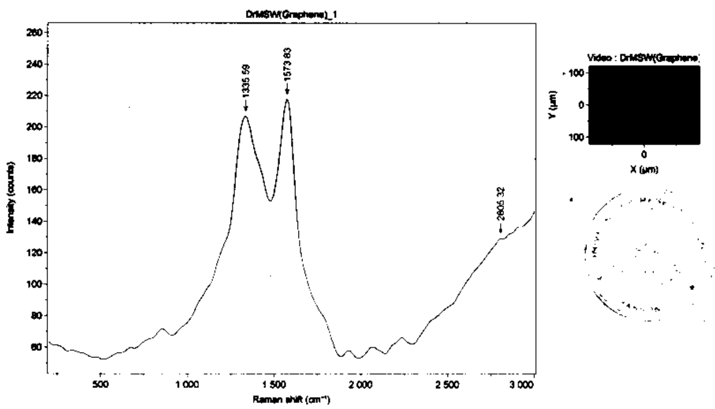


Figure 3 The SEM images of copper substrates after graphene growth on copper (some carbon nano tubes were accindently present during fabrication by CVD on some images in this temperature).

In fact, few layer and bilayer graphene were obtained on the regions where copper surface was not uniform, confirmed by Raman spectroscopy. Raman spectroscopy was used for the graphene characterization because Raman spectrum of graphene contains characteristic bands which can be used to distinguish among number of graphene layers as shown in Figure 4 and also gives information about defects in the sample. Also it is fairly easy to generate spatial Raman area maps of the order of hundreds of microns to study spatial uniformity.



Date	10.05.2019 1 ..	Acq. time (s)	5	Accumulations	5	Laser	532nm_Edge
Spectro (cm-¹)		Hole	100.021	Slit		Grating	600 (500nm)
ND Filter	10%	Objective	x10_VIS	ICS correction	Off	Range (cm-¹)	

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Figure 4 Raman spectrum of graphene contains characteristic bands

Conclusion

The main objective of this project was to optimize graphene synthesis and transfer process using CVD was selected as synthesis technique for grapheme growth as it is a simple method for large scale graphene synthesis. Copper foils were chosen as substrate quite promising because of the lower solubility of carbon in copper which is important in controlling number of graphene layers. CH_4 was used was precursor gas while H_2 annealing was used to remove native oxide as well as to grow copper grains. Ar acted as carrier gas during synthesis to dilute the precursor gas. Graphene on copper is in principle straight forward, involving the decomposition of methane gas over a copper substrate typically held at 1000°C.

The specific growth parameters that have been utilized for achieving the best graphene films on Cu. Raman spectroscopy was used as characterization technique as graphene shows characteristic raman spectrum which can be used to distinguish number of layers on a given sample. Recently graphene deposition on copper thin films has developed but it has some defects of SEM images and widely used in graphene film deposition on other substrates. CVD fabrication allows large area graphene of single layer to several layers graphene.

In this work, graphene deposition on copper foil is to be able to manufacture the most reliable and rapidly charged high energy density super capacitors in very near future. The present study provides a proficient approach to synthesize cost effective and to bring graphene to the production level.

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