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Synthesis of Single layer, Bi-layer and Multi-layer Graphene using Liquid Precursor n-Hexane

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Abstract—Humans, from Stone Age to Silicon Age, have witnessed each age lead by new materials. Each new material, so invented or discovered or synthesized has affected altogether the future technologies, research and life style of the society. Graphene is one of such type of wonder material which will affect us and will open new paths in all fields of technologies. Here, we report the synthesis process of single layer, bi-layer and multi-layer graphene films using liquid precursor n-Hexane on thin Cu-foils by using chemical vapor deposition (CVD) technology. We have also demonstrated very easy transfer process of these graphene films on any desired substrate without damage. This synthesis process opens up window for economic and simple synthesis of pristine as well as doped graphene films.

Keywords—graphene, CVD, liquid precursor, synthesis

I. INTRODUCTION

Graphene is defined as a planar monolayer of carbon atoms densely packed into a two-dimensional (2D) honeycomb lattice. It is a basic structure for all graphitic materials of other dimensionalities (3D, 2D, 1D & 0D). It can be wrapped up into 0D fullerenes, rolled into 1D carbon nanotubes or stacked into 3D graphite [1]. Furthermore, graphene can be cut into a small ribbon known as nano-ribbons, which are the subject of present-day research. As a result, understanding the electronic properties of graphene is the main importance in explaining, for example, the electronic properties of carbon nanotubes and grapheme nano-ribbons.Graphene has created a great interest in research activities during the last 16-17 years because at nano scale it shows thermal conductivity and current density on higher side, and special properties like optical transmittance, ballistic transport, chemical inertness, very high sensitivity of adsorption of individual gas molecules and super hydrophobicity [2, 3]. Due to these extra ordinary properties of graphene, it has already established an area of exciting research for new physics and potential applications in electronics. Graphene is believed to be one of the miracle materials in the twenty-first century. To study all the above properties and various applications of graphene, It is very important to synthesize high quality, uniform and continuous single and multi-layer graphene films by a consistent, simple, reliable and economic synthesis method. Early work on graphene synthesis concentrated on exfoliation of graphite and epitaxy on silicon carbide (SiC). The exfoliation process has the limitation of small size and scalability. Due to high quality graphene obtained by sublimation of the Si atoms from the crystalline surface of SiC became prominent among researchers [4].

Unfortunately, the silicon carbide substrate is predominantly expensive. It is only commercially feasible to very high, aviation performance electronics. Moreover, such sublimation processes of Si require extremely high temperatures (~1500 °C). This makes it incompatible with many substrates and also uneconomic per-unit-area cost of the synthesized material. Direct chemical assembly of benzene sub-units has also been explored [5]. Though the practicality of this approach has been demonstrated the material is as yet incapable in terms of areal coverage and graphitic quality. Perhaps the most industrially practical approach is chemical vapor deposition (CVD). CVD of graphene is emerging method of synthesizing graphene for almost all applications and preferred by so many researchers. It is attributed in part to wide process control, large-area compatibility, and technique familiarity of the CMOS foundries. In CVD process graphene has been synthesized on polycrystalline Ni [6], Fe, Au, stainless steel [7], and single crystals of Ru (0001) [8], Ir (111), Rh (111), Pt (111), and Pd (111) [1]. Since these metals can dissolve a large amount of carbon in bulk, the growth mechanism is

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mainly precipitation-based, with additional contributions from decomposition of the precursors on the metal surface. During cool-down the carbon from the bulk precipitates on the surface and forms the graphitic layers.

Nevertheless, many of these catalysts including materials processing cost are quite expensive, as most of them are single crystalline metals of extremely high purity. Furthermore, controlling the number of layers during the growth is also proved challenging. So far, only polycrystalline nickel has been demonstrated to yield reasonable quality graphene (*i.e.*, a charge mobility of 3700cm^{2}V^{-1}s^{-1}) at low cost, scalable size, and low lattice mismatch [6]. However, even nickel has been surpassed by the controlled growths enabled by copper. At present, copper-based CVD is by far the most popular production method for large-scale graphene [9]. The major disadvantage of this process is that it requires high vacuum and gaseous precursor like methane, ethane and ethylene etc. Handling and maintaining the pressure is difficult. However, liquid precursor based synthesis of graphene could be a very easy and very economic synthesis process due to easy availability, low cost and easy to use of organic solvents. Here, we report the synthesis process of uniform, large, single layer, bi-layer and multi-layer graphene films employing chemical vapor deposition techniques on Cu-foils using liquid precursor n-Hexane. The synthesis process based on liquid precursor will be beneficial over gas precursor based process due to easy availability and low cost of organic compounds in liquid phase at room temperature. Moreover, handling and transportation of gas based precursors is very difficult and expensive. Liquid precursor based synthesis process can be very helpful for synthesizing and studying the properties of doped graphene by using dopants containing organic liquid precursors (pyridine, triethylborane).

II. Experimental Details

For growing the uniform gaphene films 25 µm thick Cu-foil (99.999 % pure) was used in the chemical vapor deposition process. Cu-foil was cut into 2x3 cm^2 pieces and cleaned in DI water, Acetone and Isopropyl Alcohol by ultrasonication for 5 minutes. These cleaned Cu pieces were loaded in a quartz tube by using a small quartz tube used as a boat as shown in figure 1. After loading the Cu substrate, rotary pump was started to pump down until 2x10^{-2} mbar before flowing the H_2 gas. When desired pressure was achieved, the H_2 gas was made to flow at 50 sccm flow rate and a pressure of ~ 5.3x10^{-1} mbar. Then Cu-substrates heated to 965 ^{o}C (at the rate of ~20 ^{o}C/min) inside the quartz tube in hydrogen atmosphere. Hydrogen atmosphere prevented the chances of Cu substrates to get oxidized. When the temperature reached 965 ^{o}C, maintained this temperature for 30 minutes to anneal Cu-substrate so that large grain size could be created on the surface of Cu-substrate. After 30 minutes of annealing, the H_2gas flow was stopped and n-hexane vapor was passed in the quartz tube to maintain the tube pressure of ~0.6 mbar for 3 minutes for single layer, for 4 minutes for bi-layer and 5 minutes for multi-layer graphene films. After 3 minutes, flow of n-hexane was stopped and the flow of hydrogen is started with flow rate of 50 sccm and also the furnace was opened for cooling to room temperature with the rate of around 50^{o}C/min. After reaching the temperature of quartz tube to the room temperature, Cu substrates are taken out from the quartz tube and stored in vacuum. A schematic diagram of experimental setup for graphene synthesis has been shown in figure 1 and synthesis parameters has been shown in figure 2.

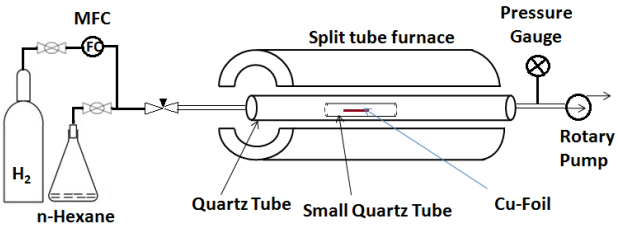

Figure 1. Schematic diagram of CVD setup for graphene synthesis

Graphene transfer process on any substrate is very important to study the properties of Graphene. Schematic diagram of simple transfer process of graphene has been shown if figure 3. Cu-foil with as grown garphene films were first spin coated with a thin layer of PMMA (poly methyl metha acrylate) only on one surface so that after etching Cu film, graphene can sustain on PMMA. PMMA with graphene was separeted from Cu-foil by dissolving the Cu-foil in dilute nitric acid from other surface as shown in figure 4. After dissolving Cu-foil, the PMMA supported graphene, which remain floating on the nitric acid solution, was washed carefully by

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placing in a petri dish filled with DI water. After washing with DI water, it was transferred on any cleaned substrate (SiO_2/Si or Glass slide or ITO coated glass). After transfering on the substrate, the substrate was soft baked so that graphene was attached properly with substrate. Then the PMMA film can be easly dissolved using accetone and got pure graphene on desired substrate for characterization of the graphene films. Raman spectroscopy (Renishaw) was used to characterize the graphene films at 532 nm laser excitation. Scanning Electron Microscopy (SEM) (Zeiss EVO MA-15) was used to see the grain formation in Cu-foil during graphene synthesis. AFM (Agilent Technologies) was used to confirm the unifromity of the films. The as grown graphene films were transferred onto silicon wafer with a 300 nm thick SiO_2 for charcterization of electrical properties. To do this, the deposition of gold elctrode was done using thermal vapor deposition with the help of shadow mask. Semiconductor device analyzer by Agilent was used for electrical characteristics of graphene at room temperature.

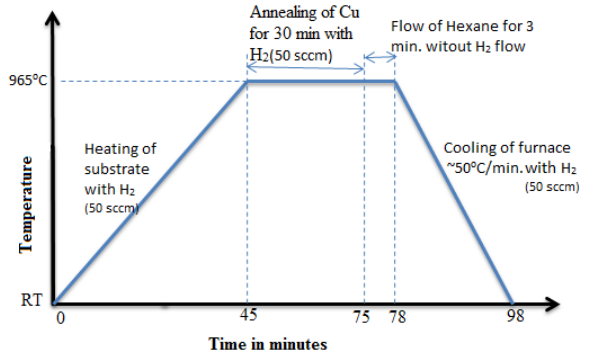

Figure 2. Time dependence experimental parameters: temperature, gas composition and flow rate

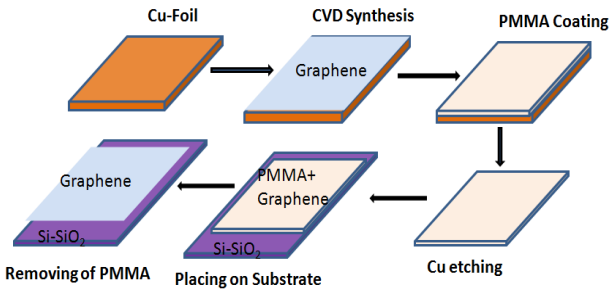

Figure 3.Schematic diagram of transfer process of graphemeon Si/SiO_2 substrate

III. RESULTS AND DISCUSSION

The Raman spectroscopy is very well-known characterization tool for characterization of number of layers and quality of graphene films. The most important bands in the Raman spectrum are the *D*, *G* and*2D* bands which occur at approximately 1350 cm^{-1}, 1580 $cm^{-1}$and 2700 cm^{-1} respectivelyfor ideal single layer graphene.The intensities ratio of 2D band and G band(I_{2D}/I_G)is goodmeasurement for finding the number of layers since this ratio is strongly affected by layer number even for graphene on different substrates.

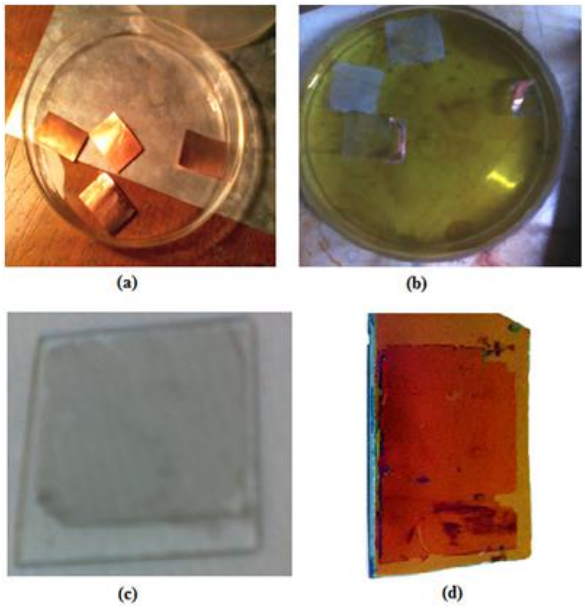

Figure 4. Graphene - (a) grown on Cu. (b) below the PMMA polymer after etching Cu. (c) on glass after removing PMMA. (d)on Si/SiO_2 after transfer process

Figure 5 shows that the I_{2D}/I_Gratio decreases as the growth times increases which points out that the number ofgraphene layers increase with the growth time. The bands intensity ratio I_{2D}/I_G> 2when the growth time is3minuteswhich indicates that single layer graphene is synthesized under these conditions and the bands intensity ratio $I_{2D}/I_G \approx 1.2$when the growth time is4minuteswhich indicates that bi-layer graphene is synthesized.While bands intensity ratio I_{2D}/I_G< 1indicates that multi-layer graphene is synthesized.

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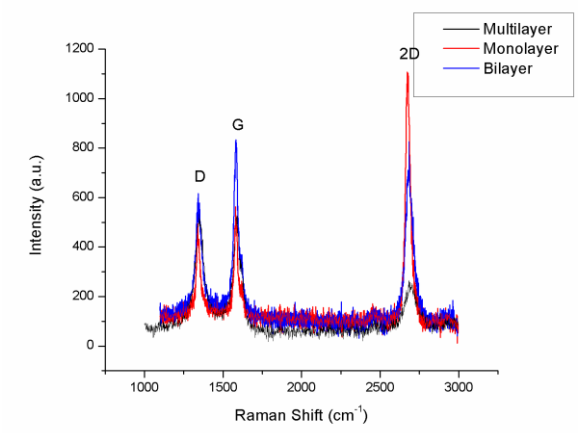

Figure 5. Raman spectrum of Single layer (red), bi-layer (blue) and multi-layer (black) graphene

The D band and G band intensity ratio (I_D/I_G)is goodmeasurement for finding the defects in the synthesized graphene since this ratio isstrongly affected by defects in the graphene due to edge defects or point defects or some impurities. Figure 5 also shows that the Defect(D) band peak increases in intensity as the growth time increases and number of layers increase.From these experiments we conclude that lowergrowth time are important parameters in decreasing number of layers during the growthstep and improving the quality in terms of defects.

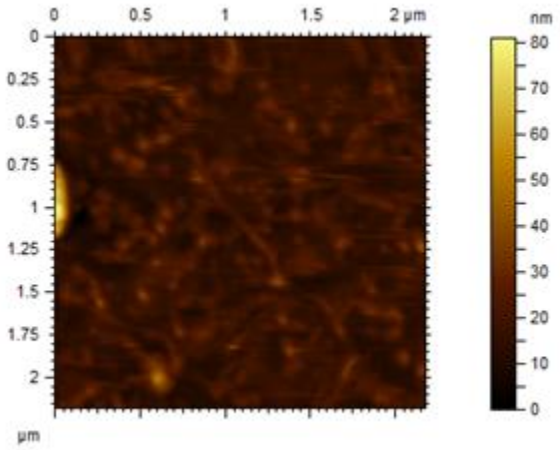

Figure 6. AFM image of graphene after transferring on SiO_2 substrate

The AFM images are taken in contact mode as shown in figure 6. AFM analysis shows that the films are highly uniform and continuous. A large number of wrinkles are also observed on these films. Wrinkles formation occur due to thermal stresses developed during cooling of the substrate after growth as there is a wide difference in the thermal expansion coefficients of Cu and graphene. Some wrinkle formation occurs during the transfer process. The observed thickness using AFM for single layer graphene is found 0.779 nm, which is also verified by ellispometer.

To measure the electrical characteristics of Graphene, gold electrodes are made by deposition gold using a copper mask having contacts size of 220 μm x 170 μm, and having the separation of 50 μm between contacts by thermal deposition. Graphene is a semi-metal so it shows ohmic characteristic as shown in figure 7.

The sheet resistance of single layer graphene is measured approximate 1000 to 2000 Ω/sq, approximate 400 Ω/sq of bi layer and approximate 200 Ω/sq of multi-layergraphene. These sheet resistances are of pristine graphene. The graphene shows a good conductivity.

IV. CONCLUSIONS

We have synthesized good quality, uniform and large size single layer, bi-layer and multi-layer graphene by chemical vapor deposition technique with n-hexane liquid precursor on Cu substrate and transferred graphene on SiO_2/Si and glass substrate for characterization of graphene. This process is very cheap and easy in handling due to use of liquid precursors.

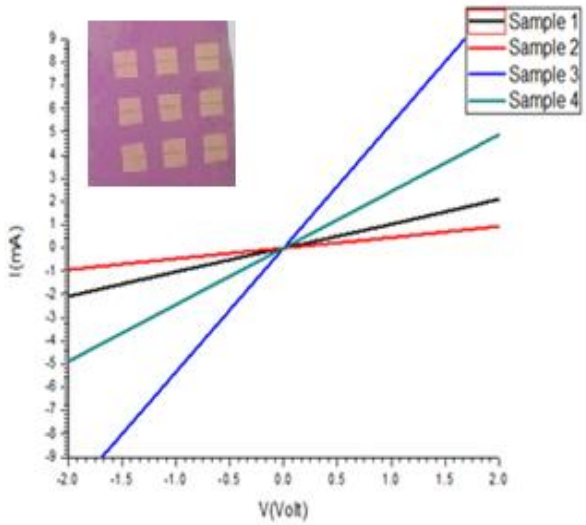

Figure 7.Electrical characteristics of single layer, bi-layer and multi-layer graphene films

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REFERENCES

[1] Deep Jariwala, Anchal Srivastava, and Pulickel M. Ajayan: "Graphene synthesis and band gap opening".Journal of Nanoscience and Nanotechnology 2011; 11(8), 6621-41.

[2] A. G. Geim and Konstantin S. Novoselov: "The rise of Graphene". Nature Materials 2007; 6(3), 183-191.

[3] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim: "The electronic properties of graphene," Reviews of Modern Physics 2009, 81(1), 109–162.

[4] Emtsev KV, Bostwick A, Horn K, Jobst J, Kellogg GL, Ley L, McChesney JL, Ohta T, Reshanov SA, Rohrl J, Rotenberg E, Schmid AK, Waldmann D, Weber HB, Seyller T:"Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide." Nature Materials2009, 8, 203-7.

[5] Cai J, Ruffieux P, Jaafar R, Bieri M, Braun T, Blankenburg S, Muoth M, Seitsonen AP, Saleh M, Feng X:"Atomically precise bottom-up fabrication of graphene nanoribbons." Nature2010, 466, 470-3.

[6] Blakely J, Kim J, Potter H:"Segregation of Carbon to the (100) Surface of Nickel."JAppl Phys1970, 41, 2693-7.

[7] Reina A, Jia X, Ho J, Nezich D, Son H, Bulovic V, Dresselhaus M, Kong J: "Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition."Nano Letters 2009, 9, 30–5.

[8] Sutter PW, Flege J-I, Sutter EA: "Epitaxial graphene on ruthenium." Nature Materials 2008, 7, 406-11.

[9] Mattevi C, Kim H, Chhowalla M:"A review of chemical vapour deposition of graphene on copper."J Mater Chem2011, 21, 3324-34.