

THE PRODUCTION TECHNOLOGY OF GRAPHENE

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ABSTRACT: *Graphene wonder and amazing material in the universe. Graphene all the excellent properties mechanical, optical, electrical, chemical, thermal, magnetic, electronics. This reason graphene is one of the material uses all application like tissue engineering, bio imaging, Polymerase chain reaction, devices, drug deliver, biomicrorobotics, testing, electronics, transistors, transparent conducting electrode, frequency multiplier, optoelectronics, hall effect sensors, quantum dots, organic electronics, light processing, optical modulator, infrared light detection, energy, generation, ethanol distillation, solar cell, fuel cell, storage, super capacitor, Electrode for Li-ion batteries, Hydrogen storage, Rechargeable battery, Sensors, Molecular adsorption, Piezoelectric effect, Body motion, Environmental, Contaminant removal, Water filtration, Plasmonics and meta materials, Lubricant, Radio wave absorption, Redox, Nanoantennas, Sound transducers, Waterproof coating, Coolant additive, Reference material, Thermal management, Structural material, Catalyst, power electronics, power transmission system, biomedical. Graphene is most important point of production required different application and different technology using high quality production of the graphene.*

KEYWORD: Graphene Properties, Application, Fabrication of Graphene, Fabrication Technology

INTRODUCTION

Graphene become the next disruptive technology, replacing some of the currently used materials and leading to new markets. Is it versatile enough to revolutionize many aspects of our life simultaneously? In terms of its properties, graphene certainly has the potential. Graphene is the first two-dimensional (2D) atomic crystal available to us. A large number of its material parameters such as graphene reported so far include high values of its Young's modulus ($\sim 1,100$ GPa)[1], fracture strength (125 GPa)[1], thermal conductivity ($\sim 5,000$ W $m^{-1}K^{-1}$)[2], mobility of charge carriers ($200,000$ $cm^2 V^{-1} s^{-1}$)[3] and specific surface area (calculated value, $2,630$ $m^2 g^{-1}$)[4], plus fascinating transport phenomena such as the quantum Hall effect[5], field-effect mobilities as high as $15,000$ cm^2/Vs and carrier velocity of $\sim 10^8$ cm/s at room temperature [6]. Graphene is composed of sp^2 bonded carbon atoms arranged in two-dimensional honeycomb lattice. The lattice can be seen as consisting of two interpenetrated triangular sub lattice, for which the atoms of one sub lattice are at the center of the triangular defined by other with carbon to carbon inter atomic length, a_c , of $1.42\text{\AA}$. the unit cell comprises two carbon atoms and is invariant under a rotation of 120° around any atom. Each atom one as orbital and two in plan p orbital's contributing to the mechanical stability of the carbon sheet. The remaining p orbital, perpendicular oriented to the molecular plan, hybridizes to form the conduction and valence band, which dominate planer conduction phenomena [7].

Structural composites and so on and so forth. Its fascinating attributes have triggered an avalanche of research publications and patent

Filings. The industry, private investors and governments, are providing substantial funding in graphene research and innovation, which will help in accelerating the pace of its commercialization. USA, Europe, Korea, UK, Japan and other Asian countries are investing a large amount of financial capital. It is expected that the market for graphene would grow by leaps and bounds in the coming decade. According to the latest report "Graphene: Technologies, Applications and Markets" released by BCC the global graphene market is projected to grow to \$67 million in 2015 and \$675.1 by 2020 at a Compound Average Annual Growth Rate (CAGR) of 58.7% within a period of 5 years. Another report entitled "world market for graphene to 2017" by the future markets, Inc. 2011 estimates that the production volume of graphene in 2010 was 28 tonnes and is projected to grow to 573 Tonnes-2017. Graphene is undoubtedly emerging as the most promising nanomaterial because of its unique combination of superb properties, which opens a way for its exploitation in a wide spectrum of applications. However, it has to overcome a number of obstacles before we can realize its full potential for practical applications. One of the greatest challenges being faced today in

Table 1 Graphene Synthesis Methods

Micromechanical Exfoliation Flakes (5Flakes to 100µm)	Carbon Nanotube Unzipping Nan ribbons (fewmicrons)	Liquid Phase Exfoliation Nan sheets (nm to a few µm)	Epitaxial Growth on SiC Thin films (>50 µm)	Chemical Reduction of Graphite Oxide Nanoflakes/ Powder (nm to a few µm)	CVD (on, Ni, Cu, Co) Thin film (<75cm)
Research Purpose	Interconnects FETs NEMs Composites	Polymer Fillers Transparant Electrodes Conductive Paints Sensors	Transistors Circuits Interconnects Memory Semiconductors	Polymer Fillers Battery Electrodes Supercapacitors Conductive Inks & Paints Sensors	Touch Screens Smart Windows Flexible LCDs & OLEDs Solar Cells
Small Scale Production High Cost High Quality Uneven Films	Moderate Scalability High Yield High Quality Potentially Low Cost	High Scalability Low Yield Moderate Quality Low Cost Impure	Low Yield High Cost High Quality High Process Temperature (15000C) Very Expensive Substrate	High Scalability Low Cost Low Purity High Defect Density	Moderate Scalability High Cost High Quality High Process Temperature (>1000oC)

Commercializing graphene is ho graphene is how to produce high quality material, on a large scale at low cost, and in a reproducible manner [8].

Fabrication of a Graphene MoS₂ Junction

Micromechanical Exfoliation

Graphite is a highly anisotropic material made of weakly coupled layers of carbon atoms bonded in a hexagonal lattice. Its buildingblock, an isolated single atomic layer (monolayer) called graphene, is only recently accessed experimentally [9-14]. Although the stacking of graphene layers is only supported by a weak interlayer coupling, the electronic properties change dramatically for the monolayer graphene as compared to the bulk graphite. As graphene is a new nano-material with unusual electronic properties, its electronic, optical, thermal and other properties have not been studied completely yet [15-19].

Knowledge of how these properties evolve from monolayer graphene to graphite will facilitate the development of graphene devices. In particular, optical detection relying on light scattering is especially attractive, because it is fast, sensitive, and Non-destructive. Raman scattering has recently emerged as a viable, nondestructive technique for the identification of mono- and few layer graphene [20-23].

Currently, graphene is prepared by different methods such as mechanical exfoliation of graphite using scotch tape [10], chemical exfoliation of graphite [11], epitaxial growth of graphene by thermal graphitization of SiC [20], chemical vapor deposition of hydrocarbon gases on transition metals [21], exfoliation of graphite by sonication [22], etc. However, at present there is no ideal method for synthesizing defect free graphene sheets. Detailed understanding of growth kinetics and production control is highly desired to prepare large-scale high quality graphene. Disadvantages of the mechanical exfoliation (cleavage) or Scotch tape method, which is the first method of obtaining twodimensional crystals, are small surface area of monolayer graphene obtained [23].

Graphene samples are synthesized by Scotch tape method, identified by optical microscopy, and characterized then by Raman spectroscopy and AFM. For synthesizing graphene samples, oxidized Si wafers (with areas of $\sim 1 \times 1 \text{ cm}^2$,

thickness of 525 μm and resistivity of 0.001– 0.005 $\Omega \text{ cm}$) are used. The thickness of SiO₂ on the top of Si substrate was 300 nm. The Raman spectra are measured by WITec Alpha300 Raman system (spectral resolution of spectrometer is 1 cm^{-1}) using a laser excitation of 632.6 nm, 514.5 nm and 487.9 nm (with a triple frequency He-Ne and Ar lasers as excitation source) delivered through a singlemode optical fiber, whose spot size is limited by the diffraction. Using a long working distance focusing objective lenses (10 $\times$ and 100 $\times$) with numerical apertures $NA = 0.90$ and 0.80 , the spot size of about 500 nm is obtained. With an incident light power of 0.2mW, heating effects can be neglected. The Raman spectra are measured using a grating with 1800 $\text{g}^{\circ}\text{mm}$ and a solid state cooled CCD detector. The Raman spectra of as-prepared and elaborated monolayer graphene samples with different areas were recorded under the same experimental conditions. The topography and height profiles of graphene samples are obtained by noncontact AFM.

Graphene samples are prepared by Scotch tape method, which is the following [20]. Graphene is produced by micromechanical cleavage or exfoliation (repeated peeling) of highly oriented pyrolytic graphite by the scotch tape, i.e. slicing this layered material by gently rubbing it against another surface on the scotch tape. After that, it is transferred to an oxidized silicon wafer covered with SiO₂ layer with thickness of 300 nm. Under an optical microscope with a 50 $\times$ or 100 $\times$ objective lens, it is possible to see plenty of thick and tiny flakes of graphite on Si/SiO₂ wafer: large, shiny pieces of all kinds of shapes and colors (Figure.1a). The optical

images of asprepared graphene samples with different magnification obtained after micromechanical cleavage of bulk graphite are shown in Fig.1. It is possible to observe monolayer graphene: highly transparent, crystalline shapes having little color compared with the rest of the substrate (Figure.1b). The ability to create graphene with such a simple procedure ensures that graphene was produced an uncountable number of times since graphite was first mined and the pencil invented in 1565.

After preparation of the graphene samples the identification of graphene layers is still a serious obstacle. It is extremely difficult to find small graphene pieces in the haystack of millions of thicker graphitic flakes, which appear during the cleavage (Figure.1a). For that reason at the beginning the surface of graphene carefully scanned in an optical microscope, which allows distinguishing mono- or few-layer graphene from bulk graphite. With the thickness of 300 nm of SiO₂ cap layer, the ultrathin graphitic flakes get visible with an optical microscope. Few layer graphene flakes are sufficiently transparent to add to an optical path, which changes their interference color with respect to an empty substrate. For a certain thickness (300 nm) of SiO₂ layer, even a monolayer was found to give sufficient contrast to differentiate graphene layers among thicker flakes scattered over a substrate. These layers have a slightly different color in the optical microscope (Figure.1b). It appears that darker color corresponds to thicker sample. The color of much thicker layers (more than 10 layers) does not follow this trend and can change from blue to yellow and then to gray (Figure.1a) [24].

Micromechanical exfoliation of graphene using PDMS stamps

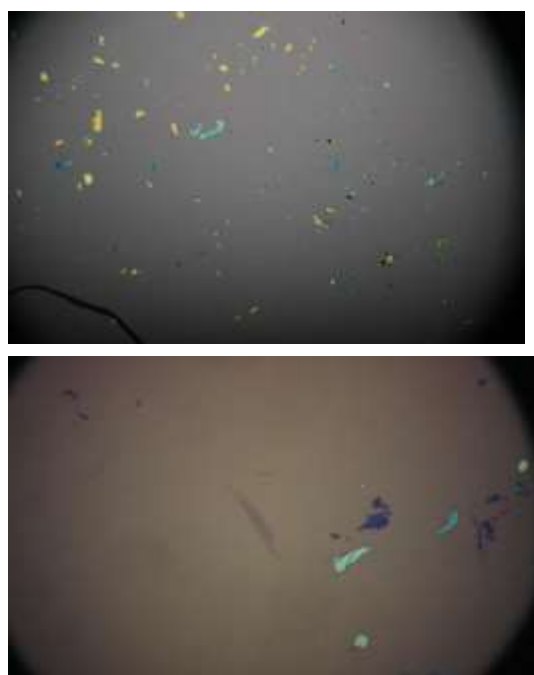


Figure: -1(a)(b). Optical images of monolayer graphene with 10× and 100× magnification

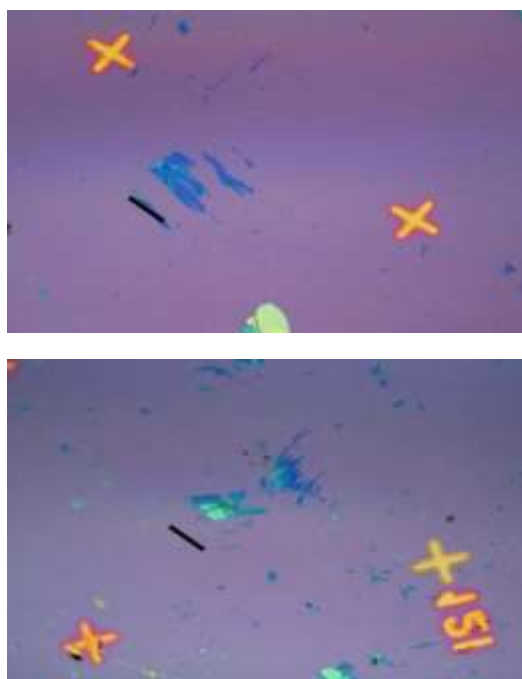


Figure: - 2 (A) MoS₂ fabricated via PDMS stamping on a 300 nm Si/SiO₂ substrate. Scale bar is 20 μ m in length. B) MoS₂ also fabricated via PDMS stamping, but on a 285 nm Si/SiO₂ substrate.

In order to isolate MoS₂, PDMS stamping was used instead of micromechanical exfoliation, due to the fact that the micromechanical exfoliation process tears apart the more brittle flakes of MoS₂, making it difficult to isolate a large-area, single-layer flake. A bulk flake of MoS₂ is first exfoliated on a piece of blue tape so that the flakes do not break apart as fast as they do on clear tape. The amount of MoS₂ on the tape is kept very dense, to allow for maximum deposition. A clean, prepared stamp of PDMS, roughly 2 x 2 cm is then placed on the tape, and pulled off quickly to grab the most pieces. This stamp is then positioned over the Si/SiO₂ wafer, where it is pressed for roughly 30 seconds. Then the stamp is slowly removed so that many thick pieces will be taken off, but thinner ones will remain. This wafer is then taken to an optical microscope where pieces of MoS₂ that are good candidates for substrate transfer are identified. Good candidates for transfer are flakes that look to be large enough in area (>70 microns) to use in a prefabricated transistor device, but also thin enough for either laser-thinning or direct deposition

A PDMS stamping technique was used to simultaneously thin and deposit MoS₂. A PDMS stamp, with MoS₂ deposited on it, was placed on a Si/SiO₂ wafer. As shown in Figure 2, thin layers of MoS₂ can be isolated using this technique. Figure 2A depicts a few multilayered flakes that are about 10-13 layers thick on a 300 nm Si/SiO₂ substrate. Figure 2B is more multilayered flakes of about the same thickness, but on a 285 nm Si/SiO₂ substrate. In both of these pictures, the crosshairs are alignment markers that are used to relocate samples after they have been identified. While this method is limited in the size of the area we can stamp, it can produce good candidates for our prospective device.

Raman Spectroscopy and Laser Thinning.

A Thermo DXR Raman spectrometer was used to perform Raman shift measurements on both graphene and MoS₂ samples. A laser of 532 nm with a normal resolution grating of 900

lines/micron is used at a power of between 0.1 and 3 mW for Raman shift measurements, and a power of 10 mW for laser thinning. The laser thinning procedure described by CastellanosGomez et al was used as a building block for this technique, with some slight alterations. [25] The same Raman spectrometer mentioned above was used to perform the laser thinning, so that there could be in situ experimentation and characterization. The thinning was conducted by finding a flake of MoS₂ that looked to be less than 7-10 layers thick (characterized under the microscope visually by having a slight lightbluish tint). Then a Raman map was used so that there could be laser impaction at the smallest resolution of this instrument (1 micron). Therefore, a flake that was 10x10 microns would have a 100 point grid overlaid on it. At each point three exposures were taken, each lasting 0.5 seconds, with a maximum laser power of 10 mW. After the map was taken, a sample spectrum could be obtained to examine the effect of the thinning; the thinning could also be verified with optical means.

Raman spectroscopy has been used to determine the number of layers and existence of twodimensional materials since their inception [20]. When looking at the output of a Raman spectrum, a few things must be considered, chiefly what the spectrum should look like in context. For graphene, the relative intensities of the G (~1580 cm⁻¹) and G" (~2700 cm⁻¹) peak are most important. The difference in intensities between these two peaks can roughly tell how many layers are being looked at. MoS₂ is not so simple; the relative intensities are of very little importance to the number of layers. The most telling characteristic of the Raman spectrum of MoS₂ is the difference between the two peaks of few-layer MoS₂. As the two peaks shift towards each other, a difference of around 20 cm⁻¹ is ideal for single-layer MoS₂.

A thin flake of MoS₂, such as that shown in Figure 2, was then bombarded with a laser to etch away additional layers. A Raman spectrophotometer can be used to do this procedure, and also characterize it in situ. Raman spectra taken from the MoS₂ being laserthinned were compared to quantify how much material is removed from the top of the target flake. The three Raman spectra in Supplemental Figure 1 represent the spectra taken before laser thinning, and after each treatment. It can be seen that as more treatments are applied to the sample, the two peaks near the right end of the spectrum shift toward each other, this is characteristic of few layer MoS₂, and can also help us in quantifying the change in number of layers between treatments [26].

Carbon Nanotube Unzipping Graphene Nanoribbons

Graphene, or single-layered graphite, with its high crystallinity and interesting semimetal electronic properties, has emerged as an exciting two-dimensional material showing great promise for the fabrication of nanoscale devices[27-29]. Thin,

elongated strips of graphene that possess straight edges, termed graphene ribbons, ngradually transform from semiconductors to semimetals as their width increases[30-33], and represent a particularly versatile variety of graphene. Several lithographic[33,34] chemical[35-37] and synthetic[38] procedures are known to produce microscopic samples of graphene nanoribbons, and one chemical vapour deposition process[39] has successfully produced macroscopic quantities of nanoribbons at 950 6C. Here we describe a simple solutionbased oxidative process for producing a nearly 100% yield of nanoribbon structures by lengthwise cutting and unravelling of multiwalled carbon Nanotube (MWCNT) side walls. Although oxidative shortening of MWCNTs has previously been achieved [40], lengthwise cutting is

hitherto unreported. Ribbon structures with high water solubility are obtained. Subsequent chemical reduction of the

Nanoribbons from MWCNTs results in restoration of electrical conductivity. These early results affording nanoribbons could eventually lead to applications in fields of electronics and composite materials where bulk quantities of nanoribbons are required [41-43].

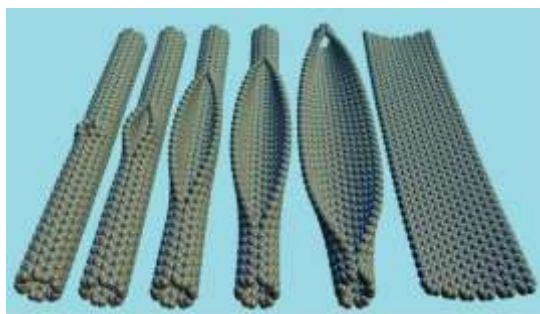


Figure: - 3 Nanoribbon formation and imaging. (a) Representation of the gradual unzipping of one wall of a carbon nanotube to form a nanoribbon.

The mechanism of opening is based on previous work on the oxidation of alkenes by permanganate in acid. The proposed first step in The process is manganate ester formation (2, Figure 3b) as the rate determining step, and further oxidation is possible to afford the dione (3, Figure. 3b) in the dehydrating medium[44]. Juxtaposition of the buttressing ketones distorts the b,c-alkenes (red in 3), making them more prone to the next attack by permanganate. As the process continues, the buttressing-induced strain on the b,c-alkenes lessens because there is more space for carbonyl projection; however, the bond-angle strain induced by the enlarging hole (or tear if originating from the end of the nanotube) would make the b,c-alkenes (4, Figure. 3b) increasingly reactive. Hence, once an opening has been initiated, its further opening is enhanced relative to an unopened tube or to an uninitiated site on the same tube. The ketones can be further converted, through their O protonated forms, to the carboxylic acids[45] that will line the edges of the nanoribbons. Finally, relief of the bond-angle strain when the nanotube opens to the graphene ribbon (5, Figure. 3b) slows further dione formation and cutting[44]. Thus, the preference for sequential bond cleavage over random opening and subsequent cutting, as occurs with nitric acid oxidation, can be explained by concerted attachment to neighbouring carbon atoms by permanganate, contrasting with the random attack on nonneighbouring carbon atoms by the nitronium species from nitric acid. The surface of the now-less-strained nanoribbon remains prone to 1,2-diol formation, which leads to the overall highly oxidized ribbon, but this is less likely to result in further oxidative cutting to the dione owing to relief of the tubular strain on the double bonds. We achieved the same unzipping process in single-walled carbon nanotubes (SWCNTs), to produce narrow nanoribbons, but their subsequent disentanglement is more difficult.

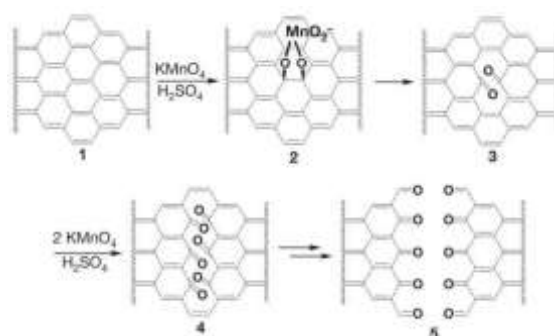


Figure :-3 Nanoribbon formation and imaging. (b)The proposed chemical mechanism of Nanotube unzipping.

We used transmission electron microscopy (TEM), atomic force microscopy (AFM) and scanning electron microscopy (SEM) to Image the ribbon structures. TEM analysis shows Nanoribbons (Figure. 1c) produced from MWCNTs with a starting diameter of 40– 80nm and approximately 15–20 inner nanotube layers (additional TEM images of untreated MWCNTs can be found in the Supplementary Figure. 3a, b). After reaction, the width of the carbon nanostructures increased to 100nm and they had linear edges with little pristine MWCNT sidewall structure remaining (see Supplementary Figure 3). The MWCNTs used were produced from a chemical vapour deposition process²²; we attempted the same H₂SO₄–KMnO₄

treatment on a single sample of laser-ovenproduced MWCNTs, but fewer nanoribbon-like structures were detected. AFM imaging (Figure. 1d) shows the presence of single atomic layers after tip sonication of the solution for 30 min to yield well-dispersed and sonication-shortened ribbons suitable for imaging. SEM imaging of nanoribbons on a silicon surface shows that the ribbons remain long (, 4 mm in this image) when not cut by tip sonication; they can be dispersed as single or thin layers and they display uniform widths and predominantly straight edges over their entire length. The degree of consecutive tube opening in the MWCNTs can also be controlled by adjusting the amount of oxidizing agent introduced into the system; using TEM, we found that in 80– 100% of the MWCNTs present, the side walls completely unravelled to form nanoribbons when 500 wt% KMnO₄ was used. The successive opening reaction was demonstrated in five iterations, each containing a stepwise increase in the amount of KMnO₄: 100 wt% KMnO₄ in the first iteration (sample I), 200 wt% in the second iteration (sample II), and so on until the final iteration, when we used 500 wt%.

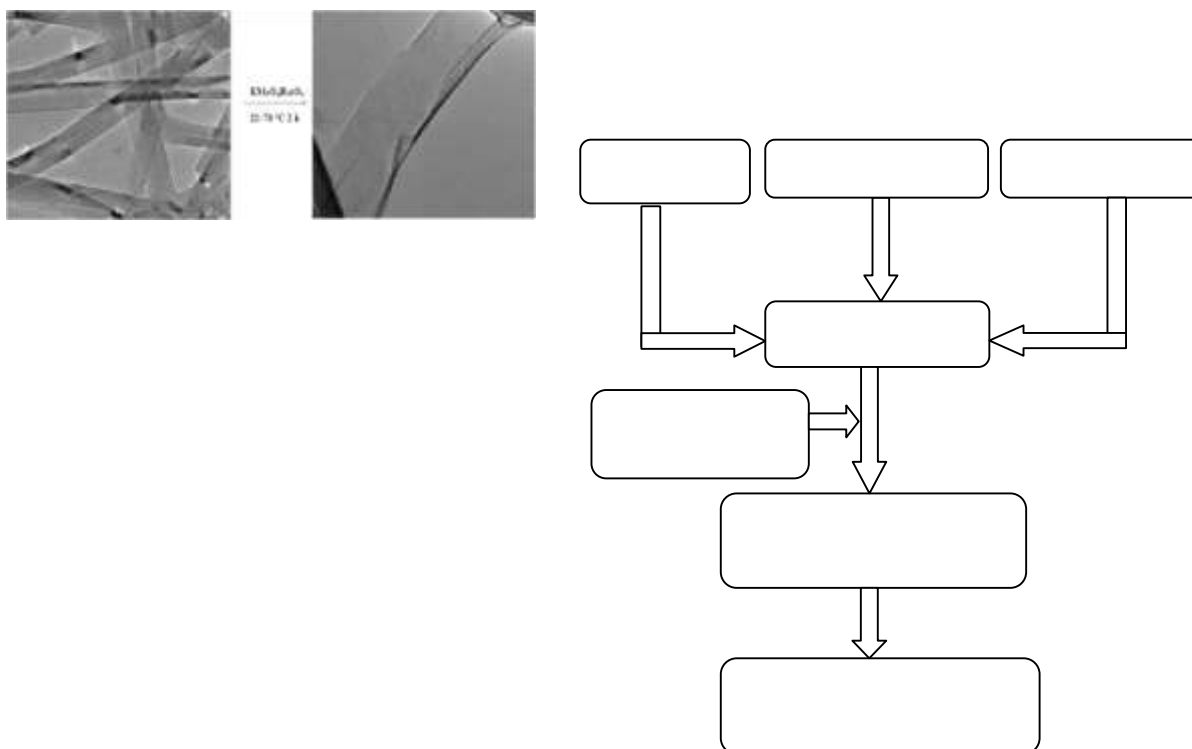


Figure:-3c, TE Mimages depicting the transformation of MWCNTs (left) into oxidized nanoribbons (right). The right-hand side of the ribbon is partly folded onto itself. The dark structures are part of the carbon imaging grid.

This resulted in consecutive unencapsulation of the different layers by unzipping of the successive MWCNTs (see Methods for details). It is evident from TEM images (that the walls of the MWCNTs open to a higher degree as the level of oxidation increases, with less MWCNT inner tube remaining in successive iterations. This is highlighted in a statistical plot showing the decrease of the average diameter of remaining MWCNTs from, 65nm to, 20nm as the amount of KMnO_4 exposure is increased. The smaller diameter tubes that remained after treatment with 500 wt% KMnO_4 were exposed to the reaction conditions for less time than the larger-diameter tubes and, thus, may not have had the chance to fully react; no difference in the rate of unzipping between smaller and larger-diameter Nanotube can be inferred from this data.

Pre-oxidation

In pre-oxidation method the MWCNT was treated with concentrated sulphuric acid (H_2SO_4) and Nitric acid (HNO_3) to enhance oxygen. MWCNT was suspended in a mixture of 50 ml of H_2SO_4 and 25 ml of HNO_3 for more than 12 hours. 50 ml of H_2O was added to accelerate the reaction. Next day stirring was done for 10 min. After 24 hours MWCNT was collected in the bottom of beaker and washed with H_2O for several times to remove acids. By help of a pH paper acidic nature was tested.

Then solution was dried to collect CNT power.

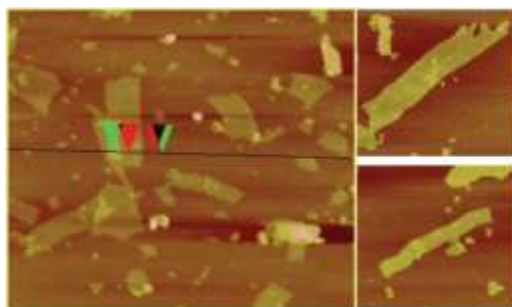


Figure:-3d, AFM images of partly stacked multiple short fragments of nanoribbons that were horizontally cut by tip-ultrasonic treatment of the original oxidation product to facilitate spin-casting onto the mica surface. The height data (inset) indicates that the ribbons are generally single layered. The two small images on the right show some other characteristic nanoribbons.

MWCNT 50 ml H₂SO₄ 25 ml HNO₃

Mixer

Additional of water (50ml)

Stirring was done for

10 min

Solution was dried to get sample

Figure:-4 preoxidation flow chart

Oxidation

MWCNT will be suspended in concentrated 50 ml of sulphuric acid (H₂SO₄) for a period of 1–12 h. Then solution was treated with 500 wt% potassium permanganate (KMnO₄). The H₂SO₄ conditions aid in exfoliating the nanotube and the subsequent graphene structures. The reaction mixture was stirred at room temperature for 1 h and then heat for 50– 700C for an additional 1 h. Now quenches the reaction mixture by pouring over ice containing a small amount of hydrogen peroxide (H₂O₂). The solution was filter over a poly tetra fluoroethylene (PTFE) membrane, and the remaining solid to wash with de-ionized water. Then dried CNT was collected[46].

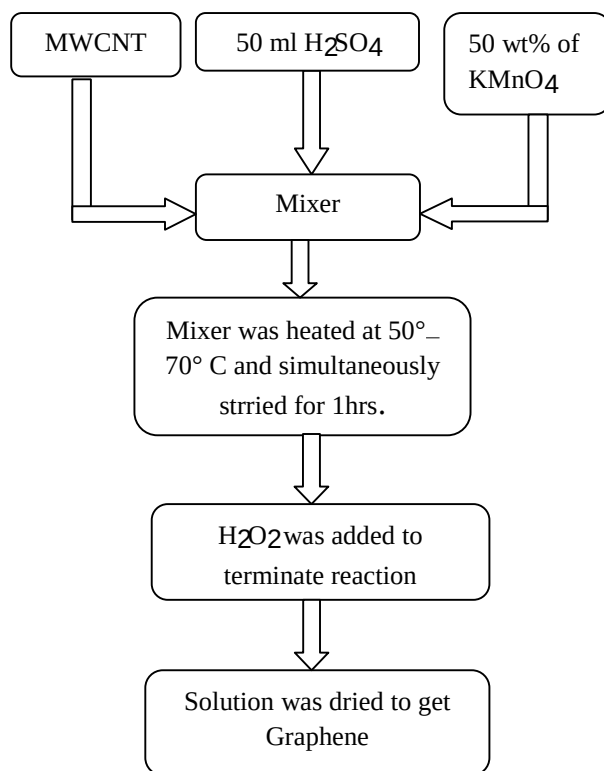


Figure:-5 oxidation flow chart

Liquid Phase Exfoliation Nanosheets

Graphene has attracted great interests during the past decade [47-49]. The excellent electrical and optical properties make it promising in a variety of devices such as high speed transistors [50-52], transparent conducting films [53,54], lithium ion batteries [55-57], and super capacitors [55,57,58]. Its electrical conductivity, which is largely affected by the presence of defects and functional groups, governs the performance of many of these devices [59]. Therefore, the preparation of graphene with low concentration of defects and functional groups is crucial for many of its applications. In addition, in view of industrial applications, high-yield production is also highly demanded. Liquid-phase exfoliation has been considered as one of the most feasible approach for industrial production of graphene due to its scalability and low cost. This approach typically involves sonication of graphite or graphite oxide powders in solvents. Depending on the graphite precursors, liquid-phase exfoliation of graphite has been studied using (1) graphite oxide, (2) natural graphite, and (3) graphite intercalation compound (GIC).

Liquid-phase exfoliation of graphite oxide is now one of the most widely used methods for preparation of graphene. This method begins with intercalation of graphite with strong oxidizing agents followed by expansion of graphite layers via sonication. The reduction of the obtained graphene oxide to graphene is usually conducted by either thermal or chemical approaches [60,61]. Although this method is capable of high-yield (>50%) production of graphene, the use of large quantity of acid and oxidizing agents requires time-consuming washing steps and produces hazardous wastes. In addition, the vigorous oxidation of graphite often leads to incomplete restoration of the sp² hybrid carbon bonds

and presence of residual oxygen functional groups resulting in poor electrical conductance [62].

Liquid phase exfoliation of natural graphite is easy to implement and can circumvent the oxidation of graphene. This method involves ultrasonic treatment of graphite in solvents such as N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), and γ -butyrolactone (GBL) [63]. Among all the solvents, NMP gives the highest graphene yield due to its surface energy approaching that of graphite that is sufficient to overcome the interacting forces between graphene layers. Although technically it is similar to the liquid phase exfoliation of graphite oxide, this method is unique with the absence of oxidative intercalation steps. Graphene prepared by this method was demonstrated to have low concentration of defects and oxygen functional groups. However, the yield is usually very low (~1 wt %) as only the surface layers of graphite were peeled off during sonication.

Liquid-phase exfoliation of GICs for production of graphene was first reported by Viculis et al and has attracted great interest recently [64-67]. This method begins with intercalation of graphite followed by expansion of graphite via rapid increase in the vapor pressure of the volatile intercalated substance under microwave or thermal treatment. As nonoxidative agents are applied for intercalation of graphite and microwave or thermal treatment of GIC leads to large expansion of graphite, high-yield production of graphene with high quality can be achieved using this method. For example, it was reported that, by solvothermal-assisted exfoliation of expanded graphite (EG) obtained from GIC in acetonitrile, Qian et al. successfully prepared monolayer and bilayer graphene with 10-12 wt% yield without significant structural defects [68]. However, these recipes are limited by using either poisonous chemical agents [65] or dangerous chemical reactions [66,67].

Natural graphite (2 g, 99.99% purity) was first mixed with an aqueous solution (300 ml) containing TEA tetrafluoroborate (0.8 g), sodium hydroxide (0.15 g), and thionin acetate salt (50 mg). After agitation for 10 minutes, the suspension was tip sonicated for 6 hours (Scientz-II D Ultrasonic Cell Disruptor, 950 W, with 90% amplitude modulation) and then vacuum filtered by Nylon membrane of 220 nm in pore size. The obtained TEA-GIC was washed with 20 ml deionized water and 20 ml ethanol for three times successively and then vacuum dried at 60 °C for 2 hours. After that, the dry graphite powders were microwave irradiated for 5 minutes (Midea microwave oven, 900 W). The expanded graphite (EG) obtained by microwave treatment was then treated ultrasonically in 700 ml NMP for 2 hours (Ultrasonic Cleaner, 250 W). The resultant suspension containing graphene was centrifuged at 5000 rpm for 15 minutes to remove unexfoliated graphite particles. A stable graphene suspension was obtained finally after the supernatant was pipetted off.

Preparation of graphene films

100 ml graphene NMP dispersion with a concentration of 0.14 mg ml⁻¹ was filtered by Nylon membrane with 220 nm in pore size. The obtained thin graphene paper was dried at 60 °C for 36 hours.

Structural characterization

The morphology of natural graphite, TEA-GIC, EG, and graphene films was examined by field emission scanning electron microscopy (SEM, Hitachi S-4800). Atomic force microscope (AFM) characterization was conducted with a Veeco Dimension 3100V scanning probe

microscope at ambient conditions using the tapping mode. The sample for AFM measurement was prepared by dip-coating. A mica sheet was immersed in 0.001 mg ml⁻¹ graphene NMP dispersion for 5 minutes to adsorb a thin layer of graphene flakes. After that, it was immersed in de-ionized water for another 5 minutes to remove unadsorbed graphene. Powder X-ray diffraction (XRD) patterns of natural graphite, TEA-GIC, and EG were recorded with Bruker AXS D8 Advanced X-Ray Diffract meter. The electrical conductivity of graphene film was measured by a physical property measurement system (PPMS) (Quantum Design Model-9). The structural information of natural graphite, TEAGIC, and EG was also obtained from Fourier transform infrared spectra (FTIR), which were acquired using a Thermal Nicolet 6700 FTIR spectrometer. Raman and X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Raman microscope (Thermo Scientific DXR) with 532 nm laser and Multifunctional XPS (Shimadzu Axis Ultradld), respectively.

Preparation of graphene

The process of preparing graphene consisted of three steps, as shown schematically in Figure 1: (a) aqueous phase intercalation of natural graphite to produce TEA-GIC, (b) microwave irradiation to obtain EG, and (c) sonication of EG in organic solvents such as NMP, DMF and GBL to obtain graphene. The TEA-GIC was produced by tip sonication (855 W) of graphite in aqueous solution containing thionin acetate salt, sodium hydroxide and TEA. Thionin cations entered graphite galleries after the intercalation of TEA to stabilize TEA-GIC while sodium hydroxide provided hydroxide anions for subsequent elimination of TEA. The TEA-GIC was further microwave irradiated in air. The release of gaseous species induced by the decomposition of TEA led to expansion of graphite. After mild sonication in organic solvent, this EG could be readily exfoliated into dispersive graphene sheets. The single-cycle yield of graphene was 5% determined by weighing the residue after filtration of the graphene dispersion. This value is four times higher than that obtained by liquid-phase exfoliation of graphite in NMP for half an hour [63] and even higher than that obtained by treatment of graphite using the same method for 460 hours [69]. The yield of graphene can be further improved with unexfoliated graphite recycled to repeat the above process.

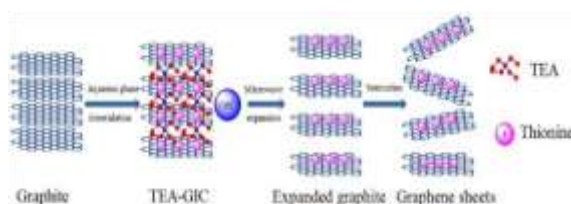


Figure:-6. Illustration of experimental procedure for preparation of graphene by liquid phase intercalation and exfoliation of graphite.

We observed the Tyndall effect with a laser passing through the dispersion, indicating that the graphene sheets were quite evenly dispersed in the solvent. This suspension was stable without noticeable sediments even after being shelved for one month. The whole experimental processes lasted only one day and were quite straightforward to implement and control

Epitaxial Growth on SiC

Graphene, a two-dimensional array of carbon atoms in honeycomb lattice, has been theoretically studied for decades in terms of the fundamental building block of carbon based materials, such as graphite and carbon nanotubes [70, 71]. However, the first observation of freestanding graphene was not realized until 2004 with mechanical exfoliation method by peeling graphene flakes from a bulk graphite crystal onto SiO₂ substrate [72]. Since then, a variety of novel properties, including quantum Hall effects, and relativistic quasiparticles with a group velocity of $1/300c$ (where c is the speed of light) [73-75] have been observed. These unique properties, together with the high values of conductance, mobility, and mechanical strength [73, 76, and 77] make graphene a promising material for a wide variety of new technological applications [78-80], such as post-CMOS digital electronics, single-molecule gas sensors, spintronic devices, etc.

To realize the application potential of graphene, reliable methods for fabricating large-area single-crystalline graphene domains are required. The most promising approach in this respect seems to be the controlled graphitization of SiC surfaces [73, 81]. In this method, single layer and/or multilayer graphene can be grown by sublimating Si atoms from SiC substrates at high temperature. In spite of a lot of efforts devoted to the improvement of synthesis methods to form large areas of uniform, electronic grade graphene by the thermal desorption process is still very challenging. In this paper, we will give a short review on the current state of epitaxial graphene research, and we will then introduce a new developed synthesis method, the “**face-to-face**” method, which allows preparing good quality monolayer, bilayer and three layer epitaxial graphene samples on 6H-SiC(0001) substrate.

Epitaxial Graphene on SiC

Although growing thick graphite samples on SiC has been a well-known process for many years [82, 83, 84], it is not until recently that the thickness was pushed down to few layers and a full characterization of the high quality graphene sample has been carried out [73, 85, 86]. The growth of epitaxial graphene on SiC is based on thermal decomposition of the SiC substrate. Both e-beam heating as well as resistive heating have been used, but no difference seems to arise from the different heating methods [87]. In order to avoid contaminations the heating is usually performed in ultra-high vacuum (UHV) environment. Similar results have been observed for high and/or low base pressure growth but so far no comparative study about the influence of the background pressure in the vacuum chamber has been conducted. From the molar densities one can calculate that approximately three bilayers of SiC are necessary to set free enough carbon atoms for the formation of one graphene layer [87]. The growth of graphene can take place on both the (0001) (silicon-terminated) or (000-1) (carbon-terminated) faces of 4H-SiC and 6H-SiC wafers. The main difference lies in the sample thickness that one can achieve. In the case of silicon face, the growth is slow and terminates after relatively short time at high temperatures giving rise to very thin samples, up to a monolayer. On the contrary, in the case of the carbon face, the growth does not selfterminate giving rise to relatively thick samples (approximately 5 up to 100 layers) [88] with larger orientational and turbostratic disorder [89, 90, 91].

Epitaxial graphene on SiC (0001) face

Hydrogen etching is performed as a normal routine of pretreatment to remove scratches from polishing and oxides and leave a surface with highly uniform, atomically flat terraces.

Although it is believed that larger graphene sheets should be obtained with a smoother graphitization surface [92], the relevance of pregraphitization SiC surface to better graphene order has not been substantiated. Recently, the relation between initial surface morphology and sample quality has been discussed by Ohta *et al.* [93]. They observed the formation of graphene on SiC by Si sublimation in Ar atmosphere, and identified two types of monolayer graphene with different shapes. It was noticed that large graphene sheets preferred to grow along the triple bilayer SiC steps, while narrow graphene ribbons formed following the surface of single bilayer SiC height. The dependence between growth mechanisms and initial surface morphology indicates the effects of H₂ etching on the formation of graphene. The result suggests that by minimizing the number of single bilayer SiC steps with H₂ etching, better graphene sample should be achieved. To compensate the depletion of Si during the precleaning process, external Si flux is applied before the SiC substrate is heated to higher temperature to grow graphene. A number of surface reconstructions prior to graphitization have been observed and studied by low-energy electron diffraction (LEED) [83, 84]. Figure 9 shows LEED patterns obtained at different stages during the growth of graphene. The initial Si-rich (3×3) phase can be obtained by exposing a well-outgassed SiC surface to a Si flux at a temperature of 800 °C. A subsequent 5 min annealing at 1000 °C in the absence of Si flux gives rise to the sharp pattern shown in panel (a), corresponding to the 1×1 spots of SiC. Further annealing for 5 min at 1100 °C produces the ($\sqrt{3} \times \sqrt{3}$) R30 reconstruction shown in panel (b). Finally, the complex ($6 \times 3 \sqrt{3}$)

6×3) R30 pattern shown in panel (c) appears after 10 min annealing at 1250°C, demonstrating the formation of graphene. In different experiments, the annealing temperature can be various. It should be noticed that the first carbon layer grown on the Si-face of SiC, referred as buffer layer, is not graphene. Although the atomic arrangement of this layer is identical to that of graphene, however, unlike graphene, one third of the carbon atoms of this layer are covalently bonded to the underlying Si atoms of the topmost SiC layer. The π -band is developed between buffer layer and following graphene layers.

Epitaxial graphene on SiC (000-1) face

Compared to the Si-face, graphene on SiC (0001) face has been less studied, due to the early conclusion that C face films were of poor quality and rotationally disordered [96]. However, a detailed study indicates that the azimuthal disorder detected by low energy electron diffraction (LEED) is not random [97]. In multiple layer graphene grown on SiC (0001) face, epitaxial layers can orient either in the 30° phase or in the $\pm 2^\circ$ phase with respect to the substrate, which is indicated in Figure. 7. The different orientations between adjacent layers cause them to decouple from each other, forming a system which preserves the transport and electronic properties of free-standing monolayer graphene [81, 98]. Due to this unique property, C-face grown graphene attracts more and more attention. The major problem with the growth of epitaxial graphene on C-face of SiC is the lack of precise control in sample thickness. The controllability has been demonstrated by Camara *et al.* [99] lately.

The Face-to-Face Method

As indicated in the review above, high quality epitaxial graphene sheets in large scales now can be achieved. However, the growth process gets more complicated because more parameters are introduced into the system, such as annealing atmosphere. In the following part, we will report a new synthesis method, the “**faceto-face**” method, which is

straightforward, simple, and economical, and yet yields good quality graphene of large length scales. Here two SiC substrates are placed one on top of the other face to face, with a small gap in between, and are then heated simultaneously. The grown samples show larger terrace sizes and better homogeneity than the one obtained by annealing SiC in ultra high vacuum, as demonstrated by LEED, atomic force microscopy (AFM), angle resolved photoemission spectroscopy (ARPES) and Raman measurements performed on the as grown sample. Moreover we show that the graphene thickness can be easily and well controlled by changing the annealing temperature. The results suggest that the method has potential for efficient production of graphene base devices. Figure 7(a) shows schematic diagram of our vacuum furnace with a base pressure $\leq 1 \times 10^{-6}$ Torr, maintained by

30 l/s hybrid turbo pump (HTP). Two rectangular pieces of SiC are stacked in pairs with spacers of Ta foil at the edges for a 25 micron gap between the two inner surfaces, the key idea of this method from which the name

“**face-to-face**”. The pieces are oriented so that the Si-terminated surfaces face each other. The two ends of the stack are wrapped by “L” shaped pieces of Ta foil at each end and connected to electrodes allowing simultaneous parallel resistive heating.

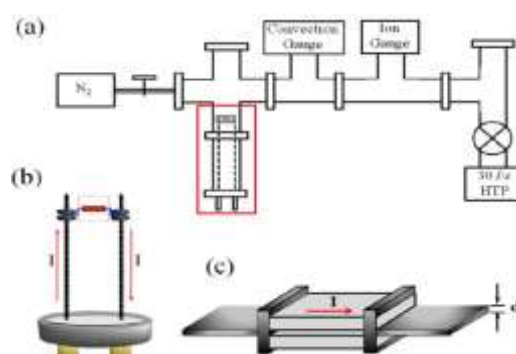


Figure:-7 (a) Schematic view of the configuration used for “face-to-face” growth method setup; (b) magnified view of the sample setup highlighted in panel (a), where rectangles in red represent SiC substrates, and lines in blue represent Ta foil; (c) magnified view of mounted SiC substrates highlighted by red lines in panel (b), the distance between Si face of the two substrates equals to the thickness of Ta foil ($d = 25\mu\text{m}$). SiC substrate is in light gray and Ta foil is in dark gray.

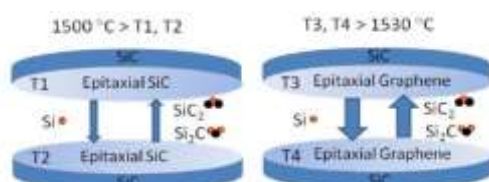


Figure:-8 two-step growth model for preparing epitaxial graphene

Panel (b) and (c). Temperature was monitored by an infrared optical pyrometer set to an emissivity of 0.96.

The simple geometry of this method results in two important effects. First, at temperatures below 1500 °C (before graphene growth has begun), both pieces act as sources as well as sinks of SiC on the opposing surface (Figure. 4a). Large atomically flat terraces form during this annealing process without careful hydrogen etching which is usually applied in other approaches as a pre-treatment for graphene preparation. By first creating large, flat substrate terraces, the eventual graphene layer can have similarly large terrace sizes. Second, the close proximity of the two surfaces partially traps Si atoms which sublime from each heated surface, increasing the local partial pressure of Si within the gap. The pressure of Si vapor next to the surfaces of the SiC crystals restricts the net rate of Si sublimation from the substrates (Figure. 4) and allows large pieces of graphene to be formed as described above. Thus, the same effect as in previous methods aiming to improve graphene annealing conditions by reducing Si sublimation (ambient pressures of Ar or disilane) is achieved in a very simple manner. We note that as Si can escape from the gap near the edges of the pieces, control of the Si sublimation from the edge of the substrates is reduced, resulting in thicker and poorer quality of graphene around the edges.

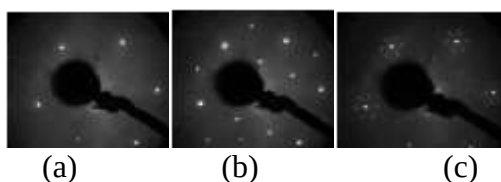


Figure:-9 (a–c) LEED patterns with a primary energy of 180 eV, obtained at four different stages during the growth of sample A. (a) 1×1 spots of SiC, after a 5 min anneal around 1000 °C followed by the initial cleaning procedure under Si flux. (b) $(\sqrt{3} \times \sqrt{3})$ R30 reconstruction, after 5 min around 1100 °C. (c) $(6\sqrt{3} \times 6\sqrt{3})$ R30 reconstruction, after 10 min around 1250 °C.

The substrates used in the experiments were cut into 4×6 mm² using a diamond saw from n-type 6H-SiC (0001) single crystalline wafers¹. The substrates were degassed at 700 °C for 4 hours followed by annealing at elevated temperatures of 1530 – 1700 °C. During the initial growth stage at 1500 °C, epitaxial SiC layers are nucleated on the two substrates creating atomically flat SiC with large terrace sizes. The sublimation of Si prevails over decomposition of SiC with higher annealing temperature than 1530 °C, which results in the formation of micrometer scale graphene sheets. As in other methods, higher temperatures lead to thicker, or more layers, of graphene. In the present method, 1530 °C results in single layer graphene, and 1700 °C results in triple layer graphene.

Chemical Reduction of Graphite Oxide

The scheme for the two classes of rGO-based thin films discussed in this Review is illustrated in Figure 1. Type one are pure rGO films, which consist of a percolating network of sheets lying flat on a substrate surface. Type two are composite films consisting of rGO as the filler and polymer or ceramic as the host material. The starting point for the fabrication of these films is the oxidation of graphite, which readily exfoliates in water, forming a colloidal suspension of GO. For electronic and optoelectronic applications discussed here, GO, which is electrically insulating, must be reduced to become electrically conductive.^[100] Various methods of reduction have been reported, resulting in varying degrees of restored electrical conductivity. Similarly, thin-film deposition techniques of GO/rGO influence the degree of coverage, number of layers, and surface

morphology giving rise to a variety of properties. In the following Sections, synthesis, dispersion, reduction, and deposition of GO are discussed.

Synthesis of graphite oxide can be achieved by placing graphite in one or more concentrated acids in the presence of an oxidizing agent. Graphite oxide was first prepared almost 150 years ago by Brodie, who treated graphite repeatedly with potassium chlorate and nitric acid.[101] This method was modified by several investigators including Staudenmaier[102] and Hamdi[103] who used a mixture of sulfuric acid and nitric acid with potassium chlorate. Hummers and Offeman[104] later demonstrated a less hazardous and more efficient method for graphite oxidation, which involves a mixture of sodium nitrate, potassium permanganate, and concentrated sulfuric acid. These and their modified versions are presently the most commonly used methods for the oxidation of graphite.[105–108] Other methods such as electrochemical oxidation of graphite have also been reported.[109]

Graphite oxide in water hydrolyzes to form thin platelets, which are negatively charged. While Brodie[84] remarked that the platelets were

„extremely thin,“ it was about 100 years later when Boehm et al.[110] concluded that the thinnest graphite oxide platelets consisted of single-carbon-thick layers. Today, the existence of monolayers of graphite oxide is widely acknowledged and recognized as graphene oxide (GO).[111,100] The term „platelets“ is often used to describe thick multilayers of GO or rGO, while „sheets“ usually indicate a monolayer to few layers.[112] Individual sheets of GO can be viewed as graphene decorated with oxygen functional groups on both sides of the plane and around the edges as described by Lerf et al.[113,114] (Figure:-11). Due to ionization of carboxyl groups, which are primarily present at the sheet edges (Figure:11), GO can be electrostatically stabilized to form a colloidal suspension[115] in water, alcohols, and certain organic solvents[116,117] without surfactants. Exfoliation of graphite oxide into individual sheets can be facilitated by ultrasonic agitation[119] or rapid heating[118,120] but excessive ultrasonication can result in decrease of lateral dimensions.[121,122] Oxidation of graphite results in a brown-colored viscous slurry, which contains graphite oxide and exfoliated sheets along with nonoxidized graphitic particles and residue of the oxidizing agents. After repeated centrifugation, sedimentation, or dialysis, salts and ions from the oxidation process can be removed from GO suspensions (see for example, Ref. [123,124,125,126]). To achieve a suspension of monolayer GO, nonoxidized graphitic particles and thick graphite oxide platelets are precipitated out by further centrifugation. Suspensions of GO flakes that are monodispersed according to their lateral size can also be obtained by density-gradient centrifugation.[122].

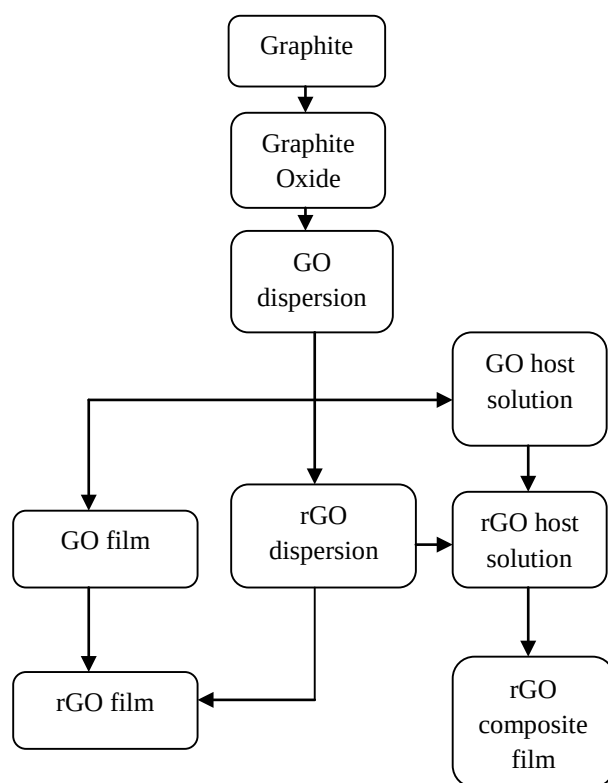


Figure:-10 Process scheme for fabricating rGO-based thin films

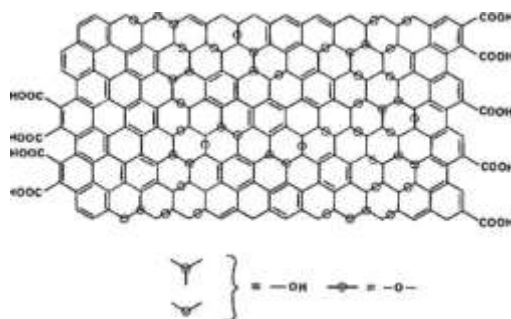


Figure:-11 Chemical structure model of GO. Position of oxygen functional groups are indicated by circles. The functional groups are attached on both sides of the graphene sheet. Reproduced with permission from [94].

The thickness of a monolayer GO sheet is approximately 1–1.4 nm, which is thicker than an ideal monolayer of graphene (thickness 0.34 nm) due to the presence of functional groups and adsorbed molecules [111,127]. Since the functional groups make GO strongly hydrophilic, multilayered GO contains trapped water molecules between the layers.[113,127,128] Studies have shown that these molecules can be partially removed from the structure during thermal reduction [127,129] (Fig. 3b). Despite the difference in their optical properties, like pristine graphene,[130,131] GO sheets are also readily visible on Si substrates with 300-nm SiO₂ [132]. Furthermore, high-contrast visualization of GO on arbitrary substrates can be achieved by fluorescence quenching microscopy.[133,134] The maximum lateral size of GO sheets is dependent on the size of initial graphite crystals, but the average size can be adjusted to some degree by the extent of oxidation procedure[135] or by ultrasonication.[121,122] Large and

small GO sheets observed with optical and atomic force microscopy (AFM), respectively, demonstrate the wide range of lateral sizes. By using large graphite crystals as the starting material and employing a multistep oxidation process, GO sheets as large as 3mm have been synthesized.[136] Due to the ease of identification on SiO₂/Si substrates and their large lateral size, GO sheets can be contacted with metal electrodes for electrical studies using standard lithographic techniques.[137] On the other hand, GO sheets having lateral sizes of few nanometers have also been observed after extensive ultrasonication.[122]

Reduction of Graphene Oxide

There are a number of routes for reduction of GO, as briefly summarized in recent reviews.[139,140] Chemical methods involve exposure of GO to reducing chemicals such as hydrazine (hydrazine

monohydrate,[111,137,138]dimethylhydrazine,

[100,123] and anhydrous

hydrazine[141]),hydrides(sodiumborohydride[1

42–145] and sodium hydride[146]), hydroquinone,[142,147] and p-phenylene diamine.[148] Reduction of GO also occurs in strongly alkaline environments[149] and in supercritical water.[150] Thermal reduction of GO is typically achieved above 200 °C in inert or reducing environments and becomes more efficient at higher temperatures.[159,160,151] It should be noted that in the presence of oxygen, GO decomposes quickly at high temperatures[111] and gradually at lower temperatures (<200 °C). Annealing GO in NH₃ atmosphere above 300 °C results in reduction as well as N doping via formation of C-N bonds.[152] Efficient chemical reduction of GO is achieved in solution, since both sides of the sheets can interact with the reducing agent while in thin films only the exposed regions are reduced.[126,153] Hydrazine is effective for the removal of in-plane functional groups such as epoxy and hydroxyls but leave the edge moieties such as carboxyl and carbonyl intact.[154,126,153] Gao et al.[154] demonstrated that these residual edge groups can be removed by additional exposure to concentrated H₂SO₄ after the initial reduction treatment. As an alternative to chemical methods, hydrogen plasma treatment has been also shown to result in efficient reduction.[137]

Other routes include electrochemical reduction,[155–157] photocatalytic reduction,[158] and flash conversion,[161] but no comparative studies on their reduction efficiencies have been conducted.

Chemical vapor deposition

The “top-down” exfoliation technique has been widely used to produce two-dimensional atomic crystals including not only graphene but also many other 2D materials, as BN and

MoS₂[162]. This process of producing graphene sheets has been found to be reliable and easy and has attracted the immediate attention of the scientific community. The best quality graphene, in terms of structural integrity, has been obtained by this method up to now. However, only flat graphene flakes (tens of microns in size) can be produced and the number of exfoliated layers is not easily controlled. As in most practical applications conceived for graphene, including microelectronics, optoelectronics (solar cells, touch screens, liquid crystal displays), graphene based batteries, super-capacitors and thermal control, large area and high

quality with low structural defects graphene is needed [163] other methods should be developed. The preparation of graphite from heterogeneous catalysis on transition metals has been known for years. Independently of this, the first report on CVD synthesis of few layer graphene (FLG) was published in 2006 [164]. Since then, the CVD “bottom-up” synthesis has evolved to scalable and reliable production method of large area graphene. Synthesis of large area and high quality graphene has been demonstrated by this method [165,166]. But comparing CVD graphene properties to exfoliated graphene, the latter goes on exhibiting better quality so far. Currently the growth and development of high quality, large-area CVD graphene on catalytic metal substrates is a topic of both fundamental and technological interest. Since the large-scale graphene films synthesized so far are typically polycrystalline, the research effort is aimed to control the domain size, the number of graphene layers, the density of grain boundaries, and the defects and so on. For graphene materials to realize the promise of “graphene based applications”, it is clearly necessary to solve those problems, preventing defects in fabricated devices.

CVD synthesis and growth of graphene

There exist comprehensive review articles and books dealing with generic aspects of the Chemical Vapor Deposition. Here we are only intent on describing elemental details of CVD applied to graphene synthesis. We encourage the readers to increase their knowledge with the fundamental aspects of Vapor Deposition Processes revisiting the cited references [167-173].

CVD chemical reactions and processes

Chemical Vapor Deposition (CVD) involves the activation of gaseous reactants and the subsequent chemical reaction followed by the formation of a stable solid deposit over a suitable substrate. The energy that the chemical reaction demands can be supplied with the aid of different sources; heat, light or electric discharge are used in thermal, laser assisted or plasma assisted CVD, respectively. The deposition process can include two types of reactions: homogeneous gas phase reactions, which occur in the gas phase, and heterogeneous chemical reactions which occur on/near the vicinity of a heated surface leading to the formation of powders or films, in each case. Though CVD has been used to produce ultrafine powders, this review article is mainly concerned with the CVD of extremely thin graphene films. So heterogeneous chemical reactions should be favoured and homogeneous chemical reactions avoided during the designed experiments. Figure:- 11 shows a schematic diagram of a typical CVD process.

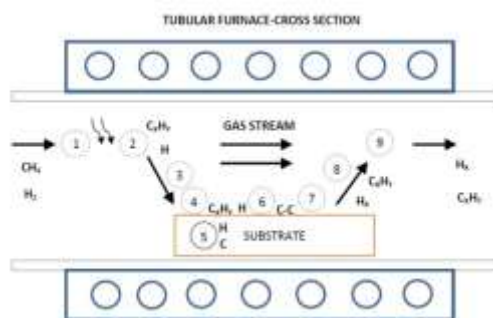


Figure.-11(a) Schematic diagram of Thermal CVD a) and Plasma Assisted CVD b) process: case of graphene from CH₄/H₂ mixtures.

Transport of reactants by forced convection.

1. Thermal a) or plasma b) activation. Homogeneous gas reaction with particles and powder production should be avoided in graphene synthesis, controlling the kinetic parameters (P,T,n).
2. Transport of reactants by gas diffusion from the main gas stream through the boundary layer.
3. Adsorption of reactants on the substrate surface.
4. Dissolution and bulk diffusion of species depending on the solubility and physical properties of the substrate
5. Thermal activation mediated-surface processes, including chemical decomposition (catalytic), reaction, surface migration to attachment sites (such as atomic-level steps), incorporation and other heterogeneous surface reactions. Growth of the film.
6. Desorption of byproducts from the surface.
7. Transport of byproducts by diffusion through the boundary layer and back to the main gas stream.
8. Transport of byproducts by forced convection away from the deposition region.

Preparation of CVD-graphene.

Chemical vapor deposition (CVD) of large-area single-layer graphene on metal films was explored widely in some respects up to now. Despite the significant progress, CVD graphene is a polycrystalline film made of micrometer to millimeter size domains. To date the graphene films grown on Ni foils or films did not yield uniform monolayer graphene. In most cases, a

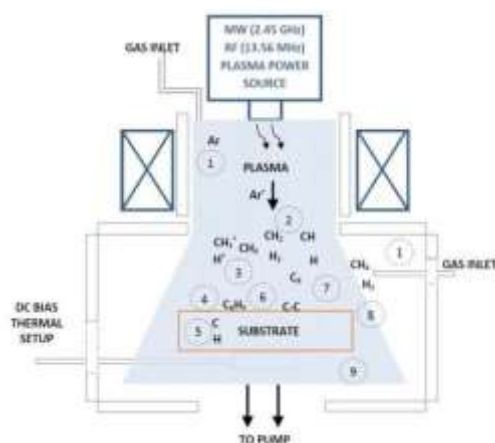


Figure.-11(b) Schematic diagram of Thermal CVD a) and Plasma Assisted CVD b) process: case of graphene from CH₄/H₂ mixtures.

Mixture of monolayer and few layers (polygraphene) was obtained. On the other hand, it was shown that Cu is an excellent candidate for making large area, uniform thickness (95%) single layer graphene films due to the low solubility of C in Cu [165]. It was

suggested and even demonstrated that the graphene growth on Cu is somehow surface mediated and self-limiting.

Processing steps

- **Heating step:** heating in controlled atmosphere the catalyst-substrate and gases (in hot wall reactors) up to the pre-process temperature.
- **Annealing step:** Maintaining the temperature and gas atmosphere so reducing the catalyst surface. This is the first chemical reaction of the whole process. It is performed to clean the catalyst surfaces and modify, as possible, the surface morphology including crystalline orientation, roughness (smoothing) and grain size of the metal catalyst. Metal evaporation should be avoided as possible.
- **Growing step:** Introduction of new precursors and growth of graphene over the catalyst substrate. During the growth process there are different strategies to growth the graphene film. There are one-step processes or manystep processes. During the steps is possible to modify the pressure or mix of gases, residence time, T, gas flow...It is important to take into account that depending on the nature of the catalyst (solubility, catalytic action and so on), the graphene may grow during this step or in the next one.
- **Cooling step:** After the growing step, the next step is cooling the reactor in proper atmosphere. The atmosphere commonly used is similar to that of the annealing or growing step, until the reactor temperature is under 200°C to prevent oxidation of the catalytic surface not covered or graphene functionalization with oxygen containing groups. When working with high solubility substrates, cooling step dynamics is critical to control the growth due to the solubility dependence.
- **Final step:** Backfill with inert gases (Ar, N) up to atmospheric pressure and open the reactor chamber.

Growth kinetics and reaction mechanisms

Hydrocarbon based reactants, being methane (CH₄) the most mentioned, were commonly used as C source. Due to strong C-H bonds in methane molecule (440 kJ/mole) its thermal (non-catalytic or non plasma activated), decomposition (step 2 in fig. 1) occurs at very high temperatures (>1200 °C) [174]. This high temperature is not easily obtained in a typical thermal CVD setup. To reduce the temperature of methane's decomposition different transition metal catalysts (e.g., Fe, Co, Ni, Cu) were widely used. This catalytic behavior is observed when growing CVD graphene on metals at low temperatures (<900°C) in a greater or lesser extent. Therefore, non catalytic activation can be considered negligible working in thermal systems [175]. On the other hand, in the case of plasma assisted CVD, the activation and decomposition of gases prior to reach the substrate is effectively performed, but surface diffusion is a thermal-mediated process and plays a fundamental role in growth kinetics.

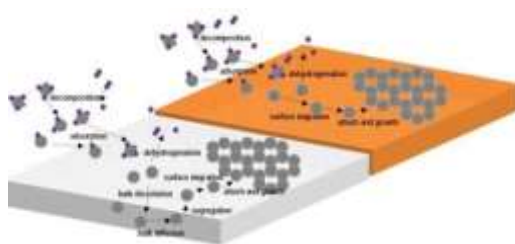


Figure:-12. Growth kinetics in CVD graphene on different catalyst: Case of CH₄ on Ni and Cu.

As the graphene synthesis process is a heterogeneous catalytical chemical reaction, the metal performs the two different roles of substrate and catalyst. Therefore, in a typical thermal catalytic CVD, the film grown over metal substrate reduces the catalytic activity due to the catalyst poisoning. This should announce the end of the reaction and the graphene film formation. If the overall process is performed on the surface (adsorption, decomposition and diffusion of molecules), monolayer graphene is preferentially grown. This is known as “selflimiting” effect and was only observed in Cu to date (and also depending on the process conditions). On Ni and other common transition metals (Co, Ru, Ir, etc.,) it was demonstrated that CVD growth of graphene occurs by carbon bulk diffusion due to the high solubility of carbon and segregation (figure 12) during cooling step. In this latter case, solid solution of a mixture of elements is formed near surface and the resulting graphene depends on the kinetic parameters selected for the synthesis. Among all the thermodynamic parameters, a fast cooling rate seems to be a critical factor to suppress the formation of multiple graphene layers [175, 176]. More complex deposition process results when an extra gas phase activation (decomposition by plasma or very high, >1200°C, temperature in figure. 2) is performed. In this case the chemical reaction evolves to a mixture of heterogeneous catalysis and decomposition in vapour phase. Then the reaction cannot be considered as totally controlled by the catalyst.

The use of carbon isotope labeling technique in conjunction with Raman spectroscopic mapping [177,178] demonstrated effectively different kinetic behavior of CVD growth of graphene on Ni and Cu. By this technique was possible to track carbon during the growth process. The two different mechanisms of graphene growth observed on Ni and Cu can be understood from the C-metal binary phase diagram, being the most important difference that solubility of C in Cu is much lower than that in Ni. Only small amount of carbon can be dissolved on Cu. The source of C is mainly CH₄ that is catalytically decomposed (dehydrogenated in fig.2) on the Cu surface. This route facilitates surface migration and monolayer graphene growth. Experiments with high temperature cycles performed on graphene films of approximately 0.5 monolayer coverage on Cu while continuously imaged using LEEM (Low-Energy Electron Microscopy) confirmed this demonstration [179]. No C precipitation or island growth was observed during cooling in agreement with preliminary reports, suggesting that the process is confined to the surface, with negligible dissolution and precipitation of C from the substrate.

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