

# Progress in Synthesis of Graphene using CVD, Its Characterization and Challenges: A Review

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**Abstract:** Diamond and Graphite both are natural allotropes of carbon. Graphene is a substance composed of  $sp^2$  hybridized carbon atoms that are similar to graphite and arranged in a regular hexagonal pattern. Graphene has astounding physical properties such as high electronic conductivity, excellent mechanical strength and thermal stability. It is capable to maintain its strength up to  $3,600^\circ\text{C}$ . It is transparent, high super hydrophobicity at nanometer scale, 100 times stronger than steel with high current density. These unique properties make graphene an interesting candidate for a number of applications currently under development, as for instance Li-ion batteries, transparent touch screens, light weight aircrafts or transistors.

Amongst the synthesis techniques, chemical vapor deposition has proved promising result for advance devices and for numerous applications where high-quality graphene films, High purity, fined grained and low structural defects film is required. CVD process is normally conducted below the atmospheric pressure and relatively lower temperatures, less than  $1000^\circ\text{C}$ . Pressure of LPCVD is 10-1000 Pascals.

**Keywords:** CVD, Graphene, Graphite, Graphene sheets.

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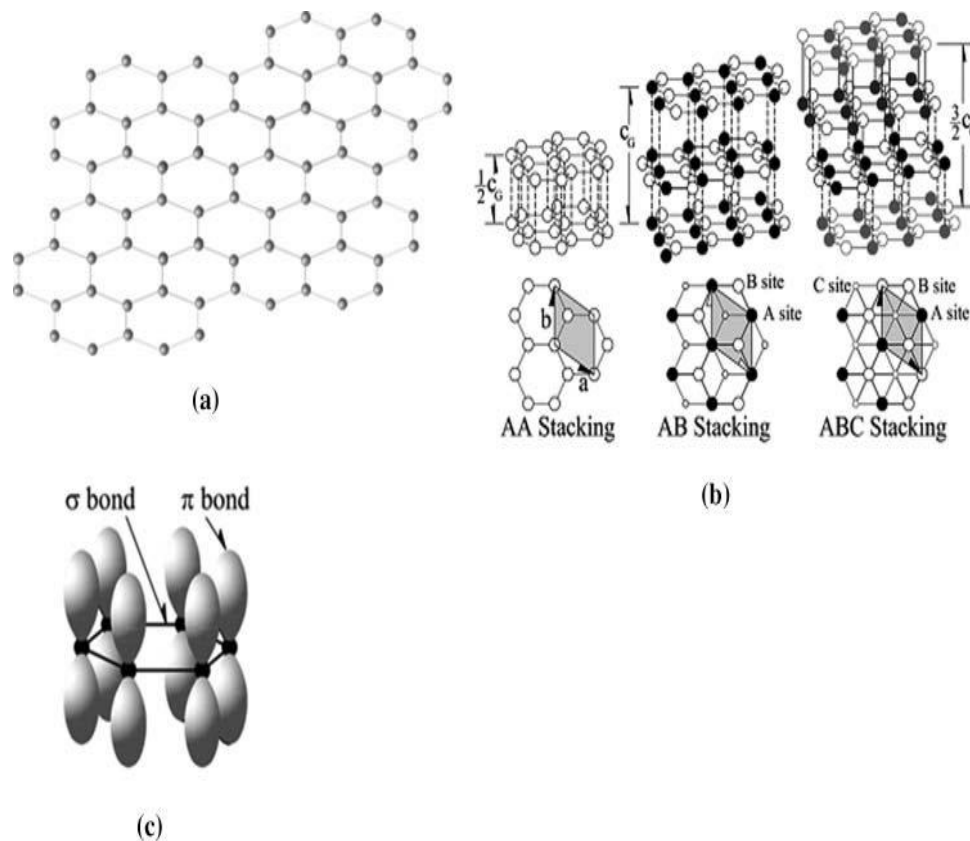
## I. INTRODUCTION

Graphene is a two dimensional and single layer sheet having  $sp^2$  hybridization. 3 million graphene sheets are combined to form 1mm thick graphite. Graphite is 3-D network of graphene. Graphite powders are used as raw materials for bulk production of graphene sheets [1]. Graphene have opened up a vast area, when combined with synthetic materials that are highly resistant and very light weight 0.77 mg. Intrinsic graphene is characterized as a zero gap semiconductor and its remarkable high electronic mobility of  $15,000\text{cm}^2\text{V}^{-1}\text{s}^{-1}$  [2]. These peculiar properties make the graphene an interesting candidate for numerous applications in flexible electronic devices, solar cells, biosensors organic photovoltaic cells, Li-ion batteries or organic light emitting diodes (OLED).

Its exemplary electronic property produce a superlative monolayer with low absorption ratio of 2.3% [3]. Graphene lacks a zero band gap around the Fermi level. Hence almost all the electron will shift from the valance band to conduction band; hence the material behaves as superconductor. Several schemes have been proposed to tune the band gap of the graphene [4]. The corresponding resistivity of the graphene layer is  $10^{-6}\text{ohm.cm}$ , which is quite less than that of the silver known for low resistivity. It have very low Johnson noise allowing them to replace silicon in the field effect transistors (FET) [5].

## II. HISTORY OF GRAPHENE

It was known graphite is a layered structure and can exfoliated by various method in 1800's. Acheson, a famous chemist had developed different exfoliation methods that he called de-flocculation to create colloidal suspensions of small graphite flakes [6,7]. Whereas, In 1859, "B.Collins Brodie" was aware of highly lamellar structure of thermally reduced graphite oxide using nitric acid and potassium chromate.



**FIG. 1 (a) Graphene structure of single two-dimensional hexagonal sheet of carbon atoms, (b) three most common structures and stacking sequences of graphene and (c) Schematic of the in-plane  $\sigma$  bonds and the  $\pi$  orbitals perpendicular to the plane of the graphene sheets [8]**

The structure of graphene was solved in 1916, by related method of powder diffraction which was done by V. Kohlschutter and coworkers in 1918, who also discover the properties of “graphite oxide”. However, the theory of graphene was firstly discovered in 1947 by P.R Wallace, as a starting point for understanding the electronic property of 3D graphite. H. P Boehm identified that by reducing it with hydrazine, mono layers of graphite oxide can be reduced to graphene in 1962 [6,9]. Then he also recognize the thickness of graphene layers using Scanning electron microscopy, X-ray scattering. Further in 1975, Van Bomme also studied that while heating the silicon carbide in vacuum, the layers of graphite are formed [10].

In 2004 **Kostya Novoselov and Andre Geim** extracted single-atom-thick crystallites from bulk graphite at the University of Manchester. The graphene layers were pulled from graphite and transferred them onto very thin Silicon dioxide which is present over a silicon wafer in a process called either **Scotch tape technique or micromechanical cleavage**. They received numerous awards for their pioneering research on graphene, notably the **2010 Nobel Prize** in Physics [1,11].

### III. PROPERTIES OF GRAPHENE

Graphene have outstanding thermal, electrical and mechanical properties

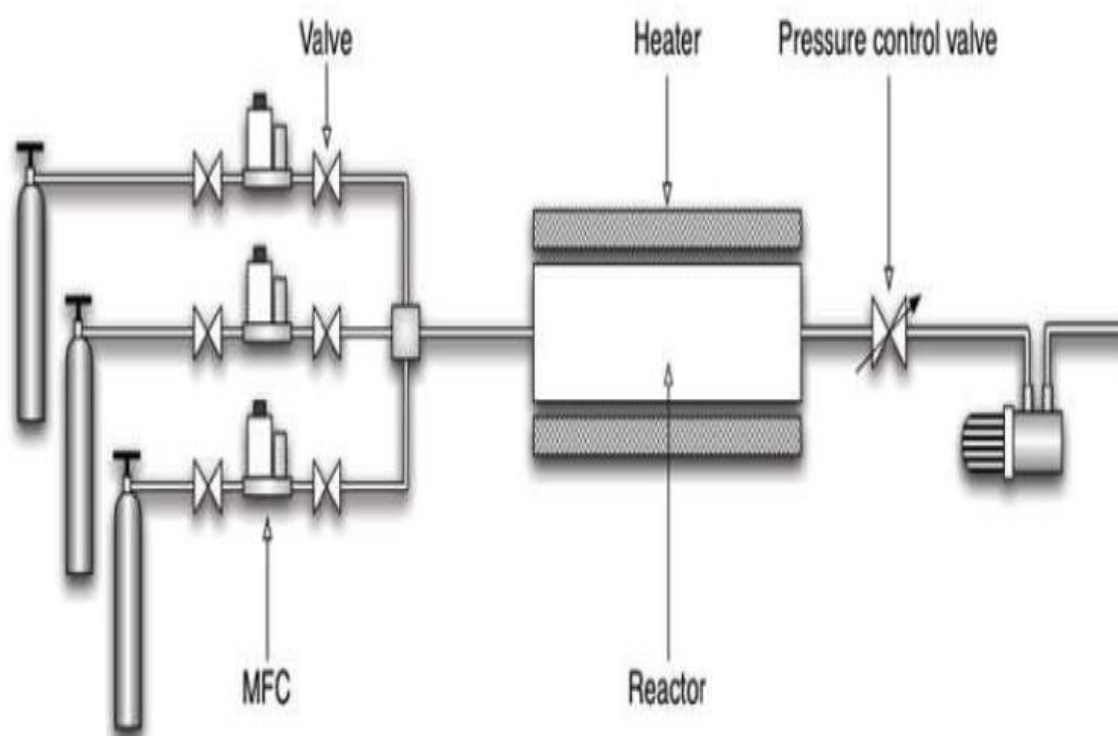
**3.1 Electrical properties:** The most interesting property of graphene is electrical property. When used as a filler in various polymers then graphene immensely embellish the electrical conductivity of composites. The filled polymer materials display a non-linear increase of the electrical conductivity as a function of the graphene based filler concentration. Graphene has high electrical properties because it has a zero band gap and high charge carrier mobility, for which the value of  $10,000\text{cm}^2/\text{v}^{-1}\text{ s}^{-1}$ . The electrical conductivity of thermally reduced GO has higher than of chemically reduced GO due to the absence of oxygenated functional groups[12].

**3.2 Mechanical properties:** Mechanical properties of graphene depend upon vander wall and hydrogen bond interaction. Graphene is 200 times stronger than steel and its intrinsic is (1TPa) and elastic modulus is (125GPa). It is stretchable up to 30% from its original length. There is increase of 76% tensile strength of GO with increase of 0.7% and also 62% of young modulus of the graphene based devices. The study erect that irregularities of graphene appears due to penetration of chemical groups and this allow graphene to powerfully interlock with molecules to avoid and reduce slippage [13].

**3.3 Thermal properties:** The thermal conductivity of any graphene based material depends on the lattice vibrations, if the lattice vibrations are more graphene has large thermal conductivity. Graphene (3,000 W/mK , at room temperature) is a material used to improve the thermal conductivity and thermal stability of the material. It is found that a small amount of graphene can considerably increase the thermal properties of polymer composites. Due to highly conductive nature of graphene and ease of inclusion into polymers and ceramics better choice for transparent conductors to increase conductivity and to make flexible devices by replacing silicon based devices[14].

#### IV. SYNTHESIS OF GRAPHENE USING CVD METHOD

Graphene can be synthesis from the various methods but one of the best practical methods for synthesis of graphene is CVD (Chemical Vapor Deposition) method. Growth involves thermal decomposition of hydrocarbons and also discharges over the substrate [15,16]. CVD follows the efficient “bottom up” approach. Chemical vapor deposition has proved promising result for advance devices and for numerous applications where high-quality graphene films, High purity, fined grained and low structural defects film is required. CVD process is normally conducted below the atmospheric pressure and relatively lower temperatures , less than 1000°C. [16]. LPCVD is being used which helps to avoid the unwanted reactions and produce more uniformity of coating on substrate. Pressure of LPCVD is 10-1000 Pascals.



**Fig. 2 The schematic diagram of a typical tube-furnace CVD system. Gas flows are regulated by MFCs, and fed into the reactor through a gas-distribution unit [17,18]**

Here, LPCVD is used that provide uniformity over the coating on the substrate and prevent unwanted reactions in the chamber. Mass Flow Control (MFC) is used to regulate the gas flow. These gases are fed into the reactor over which substrate is placed at temperature 800°C.

## V. GROWTH MECHANISM

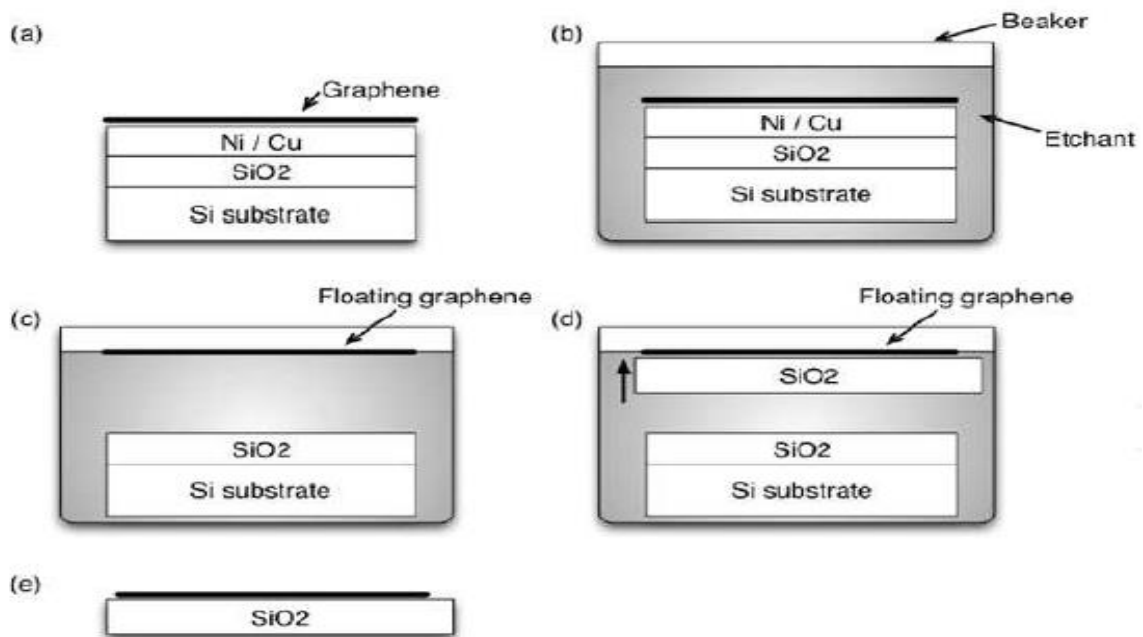


Fig.3, Schematic diagram of the etching and scooping method without using a support. (a) The CVD-grown graphene on Ni or Cu catalyst. (b) The graphene sample is submerged into the metal (Ni or Cu) etchant. (c) The Ni or Cu is etched and the graphene is floating on the etchant surface, while the remaining SiO<sub>2</sub> and Si substrate sinks to the bottom of the beaker. (d) Another SiO<sub>2</sub> is used to scoop the floating graphene out of the etchant. (e) After drying, graphene is sitting on SiO<sub>2</sub>, ready for future processing [17].

## VI. GRAPHENE SYNTHESIS

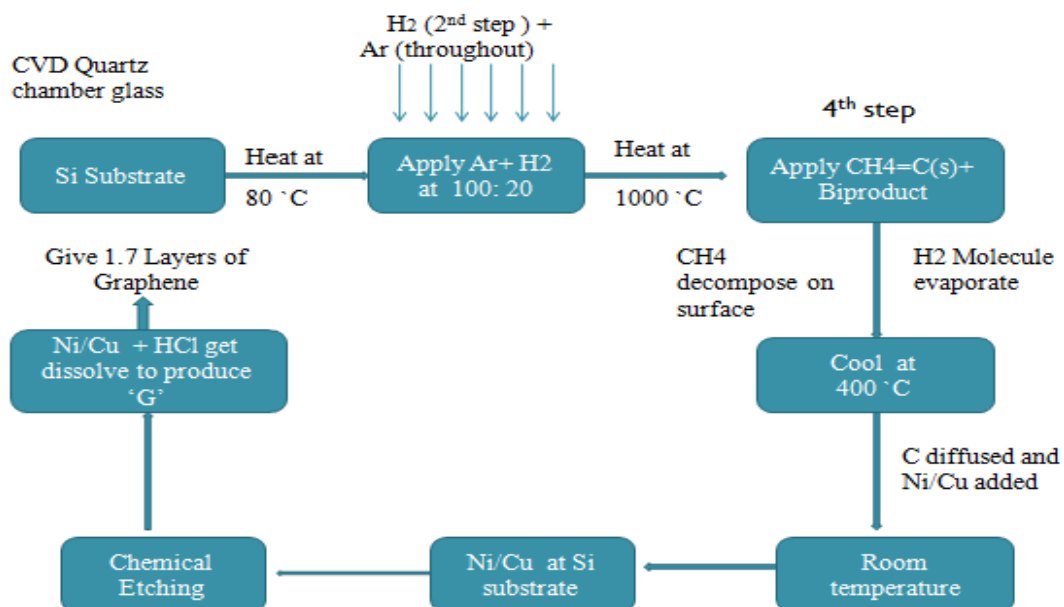


Fig.4, Detailed mechanism for synthesis of graphene growth on Ni/ Cu layer with SiO<sub>2</sub> substrate [19].

Amongst all the synthesis method, Graphene has proved the leading method for amalgamation of graphene. Over this method, Quartz is placed in the substrate at 800°C. After applying H<sub>2</sub> and Ar at 100:20 SCCM, heat the reactor at 1000°C. Methane gas decomposed over the Si substrate, H<sub>2</sub> evaporates. The process involves growing graphene films on different types of substrate that utilize transition metals like copper (Cu) or nickel (Ni). This involves the diffusion of decayed carbon atoms into nickel or copper at a high temperature, followed by the discernment of carbon atoms on the surface of the nickel/ copper during the cooling process.

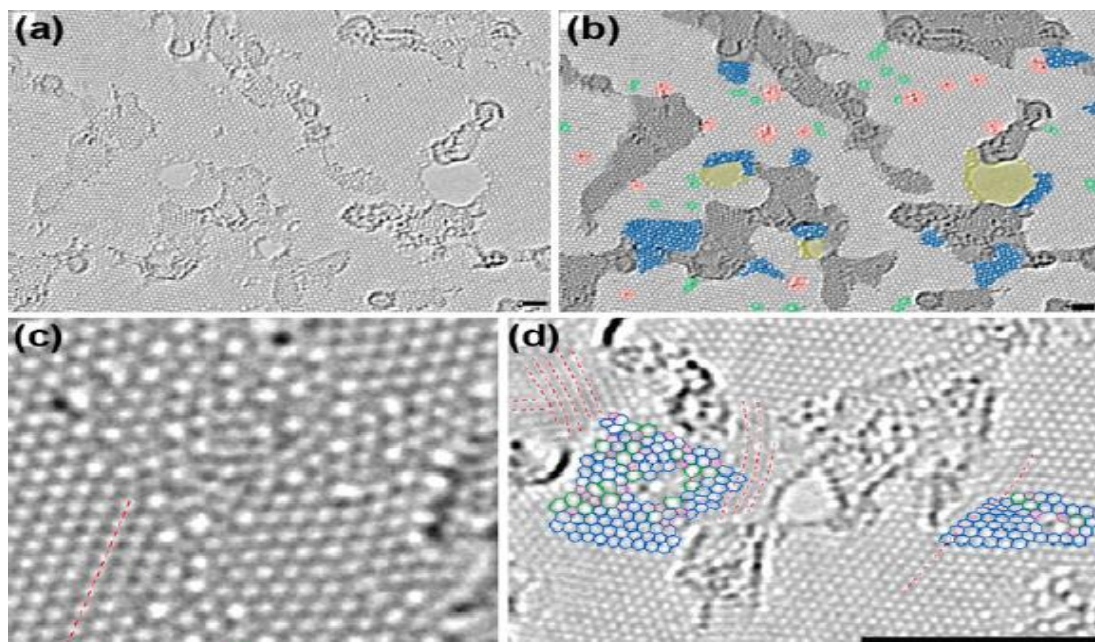
From the research, it is concluded that in Ni layer, additional time is required for carbon atoms to reach their saturation state. During the super saturation state, the carbon atoms get segregated over the Ni layer. After cooling the film at temperature from 900°C to 725°C, over the Ni film, 1.7 layers of graphene is obtained.

## VII. CHARACTERIZATION TECHNIQUE

These are the techniques which are used to examine the various aspects of graphene. It identifies **number** of layer, wafers, flakes its alignments, vibration modes micro dents or defects etc. These can be done via basic techniques like Transmission electron microscopy (TEM), SEM (Scanning Electron microscopy), Raman spectroscopy, Atomic force microscopy, X-ray diffraction (XRD).

### 7.1 Transmission Electron Microscopy (TEM)

It is a microscopy technique in which electron beam is propagated through the specimen and after interaction, on the layer of photographic film or fluorescent screen a focused and magnified image is formed which is being detected by sensors. In 1986, Ruska was awarded the Nobel Prize in physics for the development of transmission electron microscopy. TEM can able to imaging very high resolution up to 10<sup>9</sup> molecules.

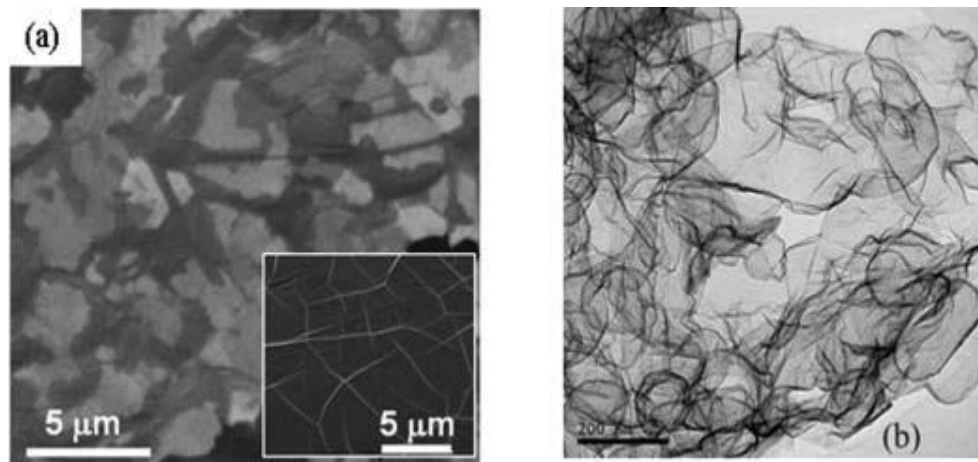


**Fig.5, Atomic resolution, aberration-corrected TEM image of a single layer H-plasma-reduced-GO membrane [20,21]. (a) Original image and (b) with colour added to highlight the different features, (c) atomic resolution TEM image of a non periodic defect configuration, (d) partial assignment of the configurations in defective areas, the inset shows a structural model showing clearly the strong local deformations associated with defects. All scale bar 1 nm.**

### 7.2 Scanning Electron Microscopy (SEM)

It is a type of microscopy technique, which produce 2-D image of a sample. SEM can capable of imaging 10<sup>3</sup> molecules. When focused beam of high energy electron is transmitted, variety of signals of specimen is generated. It is also able to analyze the particular points and location on the sample.





**FIG. 6** (a) SEM images of as-grown graphene films on thin (300-nm) Ni layers and thick (1-mm) Ni foils (inset)[22,23], (b) HRTEM image of few layered graphene, showing individual graphene sheets with the edges of the graphitized layers [22,24]

### VIII. CHALLENGES

Using CVD method, it is possible to create high Purity, fine grained and low structural defects are obtained, but stumbling block is successful exfoliation of film from the Si substrate. It is strenuous to obtain separation without affecting its properties or also damaging its structure. The second major challenge is its Band gap opening. Due to ballistic charge transport of electrons the band gap of graphene material around Fermi level became zero.

Another problem of implementing this technique is its wider cost. There is generation of corrosive and toxic gases during the CVD process, which is injurious to health as well as environment. It is also difficult to create monolayer and uniform layer of graphene on a substrate.

### IX. CONCLUSION AND FUTURE OUTLOOK

Graphene has proven the promising solution and compile the meaningful result around the world. It is concluded that due to the absence of oxides in the graphene, its conductivity is very high. By applying appropriate temperature, pressure and flow of gases, monolayer graphene is obtained. Using CVD method, 1-2 layers of graphene is formed which is highly transparent and crystalline. As the building block of carbon, graphene exhibits excellent electronic, mechanical, optical and thermal properties.

Due to emergence of graphene and its these ballistic properties, it has been used in advance devices of micro, nano scales or for numerous applications. In Aerospace for strong and light weight aircrafts. Graphene Coating on glass, prevent it from corrosion. It is also used in transparent & flexible touch screens, organic light emitting diodes OLED's and Super-capacitors.

Scientists are working on replacing the silicon in transistors and electronics equipments with graphene. Increasing the efficiency of electric batteries by coating with graphene. Scientist have demonstrated that mechanically enhanced silk fibers could be naturally produced by feeding silkworm with diet of mulberry leaves coated with Single walled graphene.

### REFERENCES

- [1] S. Sheshmani and M. A. Fashapoyeh, (2013), "Suitable Chemical Methods for Preparation of Graphene Oxide, Graphene and Surface Functionalized Graphene Nanosheets", vol. 60, no.4, pp. 813–825.
- [2] K.S Novoselov, A.K. Geim et al.(2004), "Electric field effect in atomally thin carbon films", Science, Vol.306, no. 5696,pp. 666-669.
- [3] A. B. Kuzmenko, E. V. Heumen, et al.(2008), "Universal dynamic conductance of graphite", Phys. Rev. Lett., 100, 117401.

- [4] Richard Balog, Louis Nilsson,(April 2010), “Bandgap opening in graphene induced by patterned hydrogen adsorption,” *Nature Mater., Lett.*, vol. 9.
- [5] A.K. Geim, and K. S. Novoselov, (2007), “The rise of graphene”, *Nature Mater.*, vol.6,no. 3, pp. 183 - 191 .
- [6] Walt A. de Heer, (Aug. 2011), “The Development of Epitaxial Graphene For 21st Century Electronics”, *MRS Medal Award paper Boston*, vol. 36, issue 08.
- [7] E. Acheson, “Deflocculated graphite”. *Journal of the Franklin Institute*, vol.164, issue 05, pp. 369-372
- [8] J. Hass, W. A. de Heer, et al.,(July 2008), “The growth and morphology of epitaxial multilayer graphene”, *Journal of Phys. Cond. Matter*, , Art.323202, vol. 20, no. 32.
- [9] H. P. Boehm, U. Hofmann, et al., (1962) “Dunnste kohlenst off- folien”, *Z. Naturforschg*, vol. 17, pp. 150–157.
- [10] V. Bommel, A. J., Crombeen, et al., (1975),“A. LEED and Augerelectron Observations of the SIC(0001) Surface”, *Surface Science*, vol. 48, pp. 463-472.
- [11] M. S. Dresselhaus, G. Dresselhaus,(2002), “Intercalation compound of graphite”, *Advances in Physics*, vol. 51, no. 1, pp. 1-186
- [12] R. Verdejo , L. Romasanta, et al. (Nov. 2011),“Graphene filled polymer nanocomposites”, *Journal of Material Chemistry*, vol. 21, no.10 , pp-3301-3310.
- [13] D. P Richard, S. Ruoff Rodney, et al., (2010), "Mechanical properties of monolayer graphene oxide", *American Chemical Society of Nano*, vol. 4, no. 11 , pp-6557-6564.
- [14] D. Verma, P.C Gope, et al.,(Dec. 2014), "Mechanical-Thermal-Electrical and Morphological Properties of Graphene Reinforced polymer composite : A Review”, *Trans Indian Inst Met*, vol. 67, issue 06, pp.803-816.
- [15] N. Alexander Obraztsov, (2009), “Chemical vapor deposition : making graphene on a large scale”, *Nat. Nanotechnol.* Vol. 4, no. 4, pp. 212-213.
- [16] L. Yuan and N. Chopra, (Dec. 2014), “Progress in Large-Scale Production of Graphene Vapour Methods”, *Journal of The Minerals, Metals and Materials research society*, vol. 67, no. 1.
- [17] M. Congqin, Z. Churan, et al., (Apr 2011),“Chemical Vapor Deposition of Graphene”, *Nanotechnology and Nanomaterials*, “Physics and applications of graphene” *Intech*, vol. 3, pp. 217-307, 953-978.
- [18] S. Hussain, W.I. Muhmmad, (2014), “Physical and electrical properties of graphene grown under different hydrogen flow in low pressure chemical vapor deposition”, *Nano research letters*, vol. 9, pp.546.
- [19] S. Mizuno et al.,(2010), ”Chemistry of CVD on Ni layer”, *Journal of American Chemical Society Nano*, vol.4, no. 12, pp. 7407- 7414, 2010.
- [20] C.G. Navarro, J.C. Meyer, et al., (2010), “Atomic structure of reduced graphene oxide”, *Nano Lett.* vol.10, no.4, pp.1144-1148.
- [21] P. Songfeng and H.M Cheng et al., (Aug. 2012),“ The reduction of graphene oxide”, *Journal of Carbon*, vol. 50, no. 9, pp. 3210-3228.
- [22] I. Lahiri , R.G. Seelaboyina et al.,(2010), “Synthesis of Graphene and Its Applications: A Review,” *Journal of Critical Reviews in Solid State and Materials Sciences*, vol.35, no. 1, pp.52–71.
- [23] K. S. Kim, Y. Zhao, et al., (Feb. 2009), “Large-scale pattern growth of graphene films for stretchable transparent electrodes”, *Nature*, vol. 457, pp. 706-710.
- [24] X. Wang, H. You, et al., (2009), “Large scale synthesis of few-layered graphene using Chemical Vapor Deposition”, vol. 15, pp. 53-56.