Extraordinary properties of Graphene: What makes it so powerful?

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Abstract:

According to the famous Moore's Law "In an integrated circuit the number of MOS transistors doubles every two years". But unfortunately, the time has come when the silicon transistors technology is inescapably approaching to its substantial limit. As the feature size of components on a single chip increase beyond a certain limit, the cost increases. Graphene is a promising hope as an entire circuit can be fabricated onto graphene sheet and the contact resistance and noise issues in the conventional silicon technology can be avoided. Being more conductive and less corrosive than copper, graphene has been chosen as interconnects in place of copper. Of all the carbon made materials, graphene seems to be the most talented due to its exceptionally excellent properties. In plastic industry, graphene has been incorporated with polymers which have environmentally friendly properties. To overcome the degradation of device performance graphene has been proposed as a potential candidate owing to high electron mobility, ballistic transport and stable character. In addition to this, graphene is approximately 200 times more resistant to fracture than steel therefore can be folded as many times as required without breaking. A graphene sheet is a million times thinner than a hair so can be inserted in multi-stack devices without altering its physical dimensions yet providing all its benefits. Furthermore, graphene is impermeable to most of the gases therefore can be used as shields to protect corrosive materials. Hence it is imperative to understand the discerning properties and transport behavior of charge carriers in graphene. This paper discusses the properties of graphene that make it so extraordinary.

Keywords: Graphene, Properties, Nanomaterials, Quantum Effect, Fermi Level, Klein, Dirac, Fluorographene, Young's Modulus, Conductivity.

1. INTRODUCTION

Small things have great potential and therefore interest in the area of nanomaterials has developed due to their suitability for the miniaturization of things, which yield electronic gadgets like laptops, touch screens, tablets and i-pads in place of huge desktop computers. The enormous interest in these materials is originated from the fact that: as the dimensions reduce, (a) the surface to volume ratio increases (b) distinctive chemical, electronic, optical and physical properties are observed and (c) material shows quantum confinement effect. There is a need to further miniaturize the structure and the technology involved may be coined as Nanotechnology [1]. In nanoscale, the major role is played by the surface atoms. Moreover, at nanoscale the properties also differ considerably from its corresponding bulk matter. This can be understood with the example of aluminum(Al), which is perfectly safe when used as bulk but nano-sized aluminum is reported to be highly explosive [2]. Nanotechnology is the area, which is used to fabricate and study the exploitation of substance at an atomic and molecular scale (in the range of 1-100nm). Owing to these exclusive properties at nanoscale, this technology shows interdisciplinary applications in a variety of fields shown in Fig. 1.

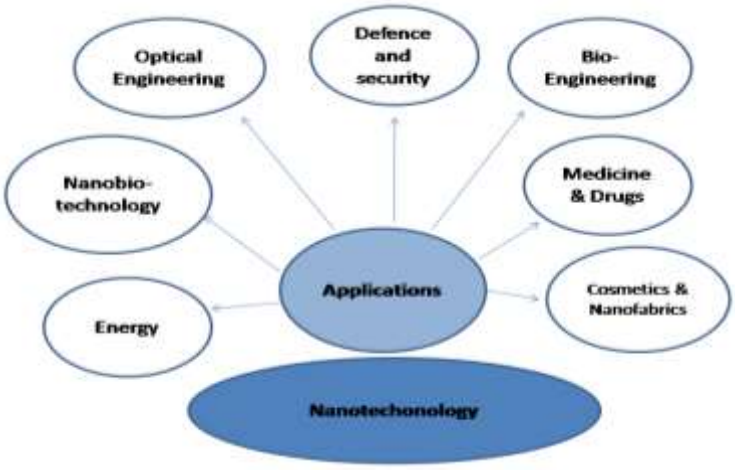

Fig 1: Various applications of nanotechnology

In low dimensions, various forms of carbon, predominantly graphitic nanomaterials have generated enormous interest in the recent years as a consequence of their distinctive properties [3-5]. Graphene (monolayer exfoliated from 3D graphite) is elected as a potential candidate, among a variety of carbon forms for low dimension electronic devices. This is attributed to the unique electronic properties [6] of graphene such as high electron mobility, ballistic transport, planar 2D structure and ease of availability. Also, it is compatible with silicon technology. Graphene is one of the thinnest (a million times thinner than paper), strongest and stiffest (Young's modulus of ~ 1.2 TPa) objects imaginable yet having an absorption of 2.3% [7]. Besides this, the thermal and electrical conductivity (mobility: 200,000 $cm^2V^{-1}s^{-1}$) is found to be highest in graphene. Scattering is negligible in the case of graphene thereby providing ballistic transport and allowing the Quantum Hall Effect (QHE) to be observed in graphene with a new twist [8, 9]. Owing to relativistic nature Klein tunneling is also observed. This paper reports the peculiar properties of graphene owing to which graphene is the most suited candidate for numerous applications. Here, we aim to introduce some of these unique properties of graphene to justify why it has gained this much popularity.

2. ELECTRONIC/ELECTRICAL PROPERTIES

The huge research interest developed so far in the field of graphene has been mainly driven because of its unique electronic properties which include following points:

- "*Conductivity even with zero charge carriers*": Minimum quantum conductivity has been predicted for Dirac fermions by both theoretical as well as experimental studies. Graphene's chiral nature and linear spectrum in pristine intrinsic graphene are responsible for the presence of conductivity despite of zero carrier concentration at neutrality point. However, in graphene supported by silicon wafer (SiO_2/Si), charged impurities arrested in the substrate, in the interface of graphene/SiO_2 and on the surface of graphene are accountable for this. In spite of the vanished carrier density at Dirac points, a minimal conductivity of order $4e^2/h$ [10] exists in graphene. To summarize, the fluctuations in graphene's electrostatic potential due to the existence of disorder in graphene (ripples, impurities, and defects) provides a minimum conductivity.

Ambipolar Nature: Another significant feature of pristine SLG which makes it different from other conventional semiconductors is that the Fermi Level at room temperature can be tuned above or below the Dirac point by applying necessary gate voltage (Fig 2). This is achieved by supplying a positive bias (negative bias) hence increasing electrons (holes) in conduction band (valance band) with the occurrence of a charge neutrality points (CNP) at zero-gate voltage. This unique characteristic is called ambipolar nature of graphene and can be utilized in device industries. However, for extrinsic graphene (practically used graphene), the point of neutral charge (CNP) is found to be shifted in reference to the zero voltage because of the unintentional doping from the environment. Some of the molecules such as water tend to accept the electron (making graphene p-type) and some such as gold, Ti contact metals tends to donate electron (making graphene n-type). The CVD graphene used in our case is p doped.

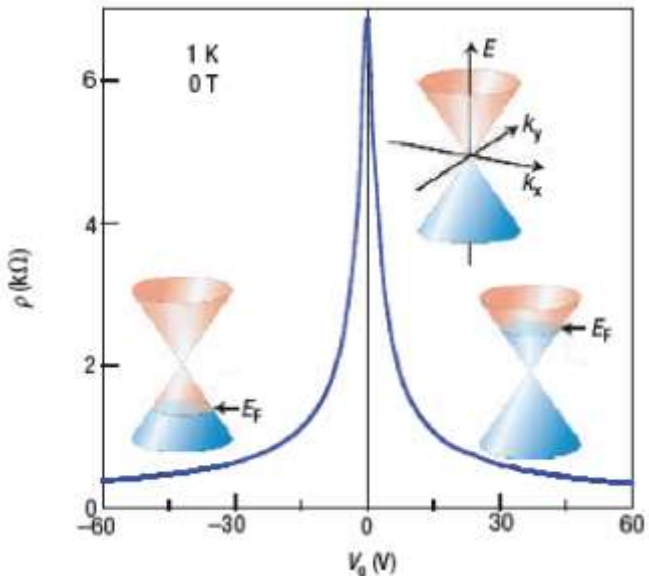

Fig 2: Figure showing ambipolar nature of single-layer graphene. Fig also depicts variations in the position of the EF of the Fermi energy with applying positive or negative gate voltage Vg [11].

- *Quantum Hall effect:* According to the prediction of E.H. Hall, "when a magnetic field is applied perpendicular to the direction of a current flowing through a metal, a potential difference (Hall voltage) is developed in the third perpendicular direction due to the Lorentz force". A most favorable technique for the calculation

of conductivity, mobility and carrier concentration is the Hall Effect measurements. However, in pristine SLG the Hall Effect is also observed as a series of equidistant steps in the Hall conductivity σ_{xy} as a substitute of the monotonic increase. The resistance is quantized. This is known as QHE and has been observed in good quality, large scale CVD grown graphene but at very high magnetic field (~14 T) or very low temperatures (~ 1.6 K) [12]. on to comprehend the electrical transport properties of CVD graphene. The large size graphene is possible only with the CVD technique which is the requirement of industries.[13]

- *Klein tunneling:* In conventional semiconductors, when an electron encounters a electrostatic potential barrier with a energy which is less than the barrier height, quantum mechanics predicts that the probability of the electron to tunnel the barrier is finite which keeps on decreasing exponentially as the barrier become more taller and wider. This is because of the decay of electron wavefuction inside the barrier. But this is not true in the case of massless Dirac fermion particles which are governed by Dirac equation. Here, the scene is reverse; the transmission probability in fact increases with the increase of barrier height. This paradox is Klein Paradox. Dirac electron will convert into a hole on striking a high potential barrier and will cross the barrier, then emerge as an electron again on the other side of barrier. This is known as Klein tunneling. This phenomenon is accredited to the fact that higher is the height of barrier, better is the mode matching between the wave functions of electron outside and hole inside the barrier. Hence the probability of transmission increases as the height of the barrier increases, accomplishing unity for an infinitely tall barrier.

3. OPTICAL PROPERTIES

Graphene has been reported to be the thinnest possible material ever made yet can be viewed through bare eyes. Now coming to the optical absorption spectra, graphene is found to absorb a noteworthy ($\pi\alpha$ = 2.3%, here, $\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$ and is defined as the fine structure constant and c is the speed of light) fraction of light coming in the IR-to-visible scope. [14]

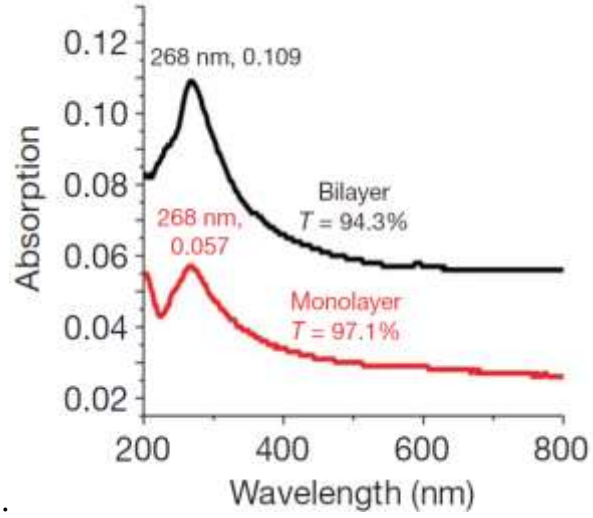

Fig 3: Absorption spectra of single layer and bilayer graphene in UV-Vis region showing absorption peak at 268 nm. The transmittance percentages are also shown measured at 550 nm (Fig adapted from paper [15]).

A transmittance of 97.1% at 550nm wavelength can be seen from the Fig 3 for monolayer graphene. However, a transmittance of 94.3% (at 550nm) is indicated by bilayer graphene [15]. This results from its unique band structure.

Owing to such a high transparency of graphene, it is hard to identify it on the majority of the substrates. For enhancement of the visibility of graphene flakes, it may be deposited on to silicon wafers which have a 300nm thick silicon dioxide layer. Graphene's optical image is shown in Fig 4 in which up to SLG is clearly visible in Fig 4(a), but even 3 layers are barely visible in Fig. 4(c). This is similar to the "rainbow effect".

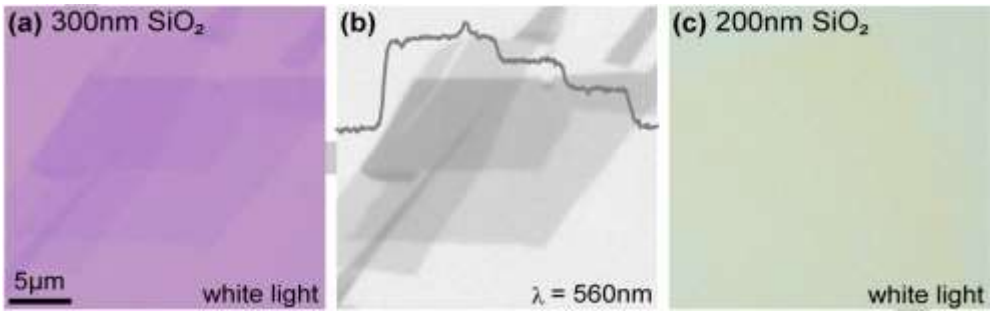

Fig 4: Microscopic image of graphene flake (a) on 300 nm SiO_2 (with white light), (b) green light and (c) on 200 nm SiO_2 (with white light). [16].

The optical path difference between the light reflected from the SiO_2/Si and graphene/SiO_2 interface makes graphene visible due to the optical interference between them and this dependent on the thickness of the oxide layer as depicted in Fig 9 [16, 17]. Moreover, Graphene's unique optical properties formulate it into a propitious suitor for various implementations in photonics and optoelectronics.

4. CHEMICAL PROPERTIES

It is likely that graphene (two-dimensional structure means huge surface to volume ratio), similar to CNT, provides a wide space (binding sites) to the foreign atoms and molecules which can be absorbed or desorbed on it. Some absorbates act as a donor by donating its electron to graphene sheet whereas some accepts an electron from graphene sheet and becomes a negatively charged acceptor [18]. In this process the graphene local carrier concentration changes thereby making graphene highly conductive. This function of graphene can be used for chemical or gas sensors applications.

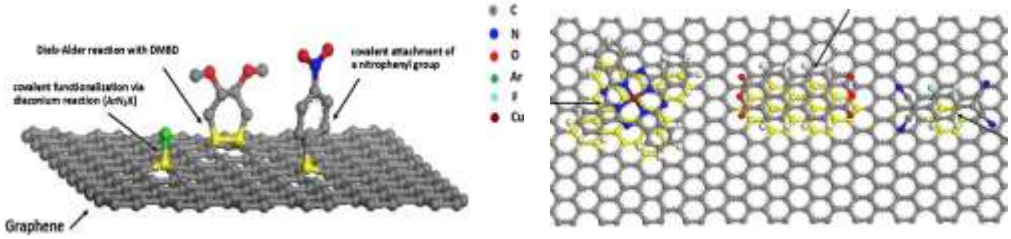

Fig 5: Illustration showing difference between (a) covalent and (b) non-covalent functionalization of graphene [18]

It may be noted that graphene has inert nature thus does not want to react eagerly until exposed to sensibly cruel reaction circumstances. Though graphene is comparatively inert, both covalent and non-covalent techniques can be implemented to make graphene chemically functionalized (Fig. 5). Covalent functionalization involves the conversion of sp^2 into sp^3 bonds via a series of reactions while the non-covalent functionalization involves Vander Waal forces. In covalent method, the structural properties as well as the electronic properties

change, for examples 1) graphene changes to graphene, which shows insulating behavior during the reaction with atomic hydrogen 2) fluorographene is formed during the reaction with fluorine. In the non-covalent method the bonding is weaker in strength π-π stacking and graphene 's basic properties are maintained because the sp^2 network of graphene remains undisturbed [18]. Moreover, SLG is more reactive than bi-, tri- and multilayer graphene. Graphene's edge is much more reactive than the lateral surface.

5. MECHANICAL PROPERTIES

These properties can be estimated by the following criteria for any material: tensile strength, spring constants, Young's modulus, weight and stiffness. For a Young's modulus of 1.0 Terrapascal (TPa), with intrinsic strength equal to 130 giga pascal and effective thickness of graphene equal to 0.335 nm, the elastic stiffness corresponds to Ca. 335 Nm^2 [19, 20]. To understand this more, suppose a graphene membrane to be stretched on a bowel and pushed by a pencil tip by putting a load of car on top! Graphene is so strong that even then it doesn't break (Fig 6). This property of graphene is attributed to the strongest C-C bond present in graphene due to sp^2 hybridization. Graphene is about 300 times stronger than structural steel with a tensile strength of 1 TPa. Graphene is lighter than feather (about 0.77 milligrams per square meter). Still graphene is so robust and stretchable.

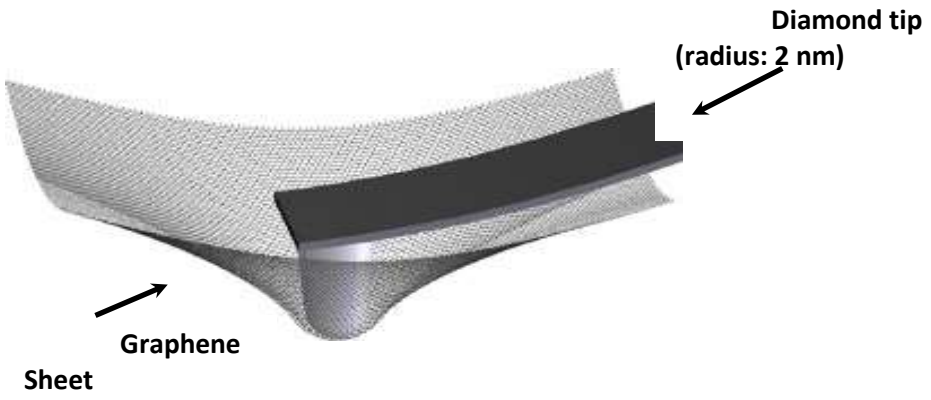

Fig. 6: An illustration of mechanical strength of graphene [21]

Defects such as vacancies or any imperfections in a material have a pronounced impact on the mechanical properties, so here come a discrepancy in the actual and theoretical values of tensile strength. Moreover, Young's modulus is reported to decreases with the increase of functionalization [22]. It is expected that due to such a high mechanical properties graphene can be employed in next era of tough and elastic composite thereby used in making flexible displays.

6. THERMAL PROPERTIES

Thermal Conductivity, K, is the ability to conduct heat, and is given by "Fourier's Law". In solids thermal conduction is mainly governed by acoustic phonons (k_p) and by electrons (k_e).

$$K = k_p + k_e$$

Unlike metals, the conduction of heat in undoped carbon materials such as graphene, is mainly due to phonons. This is attributed to the presence of strongest in-plane sp^2 hybridized bonds making its lattice like chicken wire that gives a well-organized structure which provides transfer of heat by lattice vibrations however the heat transfer, out-of-plane is restricted by weak van der Waals coupling. Graphene is a good thermal conductor. Using an optothermal Raman technique, the thermal conductivity at room temperature K of mechanically cleaved graphite was found to be ~3000 Wm/K [23] whereas in CVD graphene it was found to be 2500 Wm/K [24]. In a few layers of graphene its value increases as the layers increase from 2 to 4. Graphene shows a good thermal response in graphene based electronic devices and microelectronic systems because as a heat spreader it increases the heat dissipation, to keep electronics cool and increase the device reliability. The understanding of graphene's thermal property is important, and it has a bright future in the IC industries. It can be used as electrical interconnects replacing copper thin film which have only 250 Wm/K thermal conductivity.

The thermal conductivity at room temperature in suspended graphene is indeed very high, however its value lowers down substantially when the disorders in graphene increases. A lot of work is now in progress in the field of graphene quantum dots [25], graphene [26],

graphene nanoplatelets [27], and graphene composites[28, 29,30] as well which will be a great help for graphene based industries.

7. Conclusion and Outlook

In the present article the chemical, electrical, optical, mechanical, and thermal properties of graphene have been reviewed and the factors supporting that properties have also been discussed. It has been shown that the possibilities and capabilities of graphene in advanced engineering fields are essentially infinite which is attributed to the embellished properties of graphene. The goal of this paper was to review various unique properties of graphene. However, graphene research is still in "on state" and there is a lot to know about graphene. There are still several challenges [31] to overcome before the industries can proceed with the massive production of graphene and use it in various applications. For example, graphene obtained by mechanical exfoliation of graphite unsuitable for big scale fabrication as they are produced in ~10 μm^2 size. In addition to this the graphene obtained by exfoliation are randomly scattered over a substrate hence cannot provide a continuous path to the charge carriers, which is an utmost requirement for any of the device applications. For this purpose one can use CVD graphene but again it has its own challenges. Price is another major consideration which comes into picture in case of massive production at industrial scale. But this is also true that graphene is a miracle material if we could crack it. Companies like IBM and Nokia have been involved in research of graphene applications. The status of this miracle material is soon to be promoted as an engineering material fulfilling the requirements of industries and consumers from a research idea.

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