Monolayer, bilayer and trilayer graphene

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Abstract

Graphene is a single two-dimensional (2D) atomic layer of hexagonally packed carbon atoms. In field of material science all have vast interest on graphene for its numerous unique mechanical, chemical, electronic, optical and thermal properties. It has been observed that with increasing number of layers graphene show many interesting properties. In this article, we briefly discuss the structures, some properties and applications of monolayer, bilayer and trilayer graphene.

1. Introduction

Antoine Lavoisier coined the term "Carbone" first in his book "Traite Elementire de Chimie" as one of the newly identified chemical elements around 225 years back [1]. Graphene is recently discovered two-dimensional allotropic from of carbon. Before graphene three-dimensional (diamond, graphite), one-dimensional (nanotubes) and zero-dimensional (fullerenes) allotropes of carbon were known. Two carbon allotropes – diamond and graphite – have been known to humans since many centuries ago. Fullerenes were discovered in1985, carbon nanotubes in 1991 and graphene in 2004. Carbon is the only compound which has four dimension structures. i.e., 0D, 1D, 2D and 3D. The theory of graphene was first explored by P. R. Wallace [2] in 1947 as a starting point for understanding the electronic properties of more complex, 3D graphite. According to Landau and Peierls atoms in 2D crystals are displaced from its equilibrium position due to the thermal fluctuations [3,4] and this displacement is comparable with the interatomic distance at finite temperature. Moreover experimentally it is prove that the melting temperature of thin films rapidly decreases with the decreasing thickness. So in a film when there exist near about 12 layers [5] it becomes unstable, so they should not exit. Hence, the existence of graphene is a miracle! [6,7].

In 2004 [8], Andre Geim and Kostya Novoselov managed to extract single atom thick crystallite called graphene. Prof. Andre K. Geim, University of Manchester, UK and Prof. Konstantin S. Novoselov, University of Manchester, UK received the 2010 Nobel Prize in physics "for groundbreaking experiments regarding the two-dimensional material graphene". Graphene is the building block for carbon materials of all other dimensions. Graphite is obtained by the stacking of graphene layers. Diamond can be obtained from graphene under extreme pressure and temperatures by transforming the 2-dimensional sp^2 hybridization into 3-dimensional sp^3 hybridization and pi (π) bond into sigma (σ) bond. Carbon nanotubes are synthesized from rolled up graphene. Fullerenes can also be obtained from graphene by modifying the hexagons into pentagons and heptagons in a systematic way. Since its discovery graphene opens a new phase in the history of research and application in the field of material science. When graphene was discovered, it was monolayer. When several graphene layers are stacked on top of each other, the character of the charge carriers changes with the number of layers and type of stacking. Now-a-days research is going on multilayer graphene along with monolayer graphene (MLG). It has been observed that with increasing number of layers graphene show many interesting properties. For instance, monolayer graphene has zero band

gap whereas bilayer and certain types of trilayer graphene have an electrically tunable band gap [9-11]. In this article, we briefly discuss the structures, some properties and applications of monolayer, bilayer and trilayer graphene.

2. Monolayer graphene

Graphene, the hexagonally structured two-dimensional crystal, consisting of bipartite lattice of two triangular sublattices. One carbon atom of the hexagon is bonded by sigma (σ) bonds with three nearest carbon atoms and having a bond angle between them of 120°. The electronic configuration of carbon is $1s^2 2s^2 2p^2$. The three valance electrons of 2s, $2p_x$ and $2p_y$ orbital are bounded by sp^2 hybridization which results these sigma (σ) bonds. The slippery, soft nature of graphene is due to the pi (π) bond created due to overlapping of the half filled $2p_z$ orbital of one carbon atom with other $2p_z$ orbitals of other carbon atoms. This pi (π) bond also imparts electrical and thermal conductivity and luster in graphene [12-16]. In a unit cell of monolayer graphene (MLG) there are two carbon atoms which form a honeycomb structure. It has three sites and can be denoted as A, B and C (Fig. 1).

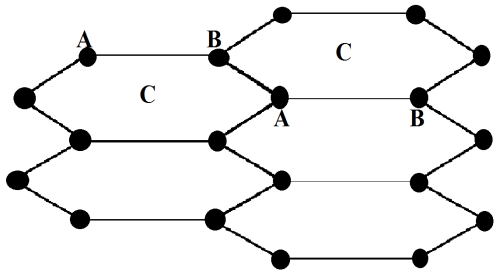

Fig. 1: Structure of monolayer graphene with A, B and C sites [25].

Electrons in monolayer graphene are obeying a linear dispersion relation (i.e. the electron energy is linearly proportional to the wave vector, $E = \hbar k v_F$) and behave as massless relativistic particles, called *Dirac fermions*. $\hbar = h/2\pi$, h is the Planck's constant, k is the wave vector and v_F is the Fermi velocity of electron in the graphene. This property implies that the speed of electrons in graphene is a constant, independent of momentum, like the speed of photons is a constant *c*. It is found that the velocity of electrons in graphene is about $10^6 m s^{-1}$. In monolayer graphene the interactions among electrons are extremely strong and graphene's dimensionless coupling constant $\alpha_{GR} = e^2/\hbar v_F \approx 1$ is larger than the dimensionless coupling constant of quantum electrodynamics (QED), $\alpha = e^2/\hbar c \approx 1/137$. Again the interaction of electrons in graphene is also different from an ordinary nonrelativistic 2D electron gas. The electrons in most of the conductors can be described by non-relativistic quantum mechanics but the electrons in graphene are treated as relativistic particles and are described by the Dirac equation rather than Schroedinger equation. This shows a possibility of studying phenomena of quantum field theory in condensed matter physics. All this makes graphene a new type of electronic system whose independent particles move relativistically, but interact nonrelativistically.

At room temperature monolayer graphene has electron mobility is 2.5×10^5 cm^2 V^{-1} s^{-1}, Young Modulus of 1 TPa; Intrinsic strength 130 GPa; High thermal conductivity of 3,000 W mK^{-1} or more [17]. It is stronger than diamond, more conductive than copper and more flexible than rubber. Monolayer graphene is used in electronics, as high frequency transistor, logic and RF transistor. Graphene can be used as non-conventional graphene switches due to its high electron mobility and high thermal conductivity.

3. Bilayer graphene

Bilayer graphene (BLG) is Bernal AB-stacked. In bilayer graphene, the Bernal stacking two layers consists of two coupled honeycomb lattices with basis atoms. The atoms are named as (A_1, B_1) and (A_2, B_2) as shown in Fig. 2. (A_1, B_1) is placed in the bottom and (A_2, B_2) in the top layers respectively.

The arranged atoms are in (A_2, B_1) fashion. That is, the A-carbon of the upper sheet lies on top of the B-carbon of the lower one [18]. The C-C bond distance is 1.42 Å and the distance between two adjacent layers is 3.35 Å.

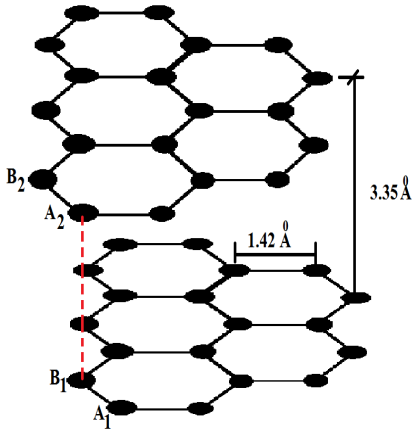

Fig. 2: Structure of bilayer graphene with Bernal AB stacking.

Electrons in MLG behave as massless two-dimensional fermions whereas electrons in BLG behave as massive two-dimensional fermions [19,20]. The density of states D as a function of particle number (or particle density) n is found to be $D(n) \sim n^{1/2}$ for massless 2d fermions (electrons in MLG) and $D(n) \sim$ constant for massive 2d fermions (electrons in BLG). Formulae for density of states are $D = \frac{1}{\hbar v_F}\sqrt{\frac{g\,n}{\pi}}$ (massless) and $D = \frac{g\,m^*}{2\pi\hbar^2}$ (massive), where g = degeneracy, and m^* is the effective mass of electrons. Thus, density of states depends upon particle density in MLG but it is independent of particle density in BLG. Massless particles (e.g. photons) have energies which depend linearly on quantum number, while the energies of massive particles (e.g. free electrons) depend quadratically on quantum number. The massless and massive dispersion relations in MLG and BLG respectively are: $E = \hbar v_F \left|\vec{k}\right|$ (massless) and $E = \frac{\hbar^2 k^2}{2m^*}$ (massive), where $\hbar = h/2\pi$, h is the Planck's constant, $\vec{k}$ is the wave vector and v_F is the Fermi velocity of massless electrons in the MLG. Monolayer graphene is more transparent than two or more layer graphene. MLG is twice transparent than BLG. Graphene shows very interesting behavior in the presence of a magnetic field at very low temperature. Graphene shows an *anomalous quantum Hall effect* (QHE) with the sequence shifted by 1/2 with respect to the standard sequence. It is found [6,14,16] that the Hall conductivity $\sigma_{xy} = \pm 4e^2/h\left(N + \frac{1}{2}\right)$, where N is the Landau level index and the factor 4 accounts for graphene's double spin and double band (valley) degeneracy. That is why; it is also characterized as *half-integer quantum Hall effect*. The QHE in bilayer graphene is more interesting. The quantized plateaus appear at the standard sequence $\sigma_{xy} = \pm 4Ne^2/h$ (same as the nonrelativistic electrons). The mobility of bilayer graphene (BLG) (~2.0 × 10^5 cm^2 V^{-1} s^{-1}2.5 × 10^5 cm^2 V^{-1} s^{-1}) is normally lower than the mobility of MLG [21–23]. Young's modulus of bilayer graphene is estimated to be 0.8 TPa which is close to the value for graphite [24]. Room-temperature thermal conductivity would be as high as about 5000 W m/K. Bilayer graphene can be used as a substitute of biological tissues, energy generation and storage, sensors and metrology.

4. Trilayer graphene

Trilayer graphene (TLG) has more complex (in comparison to monolayer and bilayer graphene) interlayer interactions that supply richer electronic structure. In trilayer graphene generally three types of stacking are possible. These are AAA, ABA and ABC stacking types corresponds to hexagonal, Bernal and rhombohedral graphene respectively (Fig. 3) [25]. Minor reflection symmetry about the centre layer among z-direction is observed in hexagonal and Bernal trilayer graphene. But rhombohedral trilayer graphene has inversion symmetry. It is observed that especially in low energy region, electronic structure of graphene is very sensitive to thickness and stacking sequence.

In case of AAA stacking all the atoms of the three layers lays one over another. For ABA stacking same atoms of the first and the third layer are exactly one over another but for the second layer that particular atom is not align. No particular type of atom in ABC stacking is in aligning with one another. The low energy band structure of ABA-stacked trilayer graphene consists of one massless and two massive subbands, similar to the spectrum of one monolayer and one bilayer graphene, whereas ABC-stacked trilayer graphene band structure is approximately cubic [26]. The AAA-stacked trilayer graphene band structure is a superposition of the band structure of its component monolayer graphenes.

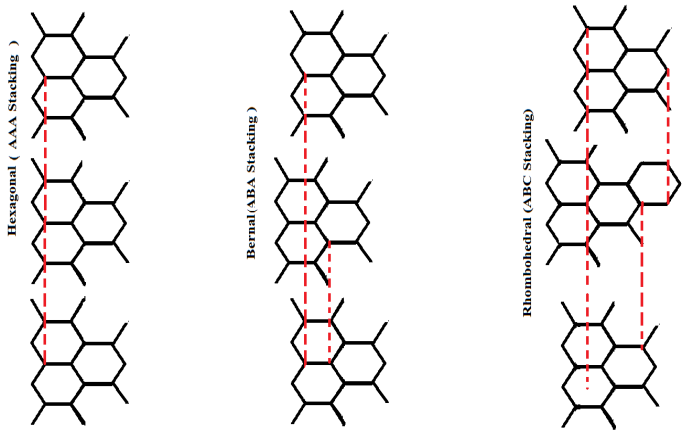

Fig. 3: Structure of trilayer graphene hexagonal (AAA), Bernal (ABA) and rhombohedral (ABC) stacking [25].

The thermodynamic properties of the electron gas in multilayer graphene depend strongly on the number of layers and the type of stacking [27,28]. At room temperature, it is observed that thermal conductivity of graphene decreases with increase in number of layers. When a strong magnetic field is applied perpendicular to the trilayer graphene planes, quantum Hall effect is observed in the material. It is found that [26] the Hall conductivity $\sigma_{xy} = \pm 4e^2/h\left(N + \frac{n}{2}\right)$, where $n = 3$ is the number of layers, N is the Landau level index, the factor 4 accounts for graphene's double spin and double valley degeneracy, $-e$ is the electron charge and h is the Planck's constant. Further, the plateau structure in σ_{xy} of trilayer graphene depends on the type of stacking. Trilayer graphene exhibits lower mobility (typically 800 cm^2 V/s at 4.2 K) compared to monolayer and bilayer graphene. Trilayer graphene can be used as LEDs, reinforcing materials, wirings, solar power aircrafts, aerospace etc.

5. Conclusions

Graphene – a two-dimensional nanomaterial, composed by covalently bonded carbon atoms in a honeycomb lattice, has been attracting the attention of the scientific community since its discovery in 2004. Due to its outstanding electronic, thermal, optical and mechanical properties it has applications in wide variety of fields, for example, spintronics, electron optics, photonics and many others. We hope, in near future it will be used in construction and telecommunication field.

Bilayer and trilayer graphene are interesting because they possess different and unique properties with respect to monolayer graphene. For example, monolayer graphene has zero band gap whereas bilayer and certain types of trilayer graphene have an electrically tunable band gap. This would make them good candidates for application in electronic industry where the control of the band gap is desirable.

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