

18. Chen, C.C., Lin, Y.P., Wang, C.W., Tzeng, H.C., Wu, C.H., Chen, Y.C., Chen, C.P., Chen, L.C., Wu, Y.C.: DNA-gold nanorod conjugates for remote control of localized gene expression by near infrared irradiation. *J. Am. Chem. Soc.* **128**(11), 3709–3715 (2006)
19. Durr, N.J., Larson, T., Smith, D.K., Korgel, B.A., Sokolov, K., Ben-Yakar, A.: Two-photon luminescence imaging of cancer cells using molecularly targeted gold nanorods. *Nano Lett.* **7**(4), 941–945 (2007)
20. Yu, C., Irudayaraj, J.: Multiplex biosensor using gold nanorods. *Anal. Chem.* **79**(2), 572–579 (2007)

Graphene

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Synonyms

[Bilayer graphene](#); [Graphite](#); [Nanoribbons](#)

Definition

Graphene is defined as an atomically thin planar allotrope of carbon. Each carbon atom in this two-dimensional (2D) crystal is bonded to three other carbon atoms, forming a hexagonal structure. Graphene is the building block of graphite, carbon nanotubes, and fullerenes. It is the thinnest crystal known at this time.

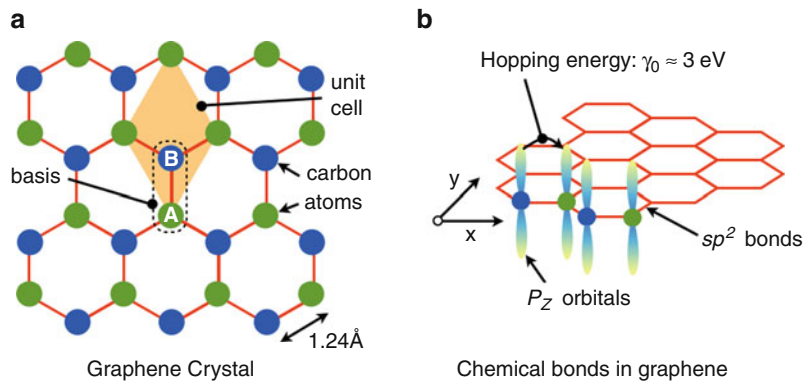
Overview

The various solid forms of carbon have been known and used since thousands of years. In three-dimensional (3D) form, charcoal is the prototype solid fuel used to sustain life through the ages. Lavoisier first showed in 1772 that diamond was composed entirely of carbon by “burning” diamond in oxygen and producing carbon dioxide. This 3D crystalline form of carbon is the hardest, electrically insulating, and most thermally conductive solid known. These properties of diamond form the basis for its many uses. Graphite is a layered solid form of carbon, and is more stable than diamond. It is remarkably different from diamond in its physical properties. It is an

electrical conductor, exhibits high anisotropy in its electrical and thermal conductivities, and is very refractory. Because it is capable of carrying copious amounts of electrical current, graphite was instrumental in the discovery of the light bulb, which converts electrical energy into photons for illumination. It is still used in arc lamps and where high currents and high temperature operation is necessary. The uses of graphite are more diverse, ranging from neutron moderation in nuclear reactors to the pencil lead, which exploits its layered structure. The rich range of physical properties of the various forms of carbon emerges from seemingly minor differences in the microscopic arrangements of the carbon atoms.

With the advent of electron microscopy, it became possible to investigate the atomic structure of solids made of carbon. Lower dimensional forms of carbon were then discovered. In semiconductor heterostructures, such as those made of silicon or GaAs, man-made quantum-size effect materials were created starting from 3D bulk semiconductors to 2D quantum wells, 1D quantum wires, and 0D quantum dots. Thus, nanostructures based on semiconductor heterostructures developed from large to small. In sharp contrast, the first carbon nanostructure discovered was zero-dimensional (0D) fullerenes (C_{60}), followed by 1D carbon nanotubes. The 2D form of carbon, graphene, has been known since the 1940s to be the building block of graphite. It was also found subsequently to be the building block of fullerenes and nanotubes. But by itself, a single layer of graphene was believed to be thermodynamically unstable. Based on the Mermin–Wagner theorem in solid-state physics, the energy cost for spontaneously broken symmetries in 2D crystals is low. This means that a perfect “flat” 2D crystal can increase its entropy by forming ripples or crumples. Thus, to a certain extent, the isolation of 2D atomic crystals in 2004 was a surprise. Using scotch tape, single layer flakes of graphene were isolated from graphite, and their electronic properties were investigated [1]. More than the isolation of single layers of graphene, the findings of the nature of electron motion in it have far-reaching consequences on the fundamental understanding of the electronic properties of solids. These findings have opened a new door to aspects of symmetry in condensed matter physics. Rapid progress has occurred in exploiting these properties in applications. To understand the origins of the peculiar properties of graphene, its atomic structure is discussed next.

Graphene, Fig. 1 Crystal structure and chemical bonds of graphene. (a) Hexagonal crystal structure showing the atomic basis of two equivalent carbon atoms, the interatomic distance, and the unit cell. (b) Chemical bonds, showing the sp^2 hexagonal structure, and the p_z orbitals that impart graphene its conductivity

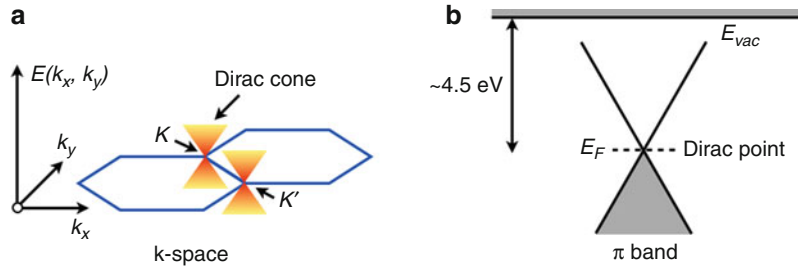


Crystal Structure of Graphene

Carbon is the sixth element in the periodic table, meaning it has six protons in its nucleus. Charge neutrality requires the presence of six electrons. The six electrons fill the lowest three orbitals in the arrangement $[1s]^2[2s]^2[2p]^2$, where the $|s\rangle$ orbitals are spherically symmetric, and $|p\rangle$ orbitals are elongated along a linear axis. When carbon atoms are brought close to each other, the two electrons in the innermost $[1s]^2$ orbitals remain close to the nucleus, and do not participate in the bonding process. The outermost orbitals start interacting, and are capable of forming chemical bonds. The four electrons in the outermost $[2s]^2[2p]^2$ orbitals can be shared between atoms in a variety of ways, each leading to a different form of carbon. For example, when four nearest carbon atoms share all four electrons of a carbon atom equally, the bond is sp^3 . An sp^3 bond is tetrahedral, and is inherently 3D. Carbon atoms bonded in this fashion arrange periodically in 3D space, forming the crystal structure of diamond. Carbon is rather versatile in its bonding possibilities; when combined with hydrogen atoms, electrons in carbon atoms can form sp^2 or sp bonds as well. This means carbon atoms can form 2D planar molecules (e.g., the hexagonal molecule benzene or C_6H_6), or long 1-dimensional chains (e.g., in conductive polymers). This versatility of electrons in carbon is the root of the complexity of organic molecules that lead to the emergence of life itself.

When a carbon atom shares electrons with *three* nearest neighbors, the bonding is sp^2 , written as $|sp^2\rangle = a|s\rangle + b|p_x\rangle + c|p_y\rangle$, where a , b , c are constants. This bonding leaves one electron behind for every carbon atom. The three chemical bonds are

separated by 120° , and are planar. This is the crystal structure of graphene, depicted in Fig. 1. The energies of the electrons forming the sp^2 bonds bunch together into bands called the σ band. The σ band is responsible for the perfectly planar nature of graphene, and determines its structural and vibrational properties, such as its thermal conductivity and Young's modulus, among others. Thus, graphene is a 2D crystal with hexagonal arrangements of carbon atoms. The atomic spacing is $a_{cc} \sim 0.124$ nm. As indicated in Fig. 1, the smallest repeating unit that can be translated to cover the entire 2D space consists of not one, but *two nearest-neighbor carbon atoms*. Though the atoms are physically identical (they are both carbon), they are labeled as A and B in Fig. 1 since the “mechanical” symmetry can be broken by the electron wavefunction associated with them. The A-B atom combination is the two-atom “basis” of the graphene crystal, similar to that in 3D diamond or silicon. The primitive repeating unit is shown as a parallelogram. By virtue of being 1-atom thick, graphene is the “thinnest” crystal. It is impermeable to small gas molecules. The structural and chemical rigidity of graphene is protected by symmetry: to form a chemical bond to graphene, one needs to convert sp^2 bonds to sp^3 . This requires buckling of the crystal since the bonds have to change from 2D to 3D, requiring the movement of atoms. If and when this is achieved, the material is no longer graphene. In addition, carbon is the lightest in group-IV of the periodic table, and the strong σ bonds lead to the highest in-plane thermal conductivity. However, the σ band does not directly influence the electronic properties of graphene. Electrons in sp^3 bonds and bands resulting from them determine the electronic *and* structural properties in conventional 3D semiconductor crystals (e.g., Si, GaAs, diamond).



Graphene, Fig. 2 Allowed energies for electrons in graphene in the k -space, and bandstructure. (a) The hexagonal symmetry of electrons in the momentum space, and the Dirac cones

originating from the mobile p electrons. (b) The bandstructure, showing electron states filled in the p band till the Dirac point energy, which is 4.5 eV below the vacuum energy level

In graphene, the electronic and structural properties arise from different bands. For understanding the electronic properties of graphene, attention is focused back to the *electron that was left out* in the formation of the sp^2 bond.

Electronic Properties of Graphene

The electrons left out in the chemical bonding process are from the $|p_z\rangle$ orbitals of the carbon atoms forming graphene. The linear axis of the $|p_z\rangle$ orbital protrudes outward from the plane, as shown in Fig. 1. These electrons can hop between the nearest neighbor carbon atoms. The energy characterizing this hopping is $\gamma_0 \sim 3.0$ eV. Thus, their wavefunctions become delocalized. Their allowed energies bunch together to form what are called π bands. Electrons in the π bands can be visualized as sliding over the hexagonal carbon atom structure of graphene. These electrons impart graphene its exceptional electrical conductivity.

The allowed energies of the delocalized π electrons depend on their wavelength, in accordance with the rules of quantum mechanics. According to the de-Broglie relation, the wavelength is inversely proportional to momentum. The momentum is given by $\hbar k$, where \hbar is Planck's constant and $k = 2\pi/\lambda$, where λ is the wavelength. The allowed energies of electrons $E(k_x, k_y)$ can be then plotted in the k -space, as shown in Fig. 2. By taking into account the basis of two atoms, the wavefunctions of electrons in graphene are represented as “spinors,” which are two-component matrices of the form $\frac{\exp[i\mathbf{k}\cdot\mathbf{r}]}{\sqrt{2}} \begin{pmatrix} 1 \\ \exp[i\theta] \end{pmatrix}$, where $\mathbf{k} = \mathbf{x}k_x + \mathbf{y}k_y$, and $\tan\theta = k_y/k_x$. Using a tight-binding procedure, the energy spectrum $E(k_x, k_y)$ is

given by the equation $\hbar v_F(\vec{\sigma} \cdot \mathbf{k})|\psi\rangle = E(k_x, k_y)|\psi\rangle$, where $\vec{\sigma} = \mathbf{x}\sigma_x + \mathbf{y}\sigma_y + \mathbf{z}\sigma_z$ is a vector composed of the three Pauli spin matrices. The term $v_F = 3a_{cc}\gamma_0/2\hbar \sim 10^8$ cm/s is a parameter characterizing the bandstructure, with dimensions of velocity. This Hamiltonian has a closer analogy to the Dirac equation rather than the Schrodinger equation used for conventional semiconductors. The Dirac Hamiltonian consists of Pauli spin matrices in the kinetic energy term, which implies that electrons have spin-like properties based on their momentum. This property is termed “pseudo-spin,” and may be pictured as a vector whose direction depends on the momentum. In traversing a path around a constant-energy circle in the Dirac cone, the wavefunction accumulates a phase of π due to the pseudospin. This phase is called Berry's phase, and has consequences on scattering and on quantum Hall effects.

The energy bandstructure obtained from this “Dirac equation” for the π band is given by $E(k_x, k_y) = E_F \pm \gamma_0 \sqrt{1 + 4\cos(\sqrt{3}k_x a/2)\cos(k_y a/2) + 4\cos^2(k_y a/2)}$, where $a = \sqrt{3}a_{cc}$ is the lattice constant of graphene. Here, E_F is the Fermi energy, which for pristine undoped graphene is ~ 4.5 eV below the vacuum energy level. This is the electron affinity or the work function of pure graphene (Fig. 2). The positive sign is for the conduction band that lies above E_F , and the negative sign is for the valence band. One can note that $E(0, 4\pi/3a) = E_F \pm 0$ eV, which implies that there is *no energy bandgap* in the π band of graphene. The points in the k -space such as $K = (0, 4\pi/3a)$ where the conduction and valence bands meet are called the Dirac points. These points form a hexagonal network in the k -space as indicated in Fig. 2, with the

nearest-neighbor points labeled as K and K' . In analogy to traditional semiconductors, graphene is a direct bandgap semiconductor. Since each K point is shared between three hexagons, there are two distinct points in the smallest repeating unit cell in k -space, called the Brillouin zone. Thus, in analogy to traditional semiconductors, graphene has a valley degeneracy of 2.

The Fermi energy is at the Dirac point for pure graphene, meaning at zero temperature and in the absence of doping, all electronic states below the Dirac point are occupied, and all above it are empty. Electrical conductivity thus occurs in graphene due to transitions of electrons between allowed states close to the Dirac point. In analogy to the effective mass approximation for semiconductors, expanding the energy dispersion around the Dirac point, say around $K = (0, 4\pi/3a)$, yields the rather interesting relation $E(k_x, k_x) - E_F \approx \hbar v_F \sqrt{k_x^2 + k_y^2} = \hbar v_F |\mathbf{k}|$. This is the equation of a cone, and owing to its origin in the Dirac-like Hamiltonian, referred to as the Dirac cone. The conical form of the energy dispersion remains valid for energies exceeding a few eVs from the Dirac point energy, which is the range of interest for all low-energy electronic and optical properties. A few intriguing aspects of this energy dispersion can be identified by comparison with traditional semiconductors.

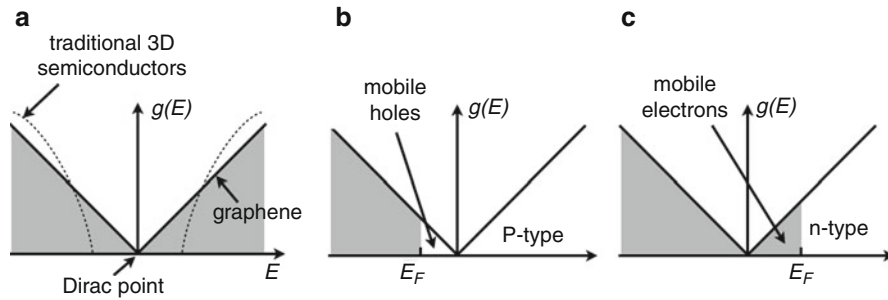
In traditional semiconductors, the kinetic energy of electrons near a band edge E_C is proportional to the square of the electron quasi-momentum $E(k) - E_C = (\hbar k)^2 / 2m^*$, with the magnitude of the kinetic energy parameterized by an effective mass distinct from the mass of free electrons. The effective mass m^* is a parameter that absorbs the details of the crystal potential. It replaces the complex motion of free electrons in a crystal by that of an electron with a different mass in free space. This is a considerable simplification, one that is heavily leveraged in the design of electronic and optical devices such as transistors, light-emitting diodes, and lasers based on traditional semiconductors. In stark contrast, the kinetic energy of electrons in graphene depends on its momentum *linearly* $E(k_x, k_x) = v_F \cdot \hbar |\mathbf{k}|$, where Fermi energy at the Dirac point is used as reference. Wallace originally derived this linear form of the bandstructure of graphene in 1947 [2].

A linear dependence of kinetic energy on momentum is characteristic of light or photons. The energy

dispersion of electrons in graphene is identical to that of photons, with the speed of light $c = 3 \times 10^8$ m/s replaced by the “Fermi velocity” $v_F \approx 10^6$ m/s. The maximum speed of electrons in graphene is $v_F/c = 1/300$ that of light in free space. In traditional semiconductors, particularly those of small bandgaps, the velocity of carriers can also approach these speeds. A consequence of the linear energy dispersion is the difficulty in associating an effective mass to electrons in graphene. The effective mass is *defined* as the curvature of the energy dispersion. By definition, the curvature of a linear curve is zero. Thus, electrons in graphene are referred to as “massless Dirac fermions.” The “massless” feature should be understood in the light of the discussion above; electrons in graphene are identical to electrons in any other material. Unlike *truly massless photons*, they need external driving forces such as electric or magnetic fields to carry currents. *What is unique about graphene is the linear energy dispersion of electrons.* In the dispersion of electrons are hidden a number of symmetries, each leading to many of its unique features.

Carrier Statistics in Graphene

The absence of an energy bandgap in graphene is related to the light-like linear dispersion. The linear dispersion also implies that the transport properties of filled states in the conduction band (see Fig. 2) and empty states in the valence bands (holes) are similar. The conduction band is a mirror-reflection of the valence band. This symmetry is special. Two-dimensional electron or hole gases in semiconductor quantum wells have multiple subbands to occupy, and can be truly 2D at very low energies or at low temperatures as long as only one subband is occupied. In stark contrast, electrons and holes in 2D graphene are truly 2D at all temperatures, since there are no higher subbands near the Dirac point. Based on the energy dispersion, the density of states (DOS) of graphene is given by $g(E) = 2|E|/\pi(\hbar v_F)^2$, which is linear in energy. Three-dimensional semiconductors have density of states that depend on energy as $g(E) \sim \sqrt{E - E_0}$, whereas the density of states of 2D subbands in quantum wells are energy-independent. The DOS of 2D graphene is shown in comparison to traditional 3D semiconductors in Fig. 3. Based on the DOS, the electron and hole densities in pristine graphene are given by $n_0 = p_0 = (\pi/6) \cdot (kT/\hbar v_F)^2$, where T is the temperature and k is the Boltzmann constant. At room temperature, there are $\sim 8 \times 10^{10}$ /cm² electrons in the



Graphene, Fig. 3 Density of states of pure graphene and p-type and n-type graphene. (a) Density of states of graphene is linear and symmetric around the Dirac point energy. It has no

energy gap, unlike conventional semiconductors. (b) and (c) P-type and n-type graphene created by moving the Fermi level into the valence and conduction band, respectively

conduction band due to interband thermal excitation, leaving behind an equal number of holes in the valence band. These carriers are mobile, and lead to a finite conductivity of graphene at room temperature even in the absence of intentional doping. They set the *lower limit* of mobile carrier concentration in 2D graphene: with any changes such as doping or field-effect, the net mobile carrier density can only exceed this number. The $\sim T^2$ dependence of intrinsic interband thermal generation of carriers is in stark contrast to traditional semiconductors, where the density depends on the bandgap as $\exp(-E_G/2kT)$ where E_G is the bandgap.

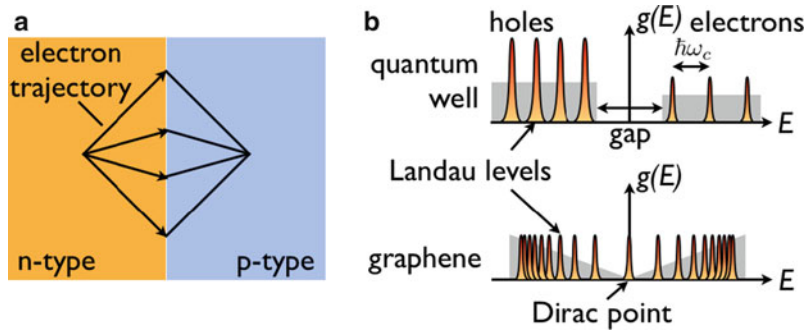
When graphene is electrostatically doped, the Fermi energy moves away from the Dirac point into the valence or the conduction band, making it p-type or n-type. Under these conditions, the carrier concentrations are given by $n = E_F^2/\pi(\hbar v_F)^2$. Thus, the Fermi energy changes as the square root of the carrier concentration, $E_F = \hbar v_F \sqrt{\pi n}$. At a 2D carrier concentration of $10^{12}/\text{cm}^2$, $E_F \sim 0.12$ eV from the Dirac point, and increases to $E_F \sim 0.37$ eV at $10^{13}/\text{cm}^2$. The Fermi energy is tunable over a wide range, which implies a tunable work function for 2D graphene. The electrons or holes thus formed in graphene are responsible for its electrical conductivity. The current per unit width that flows in a graphene sheet in response to a voltage applied across contacts made to graphene is given by $I/W = qn\langle v \rangle$, where $\langle v \rangle$ is the ensemble-averaged velocity. In the absence of any scattering, the velocity of *all* carriers in graphene is the Fermi velocity v_F , by virtue of its linear bandstructure. However, since a net current flows only along the electric field, the effective velocity is only a fraction of the Fermi velocity obtained

appropriately by angular averaging. The current drive in clean defect-free graphene is typically high, owing to the high Fermi velocity. In the presence of defects, however, the conductivity suffers due to scattering.

Carrier Transport in Graphene

The mobility of electrons in graphene is typically high, if the material is pure. Electron and hole mobilities well in excess of $50,000$ cm^2/Vs have been measured at room temperature in the cleanest samples [3]. The high mobility is typically degraded due to scattering from impurities that are not inherent to graphene itself. For example, charged impurities located outside the plane of graphene result in Coulombic scattering of mobile carriers. Similarly, integrating a dielectric in close proximity to graphene allows electrons in graphene to excite phonon modes in them, resulting in “remote” phonon scattering [4]. When these scattering processes are suppressed, the mobility of carriers in graphene is found to increase. The high mobilities lead to long mean-free paths, and ballistic transport is possible over micrometer length scales. At high voltages, when electrons gain kinetic energies high enough to excite the intrinsic optical phonon modes of graphene, they collide with the carbon atoms and create optical phonons. By virtue of the lightness of carbon atoms, the optical phonon energy is high (~ 160 meV), implying that carriers cannot emit optical phonons until they acquire an equivalent kinetic energy, resulting in high velocities.

The high mobility and velocity of carriers leads to high currents in field-effect transistor-like device applications. Due to the lack of a bandgap, the demonstrated current modulation in 2D graphene typically does not



Graphene, Fig. 4 Electron “lensing” in graphene, and Landau levels in traditional semiconductors compared to those in 2D graphene. (a) Electron transport in graphene mimics light; a p-n junction behaves as a lens for electrons. (b) At high magnetic

fields, the density of states of graphene collapses into Landau levels that are quite different from what is observed in 2D electron-hole systems in conventional semiconductors

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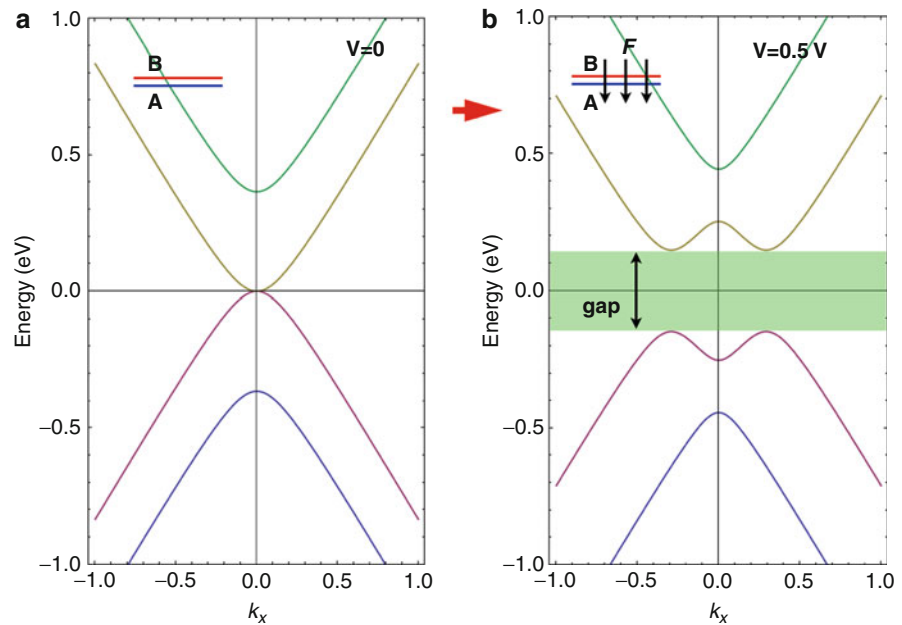
exceed a factor of 10X, currently restricting the feasibility of 2D graphene in electronic digital switching. However, applications that do not require a high current modulation stand to benefit from the high current drive and the high speed. Unlike traditional semiconductors, the symmetry of the bandstructure and the absence of a bandgap implies that graphene is as conductive when p-type as when it is n-type. Thus, when the Fermi energy is tuned from the valence band to the conduction band, the current characteristics change from hole conduction to electron conduction symmetrically; this property is termed ambipolar. The ambipolar symmetry is useful for passive applications in electronic circuits such as mixers to generate higher harmonics of oscillatory signals. In most traditional semiconductors, the valence band effective mass is higher than the conduction band effective mass, and the ambipolar nature is not protected by symmetry, as in graphene.

Adjacent regions of graphene can be electrostatically gated with opposite polarity, forming p-n junctions as shown in Fig. 4. In such a case, when electron waves are launched from a point in the n-region at various angles to the interface, they have to conserve energy and momentum when they enter the p-region. Since they have to tunnel from the conduction band in the n-side to the valence band in the p-side, the component of momentum parallel to the junction is flipped, resulting in the collimation of the electron waves. The tunneling process in graphene is unique owing to its Dirac dispersion, and is called Klein tunneling. This sort of electron “lensing” is a consequence of the light-like energy dispersion of graphene [5]. It requires the

phase of the electron waves to be coherent throughout the transport process, and thus requires long mean free paths and low scattering. Similarly, electrons can be reflected from similar interfaces, and by combining junctions, can be “waveguided” from one region to another through all-electrical controls. The similarity of the electron energy dispersion to that of light makes such processes possible in graphene.

The quantum Hall effect in graphene offers a signature of its energy dispersion. As shown in Fig. 4, in traditional semiconductor quantum wells, 2D electron and hole gases have different effective masses, and hence different density of states. Upon the application of a high magnetic field B , the DOS collapse into uniformly spaced Landau levels, with energies peaking at $E_n = \hbar\omega_C(n + \frac{1}{2})$ for each band, where $\omega_C = qB/m^*$ is the cyclotron frequency and $n = 0, 1, 2, \dots$ is an integer. As the height of each Landau level and their separation is changed by varying the magnetic field, the Fermi level passes through peaks and minima of the Landau level, causing the longitudinal magnetoresistance to oscillate. The transverse resistance is the Hall resistance. The quantized Hall *conductance* in traditional semiconductor 2DEGs is given by $\sigma_{xy} = \frac{2q^2}{h}n$. The Landau levels of 2D graphene, on the other hand, are given by $E_n = \pm v_F\sqrt{2q\hbar B}\sqrt{n}$, bunching closer as n increases, as shown in Fig. 4. The resulting Hall conductance is given by $\sigma_{xy} = \frac{4q^2}{h}(n + \frac{1}{2})$. For $n = 0$, there is a Landau level at the Dirac point for graphene, and the half-integer quantum Hall conductance is a signature of both the Dirac cone dispersion and the Berry phase of

Graphene,
Fig. 5 Bandstructure of bilayer graphene in the absence (a), and the presence (b) of an external field. Bilayer graphene is one of the first materials that has an electrically tunable energy bandgap



π for electron wavefunctions [6, 7]. The half-integer quantum Hall effect has been observed in single layer graphene grown by various methods, and the precision of the quantization is high.

Bilayer Graphene

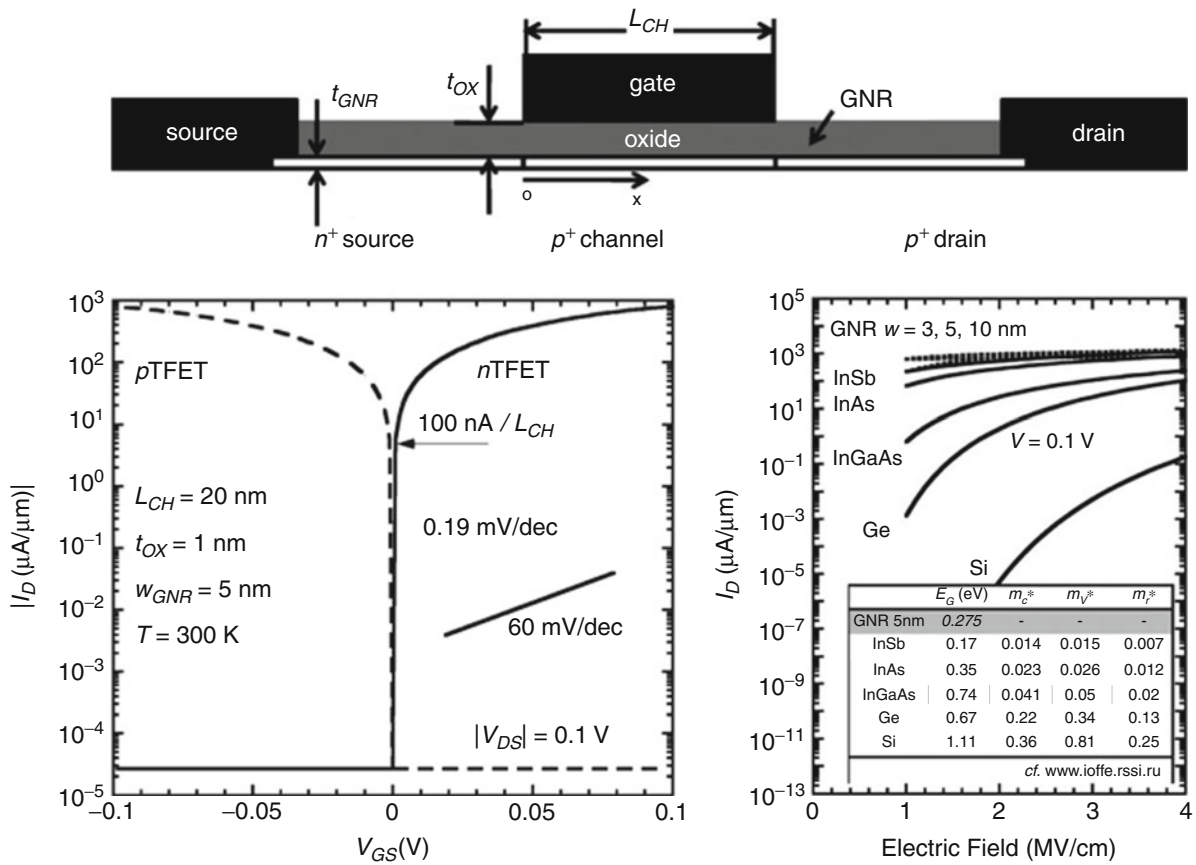
When two layers of graphene are stacked, the mutual interaction changes the electron energy dispersion, and hence its electronic properties. Bilayer graphene should not be considered as two individual layers of graphene, but one composite electronic system. Bernal stacking is a particular type of stacking, where the A atoms in one layer (Fig. 1) are vertically above the B atoms of the other. For this form of bilayer graphene, the energy dispersion changes from the Dirac cone feature of a single layer to a parabolic bandstructure characterized by an effective mass $m^* \approx 0.033m_0$, but still with a zero bandgap. This bandstructure is shown in Fig. 5. A remarkable phenomenon occurs upon the application of an electric field vertical to the graphene bilayer. The bandstructure deforms to that shown in Fig. 5b. An energy bandgap appears, which is tunable with the applied electric field [8]. The electric field breaks the symmetry of electron wavefunctions in the direction perpendicular to the bilayer, and this broken symmetry results in a bandgap. Such field-tunable energy bandgaps are rare in solid state systems, and

can be expected to lead to novel applications. Energy bandgaps opened in this fashion up to ~ 0.2 eV have been experimentally measured [9].

The symmetry of the bandstructure of graphene has also led to the proposal of interlayer tunneling devices such as the BISFET [10]. This device mimics Bose-condensation of electron-hole pairs (excitons) in two graphene layers close enough to allow strong interactions, yet far enough to prevent the formation of a bilayer. It exploits collective many-body effects in an all-electronic system at room temperature. As the number of graphene layers stacked increases, the energy bandstructure evolves toward that of bulk graphite. Graphite is a semimetal, where the conduction band minimum and the valence band maximum occur at different points in the k -space, and they overlap in energy. The semimetallic nature of graphite is responsible for its high current carrying capacity.

Graphene Nanostructures

When graphene sheets are “cut” into thin nanoscale ribbons, the size confinement results in the selection of a finite number of modes that can propagate freely along the axis of the ribbon. These structures are called graphene nanoribbons (GNRs) [11]. The edge of



Graphene, Fig. 6 Graphene nanoribbon-based tunneling field-effect transistors. Proposed device structure and predicted performance showing vast advantages over state-of-the-art silicon CMOS devices

a GNR can be armchair or zigzag, and depending on the edge and the width, the allowed propagating modes can be metallic or semiconducting. In this aspect, GNRs are similar to carbon nanotubes (CNTs), except that the nanotube has no edges. A CNT is a rolled up GNR. Semiconducting GNRs have a bandgap $E_g \approx 1.4/W$ eV where W is the width of the GNR in nm. Since GNRs lie flat on substrates, they can dissipate heat efficiently, and are capable of high current drives. In addition, the existence of a bandgap implies they can be used for electronic switching. GNRs retain the symmetry of the bandstructure of the graphene sheet they are carved from, in the sense that the valence band of a GNR is a mirror image of the conduction band. Thus, semiconducting GNRs can be ambipolar, with a high current modulation. In the process of fabrication, if the edges of GNRs are rough, scattering from this disorder can reduce the electron mobility and

carrier velocity. Nevertheless, GNRs can prove attractive for making electronic devices in the future.

If a p-n junction can be fabricated from GNRs, then the structure is very attractive for an unconventional field-effect transistor. Recently, a lot of research has focused on lowering the energy cost of digital switching by transistors. An attractive candidate for replacing conventional silicon field-effect transistor relies on the interband tunneling of electrons. The device is called a tunneling field-effect transistor or TFET; it promises digital switching of current at smaller voltages [12]. High current drives are required in transistors to maintain high performance. The tunneling currents in traditional semiconductors are typically low due to the wide bandgaps. However, devices based on GNRs can deliver among the highest current drives among all homojunction TFETs [13]. Figure 6 shows the concept of the device,

along with its predicted energy band diagram and switching performance. Owing to the symmetry of the bandstructure, a GNR TFET makes complementary operation feasible, a feature difficult to attain in similar devices made of traditional semiconductor heterostructures. In addition, the absence of out-of-plane bonds and the planar nature implies that GNRs and graphene are simpler to integrate with existing semiconductor technologies.

Optical Properties of Graphene

Interaction of light with graphene is understood from its energy spectrum. Single layers of graphene are found to absorb a well-defined fraction of visible light passing through them by interband excitation of electrons. This fraction is given by $\pi q^2/\hbar c = \pi \cdot \alpha \sim 2.3\%$ where α is the fine structure constant [14]. The absorption coefficient is *independent* of the photon energy over a large spectral window. The photogenerated electrons and holes can lead to photocurrent, and aided by the high mobility, 2D graphene can be used for fast photodetectors that operate over a large spectral window. The ease of integration of graphene with traditional semiconductors makes it attractive for applications in optical communication devices.

Electrons in graphene can also absorb photons of very long wavelengths and small energy (in the THz spectral window). This happens by the process of free-carrier absorption, and requires momentum scattering, as in a traditional semiconductor. Since the number of photons absorbed is related to the circumference of the Fermi circle in the k-space, by tuning the Fermi energy of graphene, the number of free carriers available for such absorption can be tuned over a large range. Thus, graphene is attractive for making THz modulators at a given frequency [15]. Further, graphene can be patterned into periodic structures similar to photonic crystals to enhance the absorption of certain modes and orientations of incident THz light. Such structures called graphene metamaterials are similar to photonic crystals made of dielectrics, and hold much promise for devices exploiting light–matter interaction.

Since graphene has zero-bandgap with a high mobility, an electromagnetic wave can create waves of electrons and holes that support its propagation. Such modes where free carriers on the surface of a conductor carry part of the electromagnetic energy of an electromagnetic wave are called surface plasmon modes. The high

mobility leads to a low loss, and plasmons are thus useful for confining and controlling the flow of light in dimensions shorter than its wavelength. Such sub-wavelength waveguiding is attractive for on-chip optical communications in the future. This can enable transistors far from each other on a microprocessor chip, or between chips to exchange information by using waveguided light instead of electrons in conductors that can be lossy and have *RC* bandwidths.

Methods of Fabrication

Single-layer graphene flakes were first isolated by mechanical exfoliation from graphite. They were transferred on to substrates with ~ 300 nm SiO₂ on conductive silicon. The dielectric contrast of the substrate at optical wavelengths made it possible to observe the atomically thin crystal under a microscope. Since this initial breakthrough, several methods of preparing graphene have been developed [16]. Large-area single-layer graphene is formed on the surface of single crystal SiC wafers by sublimation. Under specific conditions, the few layers of Si and C on the surface dissociate, Si atoms leave the crystal, and the remaining carbon atoms rearrange to form graphene. A larger-scale method of fabricating single-layer graphene is by chemical-vapor deposition of carbon on heated copper (or other metallic) foils [17]. Owing to the low solubility of carbon in copper, it “precipitates” out, forming a single layer of graphene on the surface. The process is self-limiting, and leads to single-layer graphene of large dimensions. The graphene is subsequently transferred on to insulating substrates by removing the metallic foil. Growth and fabrication of graphene are still at their infancy. The methods used to grow graphene, and the resulting crystalline quality is expected to improve with time.

Other Applications

At present, the high conductivity of graphene and its ultrathin nature makes it attractive for transparent conductive electrodes for flexible electronics. The high in-plane thermal conductivity of graphene can be harnessed for effective heat spreading in various nano-scale structures; graphene can scale this usage of graphite

down to nanoscale dimensions. The light mass of the atoms in graphene, the high bond strength, and atomically thin structure implies that microelectro-mechanical (MEMs) or nanoelectro-mechanical (NEMs) structures made from graphene can operate at very high frequencies, and extend the range of applicability of existing devices. The ease of field-effect of graphene also makes it especially conducive to the fabrication of gas and charge sensors in the field-effect geometry.

Other 2D Crystals and Future Directions

The symmetry of the bandstructure of graphene led to the proposal, and eventual discovery of a new class of materials called topological insulators [18]. These materials have a graphene-like Dirac cone energy dispersion for surface states, whereas the bulk states have energy bandgaps as in traditional semiconductors. The valley degeneracy of such materials is one, so in a sense they are “half” of graphene. Electron motion in the surface bands of topological insulators are protected against scattering by geometric constraints, and are currently under much scrutiny.

The discovery of graphene also opened the door to the search for other 2D crystals, and a number of them have been identified. Among them, boron nitride (BN) is an excellent example. Boron and nitrogen straddle carbon in the periodic table, and is the compound semiconductor analogue of graphene. However, the broken symmetry in the crystal basis itself creates a very large bandgap, approaching ~ 5.4 eV. Thus, BN is an excellent insulator, and quite distinct from other insulating dielectrics since it is composed of sp^2 bonds. The absence of out-of-plane or broken bonds implies that it is chemically and electronically more inert than its 3D insulating counterparts. Indeed, graphene when placed on BN in planar fashion exhibits high electron mobilities and this is attributed to the reduced electronic coupling between the two crystals. The transition-metal dichalcogenides (such as MoS_2) are an analogous family of 2D crystals that exhibit semiconducting as well as metallic properties. However, these 2D crystals are not perfectly planar, as their chemical bonds are different from sp^2 ; they involve d-orbitals. The presence of d-orbitals leads to a richer range of electronic phenomena, ranging from metallic, semiconducting [19], magnetic, to superconducting. Combining this rich range of electronic properties of 2D crystals in heterostructures is

expected to lead to new generations of more efficient and fundamentally new devices in the future. Combining 2D crystals by stacking is expected to be simpler than 3D materials since there are no out-of-plane bonds to join, or break [20].

Cross-References

- ▶ [Active Carbon Nanotube-Polymer Composites](#)
- ▶ [Active Plasmonic Devices](#)
- ▶ [Carbon Nanotube-Metal Contact](#)
- ▶ [Carbon Nanotubes for Chip Interconnections](#)
- ▶ [Carbon-Nanotubes](#)
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- ▶ [Thermal Conductivity and Phonon Transport](#)

References

1. Novoselov, K.S., Jiang, D., Schedin, F., Booth, T.J., Khotkevich, V.V., Morozov, S.V., Geim, A.K.: Two-dimensional atomic crystals. *Proc. Natl. Acad. Sci.* **102**, 10451–10453 (2005)
2. Wallace, P.R.: The band theory of graphite. *Phys. Rev.* **71**, 622–634 (1947)
3. Dean, C.R., Young, A.F., Meric, I., Lee, C., Wang, L., Sorgenfrei, S., Watanabe, K., Taniguchi, T., Kim, P., Shepard, K.L., Hone, J.: Boron nitride substrates for high-quality graphene electronics. *Nat. Nanotechnol.* **5**, 722–726 (2010)
4. Konar, A., Fang, T., Jena, D.: Effect of high- κ gate dielectrics on charge transport in graphene-based field effect transistors. *Phys. Rev. B* **82**, 115452–115458 (2010)
5. Cheianov, V.V., Fal’ko, V., Altshuler, B.L.: The focusing of electron flow and a veselago lens in graphene p-n junctions. *Science* **315**, 1252–1255 (2007)
6. Novoselov, K.S., Geim, A.K., Morozov, S.V., Jiang, D., Katsnelson, M.I., Grigorieva, I.V., Dubonos, S.V., Firsov, A.A.: Two-dimensional gas of massless Dirac fermions in graphene. *Nature* **438**, 197–200 (2005)
7. Zhang, Y., Tan, Y.-W., Stormer, H.L., Kim, P.: Experimental observation of the quantum hall effect and Berry’s phase in graphene. *Nature* **438**, 201–204 (2005)
8. McCann, E.: Asymmetry gap in the electronic band structure of bilayer graphene. *Phys. Rev. B* **74**, 161403–161406 (2006)

9. Zhang, Y., Tang, T., Girit, C., Hao, Z., Martin, M.C., Zettl, A., Crommie, M.F., Shen, Y.R., Wang, F.: Direct observation of a widely tunable bandgap in bilayer graphene. *Nature* **459**, 820–823 (2009)
10. Banerjee, S.K., Register, L.F., Tutuc, E., Reddy, D., MacDonald, A.H.: Bilayer pseudospin field-effect transistor (BiSFET): a proposed new logic device. *IEEE Electron Device Lett.* **30**, 158–160 (2009)
11. Han, M.Y., Ozyilmaz, B., Zhang, Y., Kim, P.: Energy band-gap engineering of graphene nanoribbons. *Phys. Rev. Lett.* **98**, 206805 (2007)
12. Zhang, Q., Zhao, W., Seabaugh, A.: Low-subthreshold-swing tunnel transistors. *IEEE Electron Device Lett.* **27**, 297–299 (2006)
13. Zhang, Q., Fang, T., Seabaugh, A., Xing, H., Jena, D.: Graphene nanoribbon tunnel transistors. *IEEE Electron Device Lett.* **29**, 1344–1346 (2008)
14. Nair, R.R., Blake, P., Grigorenko, A.N., Novoselov, K.S., Booth, T.J., Stauber, T., Peres, N.M.R., Geim, A.K.: Fine structure constant defines visual transparency of graphene. *Science* **320**, 1308 (2008)
15. Sensale-Rodriguez, B., Fang, T., Yan, R., Kelly, M., Jena, D., Liu, L., Xing, H.: Unique prospects of graphene-based THz modulators. *Appl. Phys. Lett.* **99**, 113104–113106 (2011)
16. Berger, C., Song, Z., Li, X., Wu, X., Brown, N., Naud, C., Mayou, D., Li, T., Hass, J., Marchenkov, A.N., Conrad, E. H., First, P.N., de Heer, W.A.: Electronic confinement and coherence in patterned epitaxial graphene. *Science* **312**, 1191–1196 (2006)
17. Li, X., Cai, W., An, J., Kim, S., Nah, J., Yang, D., Piner, R., Velamakanni, A., Jung, I., Tutuc, E., Banerjee, S.K., Colombo, L., Ruoff, R.S.: Large-area synthesis of high-quality and uniform graphene films on copper foils. *Science* **324**, 1312–1314 (2009)
18. Hasan, M.Z., Kane, C.L.: Topological insulators. *Rev. Mod. Phys.* **82**, 3045–3067 (2010)
19. Radisavljevic, B., Radenovic, A., Brivio, J., Giacometti, V., Kis, A.: Single-layer MoS₂ transistors. *Nat. Nanotechnol.* **6**, 147–150 (2011)
20. Novoselov, K.S.: Nobel lecture: graphene: materials in the flatland. *Rev. Mod. Phys.* **83**, 837–849 (2011)

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Green Tribology and Nanoscience

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Synonyms

Ecotribology

Definition

Tribology (from the Greek word τριβή “tribo” meaning “to rub”) is the branch of science and technology concerned with interacting surfaces in relative motion and with associated matters (as friction, wear, lubrication, and the design of bearings). Green tribology is the science and technology of the tribological aspects of ecological balance and of environmental and biological impacts.

Research Areas

Green tribology deals with the ecological aspects of technology involving friction, lubrication, wear, solid surfaces, coatings, as well as applications of this technology. This makes green tribology closely related to the novel areas of tribology: nanotribology, biotribology, and biomimetics. The term “green tribology” was suggested in about 2009 by several engineers and economists. In 2010, the first scientific volume was published by *Philosophical Transactions of the Royal Society* [1]. A number of symposia and conference sections devoted to ecological and green tribology took place starting from approximately the same time, as well as books prepared for publication [2].

Green or environment-friendly tribology emphasizes the aspects of interacting surfaces in relative motion, which are of importance for energy or environmental sustainability or which have impact upon today’s environment. This includes tribological technology that mimics living nature (biomimetic surfaces) and thus is expected to be environment-friendly,