

EPITAXIAL GRAPHENE

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Abstract

Epitaxial graphene, developed at the Georgia Institute of Technology, is a new material composed of one or more graphene layers that are grown on a silicon carbide substrate. It can be lithographically patterned to produce electronics devices that are similar to carbon nanotube devices. On specific faces of single crystal silicon carbide Multilayered Epitaxial Graphene can be grown in such a way, that it retains the essential features of a single graphene layer, even though it may have as much as 100 layers or more. The properties of epitaxial graphene are so compelling that it is currently recognized by the electronics industry as a possible alternative to silicon for large scale integrated electronics.

Introduction

Graphene is a two-dimensional sheet of carbon atoms in which each carbon atom is bound to its 3 neighbors to form the honeycomb structure shown in Fig. 1a. Graphene occurs naturally as the basic building sheet of graphite. In graphite, each graphene layer is arranged such that half of the atoms lie directly over the center of a hexagon in the lower graphene sheet, and half of the atoms lie directly over an atom in the lower layer, seen in Fig. 1b. This stacking of the graphene layers is called the Bernal stacking. This particular arrangement of the graphene layers in graphite greatly affects the electronic properties of graphite; other types of stacking give different electronic properties.

The covalent chemical bonds between the carbon atoms in a graphene sheet, known as sp^2 bonds, are among the strongest in nature. They are, in fact even stronger than the carbon bonds in diamond; diamond reverts to graphite when heated. This exceptional property of the sp^2 bond, that results in the exceptional stability of graphitic systems, is very important for electronic applications and especially for nanoelectronics

in which the structures are subjected to extremely large thermal and electrical stresses. Moreover, the low temperature electronic mobility of graphite is of the order of 10^6 cm^2/Vs , exceeding silicon by about 3 orders of magnitude. The very strong bonds, combined with the low mass of the carbon atom causes a very high sound velocity resulting in a large thermal conductivity, which is advantageous for graphitic electronics. The most important graphene properties actually emerge from the unique band structure of this material as explained fully below.

In contrast to the very strong bonds between the carbon atoms in a graphene sheet, the inter-sheet van der Waals bonding in graphite is more than 100 times weaker and ranks among the weakest bonds. This very weak interlayer bond causes the layers to become essentially decoupled from each other, which produces large anisotropies in the electronic and thermal properties. For example, at low temperatures in-plane electrical and thermal conductivity of single crystal graphite is several thousand times greater than perpendicular to the planes¹. It is because of the very weak interlayer bonds that microscopically thin layers of graphite are easily mechanically cleaved from a larger crystal by rubbing it against a surface, for example paper, causing the familiar pencil trace which consists of microscopic graphite flakes. In fact graphite derives its name from this property (graphein is Greek for to draw).

The recent surge in scientific enquiry into graphene gives the impression that this is a new material. This is in fact not so. It has been known and described for at least half a century. The chemical bonding and structure has been described since the 1930's while the electronic band structure of graphene had been first calculated by Wallace² in 1949. These calculations have been refined ever since, in the wake of new experimental results. In fact the word graphene was officially adopted in 1994, after it had already been used interchangeably with monolayer graphite in surface science to denote graphene sheets on various metallic, metal carbide and silicon carbide surfaces. It was known in the surface science community that the bonding of a single graphene layer on metal surface depends sensitively on the metal surface. In these experiments, graphene is grown on carefully prepared, contamination free metal samples by heating them to high temperatures in a carbon containing gas (methane, ethylene, acetylene etc.). Depending on the surface, the graphene layer may grow epitaxially (for example on a Ni surface³), whereby the graphene atoms registers with the metal atoms on the surface, or the graphene crystallites may have various orientations or even be randomly oriented (as for example on Pt surface⁴). In many cases the bonding to the surface is so weak that the properties of pristine graphene are retained.

It is also noteworthy that several recently discovered graphitic nanostructures, like, for example, carbon nanotubes, are directly related to graphene. In fact carbon nanotubes have been traditionally referred to, as rolled up graphene sheets⁵, and the carbon nanotube properties are most easily described and understood in terms of those of graphene^{6,7}. Indeed, essential properties of graphene were well understood for decades.

Epitaxial graphene layers can be grown on silicon carbide surfaces by heating single crystals to high temperatures (>1100 C) in vacuum or in other inert atmospheres⁸. First reports of single and multilayer graphene on silicon carbide substrates date back to the 1970's⁹. In this process silicon evaporates, leaving a carbon rich surface, which reconstructs into a layer composed of one or more epitaxial graphene sheets. The properties of epitaxial graphene sheets on single crystal silicon carbide had been of interest for several reasons. First of all, graphene growth on silicon carbide can occur during various silicon carbide crystal growth processing steps (for example molecular

beam epitaxy) where it affects the silicon carbide growth; methods have been developed to inhibit the effect of graphene coating. On the other hand, a thin graphitic layer on the silicon carbide had been considered as a method to electrically contact the silicon carbide for silicon carbide based electronics¹⁰.

Researchers at the Georgia Institute of Technology (GIT) pioneered graphene electronics: they were the first to propose and to actively pursue epitaxial graphene for graphene based electronics. The initial steps were taken in 2001, after preliminary calculations revealed the potential of patterned graphene for electronics in general¹¹⁻¹³. In 2002, graphene layers were grown on single crystal silicon carbide and microelectronics methods to pattern epitaxial graphene were developed. The first patent¹⁴ was issued in 2006 based on an application filed in 2003. In 2004 the GIT team published the first scientific paper describing both the vision of the epitaxial graphene electronics as well as providing the earliest results of the potential of epitaxial graphene electronics properties. This includes indications that the material could be gated¹⁵, meaning that an electrostatic potential applied to the graphene layers, thereby altering the electron density, could significantly modulate the conductivity.

Soon after, epitaxial graphene was selected as the most promising platform for graphene based electronics. In fact, epitaxial graphene has appeared on the International Semiconductor Technology Roadmap as a potential successor for silicon for post-CMOS electronics¹⁶. Below we will outline developments along these lines.

There has been a parallel development in another form of graphene called exfoliated graphene. In 2004 researchers at Manchester University developed a simple method to exfoliate graphite in order to produce thin graphitic layers on conducting (degenerately doped) silicon wafer supplied with a 300 nm thick silicon oxide dielectric layer¹⁷. The process involves repeatedly “cleaving” a small graphite crystal using Scotch tape, resulting in successively thinner graphite flakes on the tape. Pressing the graphite-flake-coated tape against the oxidized silicon wafer transfers some of the exfoliated flakes to the wafer so that the surface is sparsely covered with microscopically small flakes of various thicknesses. Most importantly, an optical microscopic method was also developed by which flakes as thin as a monolayer could be reliably identified. The first publication¹⁷ showed an electric field effect, i.e. that the ultrathin graphite flakes on oxidized silicon carbide surfaces can be gated. The paper demonstrates that these ultrathin graphite flakes could be made and that they essentially had the semi-metallic electronic properties of graphite. It was further suggested and demonstrated in following papers^{18, 19} that single layer graphene could be produced by this method. The monolayer graphene was next shown to be distinct from those of graphite and consistent with predictions. This development opened a new direction in two dimensional electron gas physics, one based on graphene rather than the more familiar two dimensional electron gases produced at the inversion layer of gallium arsenide/gallium aluminum arsenide interfaces, which had been the focus of the two dimensional electron gas community for several decades.

As is clear from various factors (i.e. the method of production, variations in the flake thickness, the microscopic size of the flakes, variations in the surface condition of the substrate), exfoliated graphene samples are suited only for research purposes into the properties of graphene and ultrathin graphite, and are not considered to have applications potential²⁰. Despite these drawbacks, research into the 2D electronic properties of exfoliated graphene has blossomed into one of the hottest new topics in condensed matter physics.

This recent great interest in graphene can be traced to the confluence of three

circumstances:

1. The development of epitaxial graphene, with its promise as a new electronics platform;
2. The development of exfoliated graphene on oxidized silicon substrates for basic research;
3. The theoretical appeal of the simple but unusual electronic structure of a single isolated graphene sheet.

The last point needs to be expanded. Two dimensional electron gasses have been studied for many years resulting in a deep understanding of their properties. The fields of two dimensional electron gas physics as well as the field of mesoscopic physics (which primarily concerns the properties of very small, i.e. mesoscopic, two dimensional electron gas structures like quantum wires and quantum dots) are of considerable importance and are well-understood. The basic electronic structure of graphene is in principle understood and several of its properties have been verified, for example in carbon nanotubes. The fact that the electronic properties of graphene are fundamentally distinct from those of “normal” electron gasses provides a bonanza for experimental and theoretical physics. It should be mentioned that theoretical research into the properties of epitaxial graphene are far less advanced. This material is more complex due to the physics at the substrate/graphene interface, which up to recently has been improperly downplayed in most graphene studies.

Here we review some properties, applications and potential of epitaxial graphene grown on silicon carbide substrates.

The electronic structure of graphene

The electronic structure of graphene is relatively easy to comprehend and it forms the foundation of its electronic properties. Graphene is not a metal: it is essentially a giant organic molecule and technically a semi-metal. The electrons follow the so-called pi-bonds that connect neighboring atoms when they travel from one atom to the next. In contrast to metals (like for example copper), the precise geometry of the carbon atoms is essential. In further contrast to metals, where the electrons behave, more or less, as if they were essentially free electrons (that is with a bare electron charge and mass), the electrons in graphene interact with the lattice in such a way that they appear to be massless (see below). Moreover, graphene electrons come in two “flavors”, which relates to the direction of their “pseudo-spin”. The pseudo-spin is an additional quantum number that characterizes graphene electrons. It actually is a label to differentiate bonding and antibonding orbitals that have identical wave numbers and energies. This combination of properties that ultimately make graphene unique graphene. Below we provide more detail.

The 4 carbon valence electrons cause the chemical bonds between neighboring carbon atoms. The orbitals of these electrons arrange in such a way to produce 3 covalent sigma bonds with neighboring atoms in the plane. The electrons participating in these bonds give the graphene sheet is exceptional strength. While electrons in the sigma bonds do not participate in the electronic transport they provide the rigid scaffolding (i.e. the rigid hexagonal honeycomb structure) of the graphitic system.

All of the electronic properties result from the forth valence electron of each carbon atom. We here provide a simplified picture of the forth electron. For simplicity, we will refer to these electrons as the electrons and ignore the sigma bonded electrons. For each carbon atom, the electron is centered on the carbon atom and oscillates up and down through the graphene plane. This up and down motion produces a quantum mechanical p_z orbital. This orbital consists of two lobes (charge density clouds): one above and one below the graphene sheet, shown in Fig. 2a. The motion of the p_z

electrons on two neighboring atoms can be in phase or out of phase with each other. Moreover, the orbitals on neighboring atoms slightly overlap. The energy of a pair of neighboring p_z orbitals decreases when their relative motion is in phase with each other, and it increases when the motion is out of phase. Hence, when the motion is in phase, the pair is said to be in a bonding (attractive) configuration, and when they are 180 degrees out of phase, they are in an antibonding (repulsive) configuration. In general, the interaction strength can have any intermediate value depending on the relative phase.

Due to the non-negligible overlap of the p_z orbitals on neighboring atoms, the electrons readily “hop” from one atom to its neighbors. In fact each electron hops at a rate of about $\nu=10^{15}$ times per second between neighbors. This hopping is so rapid that it is impossible to associate a specific electron with a specific carbon atom. Moreover, a classical description of the electron fails and a quantum mechanical picture is required.

In the quantum mechanical picture, each electron is described as a wave that extends over the entire surface of the graphene sheet. This electron wave has a specific phase and amplitude at each atom. (The amplitudes at each atom are minute: summing the magnitude of the squares of the amplitudes $\Psi(i)$ of a specific electron wave at each atom in the sheet produces unity: $\sum |\Psi(i)|^2=1$). The total energy of the electron wave is found by summing the energy at each bond, thereby by weighting the amplitude of the electron wave at each atom with a factor that depends on the relative phase of the electron ϕ_{ij} wave at neighboring atoms i, j : $E = -\gamma \sum |\Psi(i)| |\Psi(j)| \cos(\phi_{ij})$, where $\gamma \approx 3$ eV represents the energy due to the overlap of neighboring p_z orbitals. Two extreme cases of electron waves can be easily visualized: the first one is when $\phi=0$ for (all in phase) and $|\Psi|=1/\sqrt{N}$ at each atom. In this case the total energy of the wave is $E = -3\gamma$. In the other case, $\phi=\pi$ so that the wave is exactly out of phase at each atom and $E = +3\gamma$. Waves with all intermediate values can be constructed. Those waves for which the total energy is exactly 0 are special as these define the Fermi surface for neutral graphene as explained below.

As demonstrated in the two extreme examples above for neighboring p_z orbitals, the electron waves come in two varieties: π and π^* representing bonding and anti-bonding waves respectively. While for a finite graphene sheet the electron waves are standing waves, in an infinite sheet they are more aptly represented as traveling waves.

A traveling electron wave in graphene is much like a light wave (photon). It has a wavelength, a direction of propagation, energy and momentum. For simplicity and following quantum mechanical convention, we will refer to the traveling waves as electrons. As a matter of fact in quantum mechanics, an electron is a wave (actually a wave function) that is spread out over space and has an amplitude and phase everywhere on the graphene sheet. It is specifically not a small, localized charged object. Indeed, whereas the spread-out nature of a photon appears more natural, in fact when photons are absorbed, they behave like discrete particles. This particle/wave dichotomy is inherent in the quantum mechanical description of matter.

The momentum \mathbf{p} of the electron in a π (or π^*) state is given by $\mathbf{p} = h/\lambda = \hbar\mathbf{k}/2\pi$, where h is Planck's constant, λ is the wavelength and \mathbf{k} is the wave number which is a vector that points in the propagation direction. The energy of a π or a π^* electron, with wave number k propagating in the x direction (perpendicular to a hexagon edge) is $E = \pm \hbar v(1 + 2\cos(kd/2))$; (- for π ; + for π^*) where $d=0.26$ nm is the graphene lattice constant. This equation describes the π and π^* energy bands as first found by Wallace² in 1947 (Fig.2). The two energy bands cross when $k=K=+4\pi/3d$ and $k=K'=-4\pi/3d$ where $E=0$.

These energy bands have been directly measured by angle resolved photoemission by researchers at Berkeley^{21, 22}(Fig. 2d).

Electrons are Fermions (as a result of their half-integer spin which can be either up or down). Consequently, as for all Fermions, no two electron waves (of similar spin) in graphene can have exactly the same momentum and energy. This property (the Heisenberg exclusion principle) dictates the electronic structure of the graphene as follows.

The electronic structure is found by filling up in energy the π and π^* bands with all of the electrons (the 4th valence electron of each carbon atom) in the graphene sheet consistent with the exclusion principle. Hence, starting with the electron with the least energy at the bottom of the π band, electrons are added one by one, until all N electrons are included. In that situation the graphene sheet is neutral (since one electron was added for each carbon atom). This procedure fills the bands up to a maximum energy (Fermi energy), which corresponds exactly to the energy of the K and K' points in neutral graphene. If the sheet is negatively charged, the additional electrons cause the Fermi level to rise to higher energies; if it is positively charged, the Fermi level is lowered.

Note in Fig. 2c that near the K and K' points the energy E of the electron waves varies linearly with momentum (i.e with k): $E=\pm c^*p^*$ where p^* is the momentum measured from the K point and $c^*\approx 10^6$ cm/s. It turns out that taking all directions in the plane into account, this relation still holds: $E=\pm c^*|p^*|$. This is a very interesting situation that is reminiscent of the energy-momentum relation (dispersion relation) of a photon: $E=c|p|$ where p is the momentum of the photon: $p= \hbar\mathbf{k}/2\pi$ and \mathbf{k} is the wave number. In this case, c is the speed of light. Hence, the dispersion relation of graphene resembles that of a photon, which implies that the velocity of electrons in graphene (its Fermi velocity) is $c^*\approx 10^6$ cm/s, independent of its energy, unlike the velocity of electrons in copper for example, that changes with its energy. This property, that the electron velocity is independent of its energy, provides it with the massless quality of a photon, however, the speed of these particles is a factor of 300 smaller than the speed of light. We should point out that in most materials the band structure gives rise to unusual effective masses that range from 0 to infinity. These 'effective masses' reflect the property of electrons in a material and at all the actual masses of the particles involved.

Examining the graphene dispersion relation more carefully reveals that near the Fermi level it is described by two pairs of cones (Fig. 2c), one pair with its apexes touching the K point and the other one touching the K' point. In neutral graphene, the electrons fill the π and π^* bands up to the K and K' points (that is the bottom cones), while above the K and K' points (that is the top cones) are empty. The fact that there are bottom, filled, cones and top, unfilled, cones and that the electrons are Fermions, indicates that the electrons in graphene actually resemble massless Fermions, like neutrinos, rather than photons. This fact was first pointed out by Ando²³, 10 years ago, when he examined the properties of graphene in the context of his well-known investigations of carbon nanotubes. The analogy with neutrinos prompted him to identify the dynamics of electrons in graphene as determined by the Weyl's Hamiltonian²³. This property has been rediscovered and colorfully renamed so that the electrons in graphene are now considered to obey the "massless Dirac Hamiltonian". In the same vein, the cones that define the band structure are referred to as Dirac cones and the K and K' points as "Dirac points".

Knowing the band structure of graphene allows one to predict some of its electronic transport properties. An electric field \mathbf{E} applied to the electrons forces the electrons to move. Specifically, only electrons near the Fermi level (charge carriers) can move by shifting from occupied levels to unoccupied levels. Consequently, the current density \mathbf{J}

is given by $\mathbf{J}=\sigma\mathbf{E}$, where the conductivity $\sigma=e^2ND$. Here e is the electronic charge, D is the electronic diffusivity, proportional to the electron mobility μ , and N is the density of states at the Fermi level E_F . The density of states is the number of states per unit energy and per unit area that are available for electrons. Therefore, at the Fermi energy, N reflects the number of charge carriers in the material. In graphene, the density of states at E_F is proportional to the circumference of the circle that is defined by the intercept of E_F and the Dirac cones. For negatively doped graphene (electron doped), E_F is above the Dirac point and for positively doped graphene (hole doped) E_F is below the Dirac point. Moreover, note that N varies linearly with E_F and that for neutral graphene $E_F = 0$ so that $N=0$.

The vanishing of the density of states at E_F in neutral graphene is reminiscent of a zero gap semiconductor (graphene is actually a semi-metal). In either case, it might be expected that the conductivity of graphene increases with E_F (i.e. with the degree of electron doping) and that it vanishes at zero doping. It turns out, however that the situation is not so simple: the physics near the Dirac point is complex.

A second important property of graphene is its relatively immunity to scattering from impurities and phonons. This property is perhaps one of the most important features of carbon nanotubes and leads to its ballistic conductance at room temperature^{23, 24}. The origin of this property can be understood, in principle, from the band structure. Specifically when absorbed, a phonon can impart a rather large momentum change to an electron but with very little energy change. Hence, only electrons at the Fermi level can be scattered and they will be scattered only to other points at the Fermi level. This already greatly restricts which electrons can interact with a specific phonon. There is even a further restriction. In order to back scatter an electron, say one going in the $+p_x$ direction, to one going in in the $-p_x$ direction, will require not only a phonon with a momentum of $2 p_x$, it must also change the electronic wave from one occupying a bonding orbital to one occupying an anti-bonding orbital. A single phonon cannot perform this feat and so electron-phonon backscattering is inhibited. A similar argument demonstrates that backscattering from long-range scatterers (charged particles on the surface for example) is forbidden, however electrons can scatter from defects in the graphene structure.

As mentioned in the introduction, graphite consists of graphene sheets that are Bernal stacked. Even though the layers are only very weakly coupled, the electronic structure especially near the Fermi level is profoundly affected. This is because of the fact that once a second layer is placed over the first one, every other carbon atom in one sheet has an atom in the other sheet directly above it. This causes a lifting of the graphene symmetry in which all atoms are essentially identical. As a consequence the Dirac cones develop into touching paraboloids and the electrons become massive and many of the distinguishing properties of graphene vanish.

Properties of structured graphene

The electronic structure described above applies for an infinite single graphene sheet and serves as a starting point for patterned and other forms of graphene. Perhaps the best known graphene structure is the carbon nanotube. A simple carbon nanotube consists of a graphene sheet that is rolled in a seamless tube. Its electronic structure is described in many review articles^{7, 25} and has traditionally been derived from the band structure of graphene by imposing appropriate boundary conditions. For a nanotube, electronic motion about its axis results in discrete angular momentum states about the axis while motion along the axis is unconfined. Hence, a nanotube is quantum mechanically a one dimensional conductor or semi-conductor. Most significantly, the confinement effect causes (for semiconducting nanotubes) a band gap to open of the order of $1 \text{ eV}/D$ where D is the diameter of the nanotube.

Likewise, quantum confinement effects also affect a graphene ribbon of width W . Specifically, whereas the motion along such a ribbon is unbounded, the motion perpendicular to the ribbon is confined to produce standing waves, resulting in normal modes (or states) that resemble the electromagnetic waves in a waveguide. Since the electronic speed is constant (like for photons) this analogy has merit and is useful to understand electronic propagation through graphene ribbons. Narrow graphene ribbons should be semiconducting, and according to theory their band gap depends on the way the ribbon is “cut”. For semiconducting ribbons, the gap is inversely proportional to its width and is predicted to be of the order of $1\text{eV}/W$ where W is the width in nanometers^{12, 13}.

Hence, the electronic properties can be tuned by shape. This property, which is shared with carbon nanotubes, is probably the single most important property of graphene ribbons. However, in contrast to carbon nanotubes, graphene ribbons can be rationally patterned using relatively standard microelectronics methods. This overcomes one fundamental problem of carbon nanotubes, which need to be accurately placed for electronic applications purposes. Complex graphene structures can be patterned to produce differently shaped interconnected graphene devices, thus avoiding problems of interfaces and interconnects. This resolves a second major problem of carbon nanotube based electronics. It was precisely these considerations lead to pioneer graphene electronics¹⁵.

Epitaxial graphene on silicon carbide.

Graphene has been grown on metallic substrates (transition metals and carbides) for many years by pyrolysis of carbon containing gasses on heated metal surfaces (Refs^{26, 27} and ref therein). Most studies were motivated by heterogeneous catalysis, because deposit of graphitic layers occurring as a by-reaction were found to be a major reason for catalyst deactivation. This is because a layer of graphite is inert to most chemical reaction.

In some cases (for example on Ni(111)³ or Ru(0001)²⁶), the carbon grows epitaxially which means that the graphene registers with the crystal lattice of the substrate. The properties of these epitaxial films have been extensively studied, however since these films are grown on conducting substrates, they have little electronics applications potential which requires insulating substrates. Consequently, this large body of original graphene work remains relatively unknown to surface-science outsiders.

Silicon carbide is a semiconductor with the chemical composition SiC. It forms in a wide variety of crystal structures (polytypes). We will concentrate on two hexagonal (H) phases, namely the 4H and 6H structures. The 4 and 6 refer to the number of SiC bilayers that make up a unit cell of the crystal. We further focus on the 0001 and 000-1 polar faces (i.e. surfaces). The 0001 face is one where the surface presents Si atoms, whereas the 000-1 face (on the other side of the crystal) presents C atoms. Ultrathin graphitic material can be grown on silicon carbide crystals simply by heating the material in vacuum at high temperatures (>1100 C). The process involves the evaporation of silicon from the surfaces causing them to become carbon rich. The carbon rearranges to form graphene layers. The layers form epitaxially on the silicon carbide surface. This is clearly a growth process that proceeds in a different way than commonly associated with epitaxial growth on surfaces in which the materials from which the films grow are supplied externally. Nevertheless, the process is relatively simple and has been known for many years^{9, 28}. It was also known that growth on the Si and on the C terminated surfaces are different. Material on the C face usually consists of several graphene layers while that grown on the Si face has few and even only 1 layer⁸.

However, several aspects were not known and discovered by the GT team^{15, 29-33}. The graphene grows over steps on the surface to produce continuous films, seen in Fig. 3a. This is clearly important for applications. Furthermore it was found, that the interface layer is charged due to the Schottky barrier at the interface to produce charge densities of the order of $n=10^{12}$ electrons per cm^2 on the graphene layer at the interface^{15, 21, 22, 29, 33, 34}. The other layers are essentially uncharged^{35, 36}. This intrinsic charging is advantageous for some applications since it enhances the conductivity.

Si-face epitaxial graphene

Graphene grown on the Si face typically consists of one to about 5 layers. Like bulk graphite it is Bernal stacked. The interface layer is charged^{21, 22}: $n \approx 5 \times 10^{12}/\text{cm}^2$ so that the Fermi energy $E_F \approx 0.3$ eV. The interaction with the substrate is found to cause an energy gap of about 0.3 eV at the interface while this gap rapidly closes as more layers are added³⁷ (Fig. 1 of ref³⁷). The graphene/SiC interface is found to be complex, and composed of various layers³³. It is possible to grow graphene monolayers on the Si face³⁷⁻⁴² although up to now, the electronic mobility is found to be relatively low (i.e. comparable to Silicon $\mu \leq 1000$ cm^2/Vs at room temperature)^{15, 42}. The low mobility, which appears to be related to defects in the structure, will need to be overcome before graphene grown on the Si face can be considered for electronic applications.

C-face epitaxial graphene

Graphene grown on the C-face has exceptional properties. Fig 3c shows a large area of graphene free of SiC steps that was achieved by utilizing step bunching of SiC. C-face graphene is typically multilayered from about 5 to about 100 layers, as seen in Fig. 3d, and it turns out to be very difficult to grow only a single layer. Like for the Si-face, the interface graphene layer is charged with a similar charge density $n \approx 5 \times 10^{12}/\text{cm}^2$. Electrical transport measurements reveal that the interface layer dominates the electronic transport, at least for relatively narrow ribbons (width < 1 μm) and that the mobility of that layer exceeds 10^4 cm^2/Vs ²⁹. Moreover, quantum coherence has been established over micron distances in relatively narrow ribbons²⁹. Both these properties are very important for applications. In particular, high mobility material is advantageous for high speed, and low dissipation electronics, whereas long phase coherence lengths indicate that quantum coherent devices can be realized in epitaxial graphene devices.

The most important feature of the C-face material is that the layers are not Bernal stacked, but rather exhibit rotational disorder^{33, 43}. For this material, the successive layers prefer to be rotated at several specific angles with respect to each other, forming Moiré patterns, shown in Fig. 3b. The reason for this is not understood, but as a consequence, the electronic structure is the same as that of a single graphene layer. The material behaves like a stack of independent decoupled graphene layers, rather than exhibiting the properties of graphite. This material is therefore multilayered epitaxial graphene (MEG) and it is not simply thin graphite. We believe that this will lead to very important new developments both in fundamental physics and in new device architectures.

The layers above the first one are found to be essentially undoped^{35, 36}. In fact infrared absorption measurements in a magnetic field reveal that for these layers $n \leq 5 \times 10^9/\text{cm}^2$ so that the Dirac point is only a few meV below the Fermi level. Hence, for these layers the Fermi wavelength is of the order of 1 μm , compared with the first layer where the Fermi wavelength is of the order of 10 nm. This is very important, especially for nanostructured devices. For example a MEG ribbon that is 100 nm wide, for example, will only conduct through the interface layer and not the top layers, because the wavelength is smaller than the ribbon width only for the interface layer^{34, 44}. Hence,

even though the top layers are graphene, they do not conduct which is consistent with observations. On the other hand, in ribbons that are larger than 10 μm , the top layers will also contribute to the transport. This is also seen in experiments.

The top, essentially undoped layers have been recently probed by infrared spectroscopy in a magnetic field B . In this situation, the electrons bunch in separate energy levels, the Landau levels, which are labeled by a Landau level index N . The energy of the Landau levels in graphene is: $E_N(B) = C \text{sgn}(N) \sqrt{B |N|}$. The \sqrt{B} dependence is directly related to the Dirac cone and serves as its signature. The Landau level spectrum has been probed by monitoring the absorption of infrared light (Fig. 4a) The analysis of these spectra have revealed that the bandstructure of MEG is indeed described by Dirac cones (Fig. 4b) and more importantly that the mobility of the material at room temperature exceeds 250,000 cm^2/Vs . This is in the same range as measured in thoroughly cleaned suspended graphene flakes^{45, 46}, but at low temperature.

Chemically modified epitaxial graphene

One extremely important feature of epitaxial graphene on silicon carbide, as graphene in general, is that it can be chemically modified which greatly enhances its utility. For example, it is possible to convert MEG to semiconducting graphene oxide by a chemical treatment⁴⁷. Moreover, it is possible to mask the material with a chemically inert coating and to produce openings in the mask where the chemical reactions take place. In this way graphene oxide regions can be patterned on the surface. This process is reminiscent of patterned doping procedures that are employed in silicon processing technology. This is a very promising new direction in graphene processing. Epitaxial graphene also lends itself very well to surface chemistry in order to chemically modify the surfaces. This is primarily so, because the surface is so well organized and well adapted for organic chemistry processing. Chemical modification and functionalization is important from a technological point of view because this will allow the fabrication of precise dielectric coatings that inevitably will be very important for most applications.

Another aspect is the possibility of functionalization of edges of patterned graphene ribbons. Because a carbon atom at an edge has missing a bond, edges in general are expected to be very reactive, contrary to graphene surfaces which requires strong chemical agents for functionalization. It is envisioned to bind molecules to graphene ribbon edges, for doping of sensor purposes.

Epitaxial graphene electronics

Graphene, why bother?

Graphene is a semi-metal (and often referred to, less accurately, as a zero gap semiconductor). That means that in neutral graphene there is no energy gap between occupied and unoccupied states. Semiconducting devices rely on this gap since it is ultimately this gap that allows a semiconductor to be switched from conducting to non-conducting. In fact, for many applications, the larger the gap the better since it insures a large on to off ratio for switching devices. However, as mentioned above, graphene has the interesting property that a band-gap develops in confined structures, of which carbon nanotubes are prototypical. Hence, the electronic properties are structure dependent. Indeed, a graphene ribbon with a width of 1 nm has theoretically a band gap of about 1 eV. An energy gap of this magnitude is very well suited for electronics applications, while the size scale of 1 nm is in the range of anticipated ultimate lithographic methods. Hence, in general, graphene based electronics is intrinsically nanoscopic and in line with micro-electronics developments. Besides this property,

graphene, like nanotubes, can sustain very large current densities that will necessarily occur in nanoscopic electronic devices.

But why should bother with graphene nanostructures since nanotubes can be produced relatively easily and they too have these properties? The reason is twofold. First of all it has been proven to be very difficult to accurately place well defined and shaped carbon nanotubes on a prepared substrate. However, such problems don't exist in epitaxial graphene. Since epitaxial graphene is a two dimensional material and can be grown in large area, devices can be simply patterned using lithographic method. For example, in Fig. 5, hundreds of graphene devices are made in a 3-by-4 millimeter SiC substrate at a time. Next, and very importantly, even though carbon nanotubes (like graphene ribbons) are ballistic conductors^{24, 48}, it is impossible to inject electrons into a nanotube without causing significant heating of the contact. This is due to the nature of the contact between a metal and a carbon nanotube, which conducts by virtue of its pi electron bands. This heating not only consumes energy, it also causes large electrical stresses at the contact giving rise to electromigration of the metal atoms that will ultimately cause the contact to fail. Patterned graphene does not suffer from these problems. Since graphene is rationally patterned, the placement problem does not exist. Furthermore, narrow graphene ribbons can be seamlessly connected to their graphene leads. In that case, the pi electron system of the leads continues into the ribbon and essentially eliminates contact heating. A further advantage, and probably one that will only become in the more distant future, is that all graphene electronics may be phase coherent^{29, 49, 50}. From a quantum mechanical point of view, electron wave propagate through the entire structure or ribbons and leads much like microwaves propagate through wave guides. Because of that, the electronic phase is well defined everywhere and can be utilized as a "state variable", that is, it can be used to propagate information.

Ballistic transport

One of the most remarkable features of carbon nanotubes and graphene is that electrons can travel large distances without scattering. This property already mentioned above, has important consequences for electronics. Not only does this provide for efficient (low power) electronic devices, it also is an important enabling property for very high speed (THz) electronics. In fact it is anticipated that ultrahigh speed electronics will be one of the most important applications of graphene electronics, at least initially.

Gate doping

It is possible to controllably change the number of electrons in a graphene sheet by the gate doping. A gate is produced by covering the sheet with a metal-coated insulating layer. Applying an electric potential between the graphene and the metal induces charges on the graphene^{15, 17-19}. If electrons are added, then states in the upper cones will become occupied, so that the Fermi energy is raised. If electrons are removed then electrons are drained from the lower cones and the Fermi energy is lowered. This, in turns affects the conductivity σ , since $\sigma = |n|e\mu$, where n is the additional number of electrons per unit area (the doping density), e is the electronic charge and μ is the mobility. Furthermore, the electronic wavelength depends on n : $\lambda_F = \sqrt{4\pi/n}$, so that this wavelength can be tuned. Gate doping has been demonstrated in prototype field effect transistors and quantum dot devices^{15, 17-19, 51, 52}.

Conclusion

In summary, epitaxial graphene grown on silicon carbide substrates is a complex but promising material for graphene-based electronics because high quality graphene can be grown to uniformly cover the entire crystal. It can be chemically converted to a semiconducting. The material can also be patterned using standard microelectronics patterning methods, which is attractive for technology.

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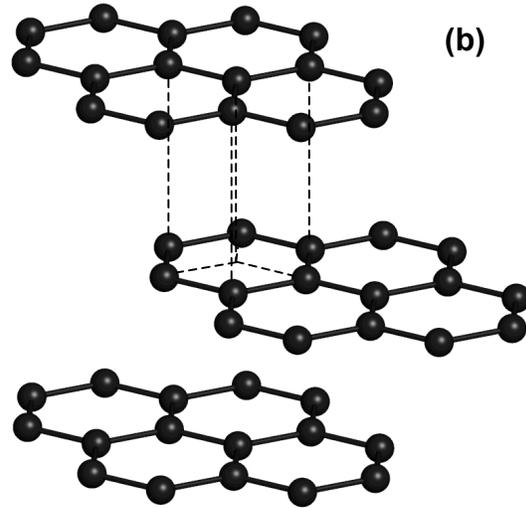
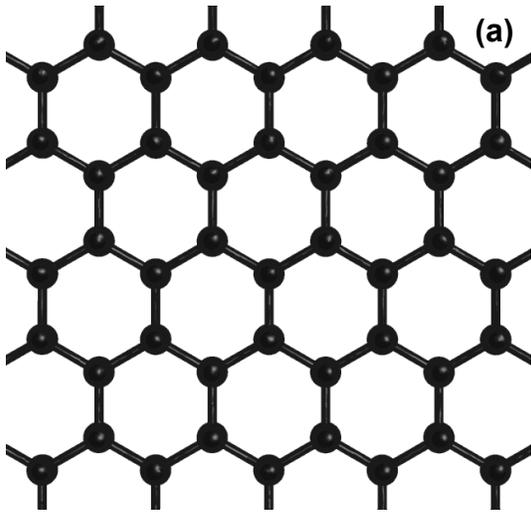


Figure 1 (a) Crystal structure of graphene honeycomb structure. (b) AB stacked graphite. One set of carbon atoms are over the center of the hexagons in the adjacent layers.

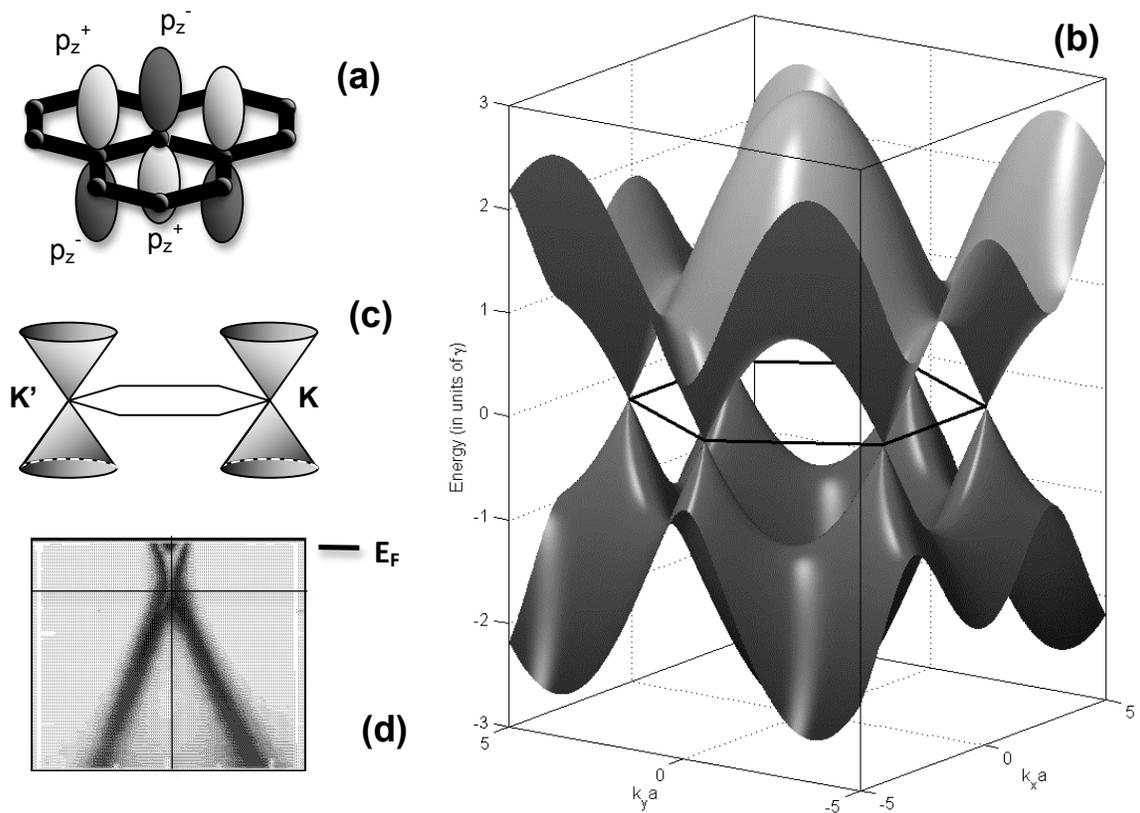


Figure 2 (a) p_z orbitals of carbon atoms are slightly overlapped in graphene. Depending on the relative phase of electron waves in neighboring atoms, the pairing of p_z orbitals can change from bonding to antibonding. (b) The band structure of graphene calculated from the tight-binding model. The valence band meets the conduction band at Dirac points. (c) In the vicinity of Dirac points, the energy of electron waves is linear in momentum. (d) Band structure of epitaxial graphene measured by ARPES shows a linear dispersion and a Dirac point.

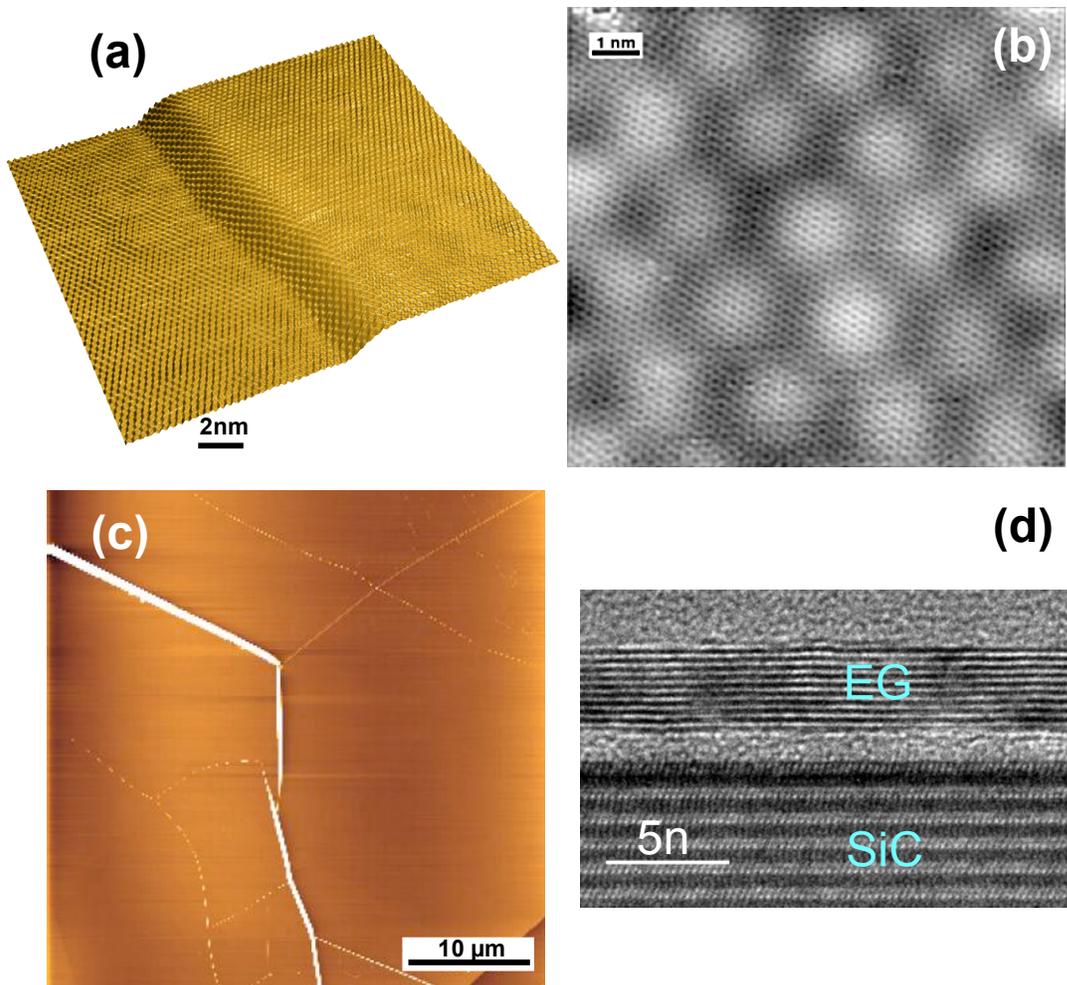


Figure 3 (a) STM image of an epitaxial graphene layer over a 4H-SiC substrate step on the Si-face. (SiC step height 0.25nm). The EG is grown in UHV. (b) STM image of epitaxial graphene on the C-face of 4H-SiC grown in a levitation furnace, in low vacuum. The Moiré pattern arises from a rotational stacking of the graphene layers. (c) AFM image of epitaxial graphene on the C-face of 4H-SiC. The white lines are 'puckers' in the graphene sheets. Flat graphene terraces extend over several tens of micrometers. (d) TEM image of the cross section of multilayer epitaxial graphene on the C-face of 4H-SiC.

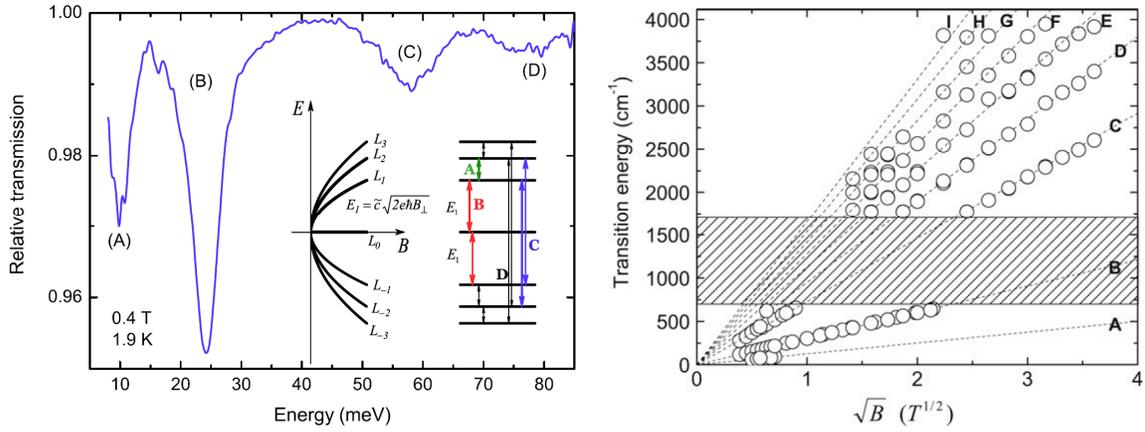


Figure 4 (a) Infra-red transmission spectrum of epitaxial graphene, where transitions occurs as a valley. Transitions happen when electrons absorb photon energy and jump from one Landau level to another. As a result, the transition energy corresponds to the distance between two Landau levels. (b) \sqrt{B} dependence of the transition energy, as expected for the Dirac spectrum in graphene.

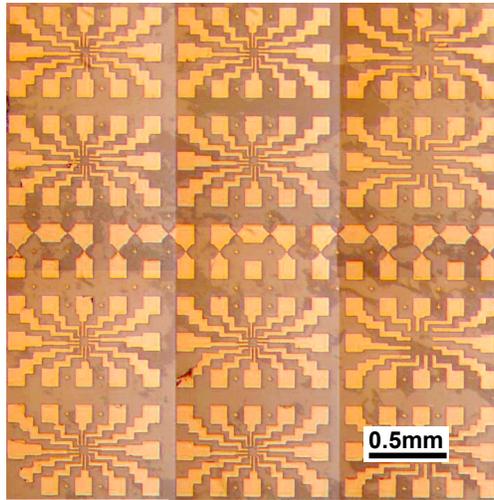


Figure 5 Picture of patterned EG on a $3 \times 4 \text{ mm}^2$ SiC chip. Pd/Au electrical contacts (bright color) connect about a hundred graphene devices.