

GRAPHENE

Nanoelectronics goes flat out

The unique electronic band structure of graphene has led to a number of exotic effects that have fascinated fundamental researchers and may also lead to improvements in the performance of electronic devices.

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When drawing a line with a pencil, small fragments of graphite are left behind on the paper, but it wasn't until four years ago that researchers discovered that single sheets of carbon atoms called graphene could exist among

the debris. They went on to demonstrate that this two-dimensional material had electronic properties quite unlike those observed in most other systems. Since then the number of papers on the subject has mushroomed and shows no sign of slowing down as researchers explore new ways of producing graphene and exploiting its remarkable electronic properties in devices.

Graphene is a semiconductor but it has the unusual feature that its band gap

is exactly zero. Moreover, the velocity of the charge carriers in graphene does not decrease at the top of the valence band and the bottom of the conduction band, as is usual for most materials, but instead stays constant throughout the bands, including at the Dirac point where the conduction and valence bands meet (see Box 1). A gate voltage can, however, modulate the density of states in graphene and switch between the low-conductivity

Box 1 A fascinating new material

Being composed entirely of carbon, graphene is part of an illustrious family of materials that includes insulators (diamond), semi-metals (graphite), quantum dots (fullerenes), and one-dimensional semiconductors or metals (carbon nanotubes). Graphene is a two-dimensional material in which the atoms are arranged in a honeycomb lattice that is just one layer of atoms thick (Fig. B1a). Graphene can be considered as the building-block of all sp^2 -hybridized carbon materials (in which each atom has three nearest neighbours): it can be rolled-up into cylinders to make carbon nanotubes; it can be bent into closed cages by incorporating 5- and 7-membered rings to produce fullerenes; and layers of graphene can be stacked on top of each other to make graphite. The carbon-carbon bond in graphene is stronger than that of diamond, making it extremely stable and chemically inert.

The low-energy electronic band structure of graphene is unique, consisting of conduction and valence bands that meet at the charge neutrality level (Fig. B1b). This makes graphene unusual in that it is a semiconductor with a band gap of zero, whereas the semiconductors used in electronic devices typically have band gaps of between 1 and 2 eV. Moreover, the electron energy is a linear function

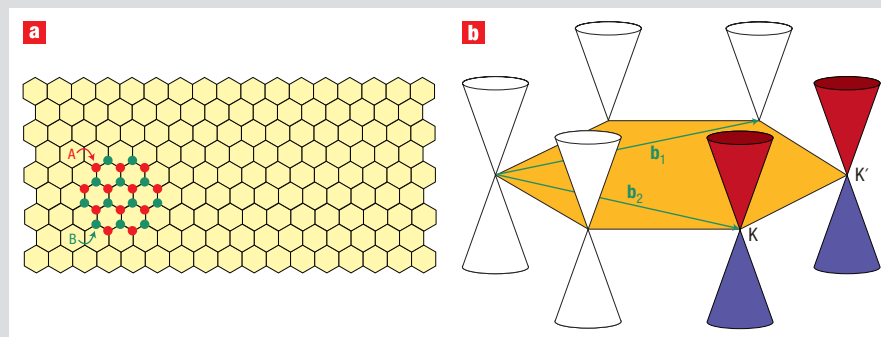


Figure B1 Graphene lattice and band structure. **a**, Real-space honeycomb lattice of graphene. The two equivalent triangular sublattices of carbon atoms (A and B) are shown in red and green. **b**, The low-energy electronic structure of graphene. The vertical axis is energy and the horizontal axes are momentum in the x and y directions. The conduction band (red) and the valence band (blue) meet at six points — known as Dirac points — at the corners of the Brillouin zone (shown in orange) in momentum space. The charge-neutrality level, which corresponds to the Fermi level in undoped graphene, lies exactly at the Dirac points. Two of the cone-shaped structures (K and K') are independent, whereas the others can be constructed from K, K' and reciprocal lattice vectors (shown in green).

of momentum in single-layer graphene, whereas it is proportional to the square of the momentum in all other quasi-two-dimensional materials, including semiconductor heterostructures and bilayer graphene.

The linear energy-momentum dispersion relation in single-layer graphene is similar to that of a photon in free space, which is described by the relativistic Dirac equation. This

means that the electrons all move with a constant speed (approximately the speed of light divided by 300), independent of their momentum, and behave as if they do not have any mass. This is true even at the Dirac point, where the density of states vanishes. The unique electronic structure of graphene has led to many effects, such as a novel integer quantum Hall effect^{10,11}, being observed in this remarkable material.

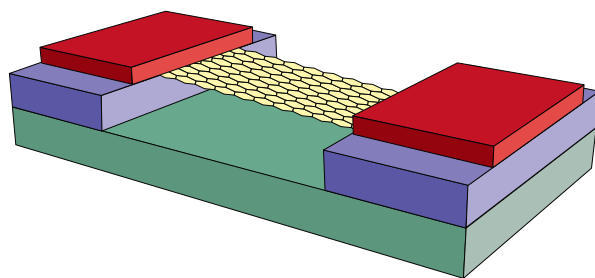


Figure 1 Suspended graphene transistor. Metal electrodes (red) contact a single graphene sheet (yellow) that is fully suspended over a silicon substrate (green). The spacer layer (blue) below the electrodes is silicon oxide. Groups at Rutgers University¹ and Columbia University^{2,3} have shown that these devices have ultrahigh charge mobilities and a very sharp transition at the Dirac point (see Box 1).

state at the Dirac point and the high-conductivity states elsewhere.

Such a switching action is at the heart of the field-effect transistor — the central element in modern computer chips — which is why there is so much interest in graphene, and its close relative, the carbon nanotube, for applications in nanoelectronics. However, there is a crucial difference between the two: semiconducting nanotubes can have band gaps of about 1 eV, which effectively blocks the current in the off state, whereas the low-conductivity state in graphene carries a finite current, even at temperatures close to absolute zero. The minimum conductivity in graphene is also compromised by defects, impurities and the substrate on which it has been placed.

Now, Eva Andrei and co-workers at Rutgers University¹, reporting on page 491, and independently, Philip Kim and colleagues at Columbia University^{2,3} have explored the intrinsic electronic properties of graphene close to the Dirac point by suspending graphene devices to remove the influence of the substrate (Fig. 1). The Columbia group has also removed contaminants in a current-induced thermal annealing process. All substrates can trap electric charges, producing image charges in the graphene. One consequence of this is the formation of electron–hole ‘puddles’ where, for gate voltages close to the conduction minimum, parts of the graphene sheet act as electron conductors, while other parts of the same sheet act as hole conductors.

Changes in the gate voltage can redistribute the charges in the puddles, but they can not reduce the conductivity below a certain value, which depends on the amount of disorder. (Again, graphene is unusual in this regard because high levels of disorder would cause the conductivity to drop to zero in most materials). In suspended graphene, on the other hand, the minimum conductivity at the Dirac point approaches

a universal (geometry independent) value of $4e^2/\pi h$ at low temperatures¹, where e is the electron charge and h is Planck’s constant, as predicted by several theories. Moreover, the transition between high and low-conductivity states as a function of gate voltage becomes very sharp, and the charge density at the Dirac point drops to below 10^{10} electrons per square centimetre (which is just one electron in an area of 100×100 nm), making it conceivable to study, in the future, the last few electrons that are free to move.

Both groups have also measured electron mobilities in excess of 10^5 cm² V⁻¹ s⁻¹ at carrier densities above $\sim 10^{11}$ cm⁻², which is an order of magnitude improvement over substrate-supported devices. At room temperature, mobilities are closer to $\sim 10^4$ cm² V⁻¹ s⁻¹, limited by acoustic phonon scattering, but this is still much better than current silicon devices. The reported mobilities imply that electrons can travel from one contact to the other with only a few scattering events in the channel or at the channel boundary. This could one day enable ballistic graphene electronics to be used for high-frequency applications.

But what happens at the edge of a graphene device and at the contact between the graphene and the source and drain electrodes in a transistor? Eduardo Lee and co-workers⁴ at the Max Planck Institute in Stuttgart and the EPFL in Lausanne have addressed the questions by focusing a laser onto substrate-supported graphene and measuring the resulting photocurrent as a function of position. They found that in addition to the randomly doped electron–hole puddles, the edges of the graphene sheet display p-type doping. This means that when devices are switched from n-type to p-type conduction by changing the gate voltage, the edge region switches before the centre region does, contributing to a broadening of the transition. It will be interesting to see if chemistry can be

used at the edges to reverse this effect (which is related to symmetry-breaking), or if this doping can be used in novel effects where carriers are funnelled either through the interior or along the edge. Lee and co-workers also observed charge transfer between various metal contacts and graphene, and determined the relative positions of the different energy levels at the interface. These kinds of measurements are useful for reducing contact resistances and controlling the alignment of energy levels in devices.

For graphene to become a viable channel material for transistor applications, its band gap has to be opened. An elegant approach would be to construct a potential that acts differently on the two sublattices of graphene (Fig. B1a). After all, hexagonal boron nitride, which has a similar structure, boasts a gap of about 7 eV. A periodic potential that varies on the same length-scale of the carbon–carbon bond could, in principle, be provided by epitaxial growth on a lattice-matched material, but this has not been demonstrated yet. Maybe bilayer graphene will come to the rescue.

The coupling of two graphene sheets in bilayer graphene produces four bands, two of which still touch at the charge neutrality level, so bilayer graphene is also a zero-gap semiconductor. There are, however, two important differences: first, the electrons in graphene are massless, whereas those in bilayer graphene have mass (see Box 1); second, and more important, an energy gap is expected to open up when the two layers of graphene become non-equivalent, which could be done by simply applying a perpendicular electric field. Researchers at the Delft University of Technology have shown that they could open a small gap on the order of 10 meV using this approach⁵. However, it remains to be seen if this effect can be enhanced to a point where the room-temperature characteristics of the transistor are substantially improved.

It is possible to open up a gap in single-layer graphene by constricting the lateral dimensions to produce zero-dimensional structures, which are called quantum dots, or one-dimensional structures such as nanoribbons. Nanoribbon devices have been fabricated by lithography and etching^{6,7}, and also by a combination of thermal and ultrasonic exfoliation of graphite in solution and deposition onto the substrate⁸. The nanoribbons produced by the latter method should have smoother edges, which will be necessary to preserve high carrier mobility.

In this context, the recent demonstration that iron nanoparticles can be used to etch few-layer graphene along specific crystallographic directions to produce

nanoribbons is of interest⁹. If this technique could be shown to produce atomically smooth zigzag or armchair edges, this would be a major feat. Certainly, some kind of lithography/etching technique that makes use of large-scale two-dimensional graphene would be more promising for integration purposes than the defect-free assembly of nanostructures over large scales.

In fact, the prospect that high-performance graphene devices could one day be patterned in a top-down fashion

is the biggest advantage that graphene has over its slightly older sibling, the carbon nanotube. It will be fascinating to see if researchers of any of these new materials can step up to the task and develop them into a viable technology.

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NANOMATERIALS

Let's twist again

A dislocation running through the trunk of a nanowire offers a new twist to the growth of chiral branched nanostructures, producing beautiful tree-like structures in the process.

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The Turning Torso, a 52-storey building in Malmö, designed by the Spanish architect and sculptor Santiago Calatrava, will look familiar to anyone who has read two recent papers about chiral-branched nanowires. Song Jin and co-workers¹ at the University of Wisconsin–Madison saw similar ‘nanotree’ structures in lead sulphide nanowires and, independently, reporting on page 477, Yi Cui and co-workers² from Stanford University observed them in lead selenide nanowires.

The central trunks of the twisted structures grown by the two teams had a dislocation contrast running along them. This contrast can be explained by the presence of a screw dislocation with a Burgers vector component parallel to the long axis. The Burgers vector quantifies the difference between the distorted lattice around a dislocation and the perfect lattice. This dislocation will lead to an induced torque, which will slowly rotate the lattice of the nanowire as it grows along the length axis. This is known as the ‘Eshelby Twist’ following the theoretical work on screw dislocations carried out by John Eshelby



Figure 1 The Turning Torso in Malmö, Sweden. The building has a rotating trunk similar to the nanotrees with an Eshelby Twist that researchers have recently created.

in the 1950s³. When a second generation of nanowires is grown epitaxially on these twisted trunks, the resulting branches directly visualize the crystal defect that runs through the tree.

The lead sulphide nanowires were created using chemical vapour deposition to combine lead chloride and elemental sulphur. The lead selenide nanowires, on the other hand, were grown by co-evaporating a low-melting-point metal such as bismuth, which acts as a catalyst, with lead selenium powder.

The formation of these branched nanowires is significant for a number of reasons. First, the decoration of the axial dislocation by the branches allows for a much simpler observation of the crystal defect, as the use of tedious transmission electron microscope studies can be replaced by fast inspection with a scanning electron microscope. What is more, these new structures follow the first theory proposed for the growth of highly anisotropic crystal shapes, which was suggested by Charles Frank in 1949⁴. Screw dislocations have rarely been identified in the whiskers and nanowires produced since the theory was proposed. In fact it took until 1965⁵ before they were observed experimentally, in single-crystal whiskers of aluminium nitride and later in the mineral chalcotrichite, which is a fibrous form of cuprite⁶. Owing to a shortage of examples of this type of growth, alternative models have been developed, such as the vapour–liquid–solid⁷ growth mode and, later, the vapour–solid–solid⁸ growth mode.

The work at Wisconsin–Madison and Stanford demonstrates that in growing nanotrees it is possible to combine growth by the Frank screw-dislocation mechanism in the trunk with vapour–liquid–solid or