GRAPHENE

From strength to strength

With exciting new results appearing every week, graphene is one of the hottest topics in physics, and may also form the basis of a new approach to electronics a decade from now.

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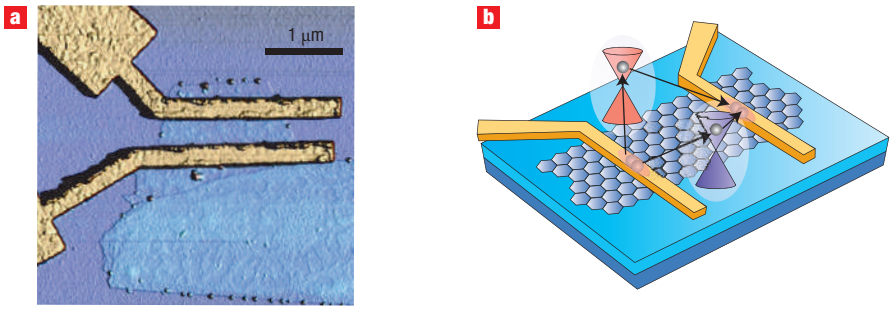

Figure 1 Graphene-based superconducting transistor. **a**, An atomic force microscope image and **b**, a schematic representation of a layer of graphene between two superconducting electrodes (yellow). Graphene is not a superconductor but it can support a supercurrent when placed between two superconductors. A gate electrode (not shown) is used to control the supercurrent, which can be carried by electrons or holes[6]. The red and blue cones in **b** represent the valleys in the electronic structure of graphene (see Box 1).

It is one of those seemingly simple questions that kids come up with: "How does a pencil work?" A scientifically knowledgeable parent will dutifully explain that the grey stuff inside the pencil is called graphite, that graphite is like a stack of pancakes with each pancake being a layer of carbon atoms, and that when the pencil is moved across a piece of paper, the pancakes peel off to leave marks on the paper. But parents know that such an answer will only provoke more questions such as: "can you see one of the pancakes?"

Less than three years ago Andre Geim, Kostya Novoselov and co-workers at Manchester University in the UK and the Institute for Microelectronics Technology in Chernogolovka, Russia, discovered that single layers of graphite — also known as graphene — really can be seen[1]. The technique they used basically involves drawing with a piece of graphite on a silicon substrate. If the substrate has been prepared with an ultrathin layer of silicon dioxide on top, the graphene flakes, which are just half a nanometre thick, become visible under an ordinary optical microscope.

More surprises followed in 2005 when Geim, Novoselov and co-workers and, separately, Philip Kim, Horst Stormer and colleagues at Columbia University in the USA, drove an electrical current through a graphene sheet[2,3]. In addition to various novel electronic phenomena (see Box 1), they found that the electron mobility of graphene can be as high as 10,000 $cm^2\ V^{-1}\ s^{-1}$ at room temperature, which is about ten times higher than the mobility of commercial silicon wafers.

Mobility is often severely limited by structural imperfections, but the structural purity of graphene means that electrons can travel huge distances — 300 nanometres or more — without being scattered. Moreover, this impressive mobility is little affected by changes in temperature or by the presence of excess charge on the graphene sheet. There also seems to be ample room for optimizing the manufacturing process of graphene, so it is little wonder that researchers at companies like Intel and IBM have started to work on graphene. But will physicists and engineers be able to convert the undoubted promise of graphene into real-world electronic devices?

Three recent discoveries indicate that things are moving in the right direction. Writing in *Science*, Novoselov and co-workers report further evidence of the remarkable electronic properties of graphene[4]. It has been known for more than two decades that the resistance of a very pure two-dimensional conductor changes in a very particular way when an external magnetic field is applied.

In the classical Hall effect, which was discovered in 1879, the Hall resistance is proportional to the magnetic field. But in the quantum Hall effect, which was first observed in very pure semiconductors in 1980, the Hall resistance is quantized and increases in units of $h/\nu e^2$ as the magnetic field is increased, where h is Planck's constant, ν is an integer and e is the charge on the electron.

This quantum Hall effect cannot be observed in conventional semiconductors above about 30 K because thermal fluctuations wash out the delicate quantum effects that are responsible for it. Novoselov *et al.* have now seen the quantum Hall effect in graphene at room temperature. This is possible because the energy that sets the scale for the quantum Hall effect in ordinary semiconductors is proportional to the inverse effective mass of the electrons, but in graphene, owing to its unique electronic structure, the effective mass of the conduction electron vanishes.

Moreover, in work submitted for publication, Leonid Ponomarenko, Fredrik Schedin, Novoselov and Geim report the first results on an all-graphene single-electron transistor (SET) that also operates at room temperature (ref. 5; L. A.Ponomarenko, F. Schedin, K. S. Novoselov and A. K. Geim, manuscript in preparation). As its name suggests, the SET is the ultimate transistor — operating at the smallest possible length scales and manipulating the smallest possible currents. The SET can be viewed as a quantum dot or 'box' for holding electrons, with the electrons being able to enter and leave the quantum dot via separate electrodes.

The operation of a SET relies on electrons hopping between the quantum dot and the leads. The key point is that electrons can only pass through the dot one by one — because of the Coulomb repulsion between the electrons it is simply not possible for two electrons to be on the dot at the same time. If the device is 'open', current can flow from one lead to

Figure 2 The structure of graphene. **a**, In graphene, each carbon atom is bonded to three other carbon atoms to form a two-dimensional honeycomb structure that displays a variety of novel electronic properties. **b**, **c**, Scanning electron micrographs showing a single graphene sheet (**b**) and thicker layers of graphite (**c**).

the other via the quantum dot. However, if a single electron is kept hostage on the dot by, for instance, applying an external electric field, other electrons cannot pass and the SET is 'closed'. The electric field that opens and closes the SET is supplied by a gate electrode near the quantum dot. The Manchester team used electron-beam lithography and isotropic dry etching to make the quantum dot, the leads and the gate electrodes — all from the same sheet of graphene.

Writing in *Nature*, meanwhile, Hubert Heersche and co-workers from the Delft University of Technology in the Netherlands report the first graphene-based superconducting transistor[6]. In principle, superconducting electronic devices consume less power than ordinary electronics and also offer ultrafast switching times. Graphene is not superconducting by itself but, like most normal conductors, it can support a supercurrent over short distances when placed between two superconducting electrodes owing to a phenomenon known as the Josephson effect. For this to happen the graphene must not destroy the quantum coherence between the electrons in the Cooper pairs that enter the graphene sheet from the superconducting electrodes. By reducing the dimensions of their device to the nanoscale, and by taking advantage of the intrinsic cleanliness of graphene, the Delft team was able to maintain the quantum coherence needed to make a superconducting transistor (Fig. 1).

Just as the current in a conventional transistor is controlled by a gate voltage, the supercurrent in the Delft transistor is manipulated by a gate electrode placed under the graphene sheet. The voltage on the gate electrodes controls the density of charge carriers that are injected onto the sheet, and the sign of this voltage determines if these charge carriers are electrons or holes. As the supercurrent can be carried by electrons or holes, the transistor is said to be bipolar. Another unusual feature is that the graphene supports a finite supercurrent, even when the

Box 1 Why is graphene so special?

In a graphene sheet, each carbon atom forms bonds with three other carbon atoms to produce a two-dimensional honeycomb structure (Fig. 2). These carbon–carbon bonds are very strong, which renders graphene stable, even when it has been cut into nanoscale structures. Indeed, last month Jannik Meyer of the Max Planck Institute in Stuttgart and co-workers reported that they had been able to freely suspend a graphene membrane on a microfabricated scaffold in air[10]. Although the membranes are strongly rippled and corrugated, they do not rupture. It is this mechanical stability that sets the stage for electronic stability.

Graphene is a zero-gap semiconductor, an electronic state of matter that is precisely in between a semiconductor and a metal. Semiconductors are characterized by an appreciable energy gap between the valence and conduction bands, whereas in metals these two bands largely overlap. In graphene the interaction between the electrons and the periodic potential of the honeycomb lattice results in a band structure in which the valence and conduction bands touch at just two points, rather than overlapping, and this leads to the formation of 'valleys' in the electronic structure (Fig. 1b). At these so-called Dirac points, the electrons behave as relativistic quasiparticles called Dirac fermions. At first this came as a surprise but it is now well established.

Dirac fermions always move with a velocity that is independent of their energy and direction. This is a property that they share with photons, which always move at the speed of light, c, irrespective of their energy. Although the Dirac fermions in graphene are much slower — only moving at about $c/300$ — the important point is that it is impossible to slow them down, which means that the charge mobility is very high[11].

So far, most theoretical predictions about graphene have been confirmed by experiment, but there is still a lot for theorists to think about, including the recent prediction that p–n junctions in graphene could be used to focus electrons and, possibly, demonstrate the electronic equivalent of a negative refractive index in optics[12]. The electrons in graphene also have a degree of freedom that is not found in other electronic systems because they can be at one of the two Dirac points, and theorists are exploring the possibility of exploiting this in devices[13].

Other condensed-matter theorists are, for example, taking on the basic challenge of exploring the consequences of the Coulomb interactions between Dirac fermions, and their colleagues in other fields are also getting involved. Cosmologists, for instance, are interested in the behaviour of relativistic quantum particles in curved spaces, so the results of experiments on curved graphene sheets could provide them with food for thought[14].

density of charge carriers is zero. Moreover, all the superconducting transistors made by the Delft group can support a supercurrent, making the ability to sustain a Josephson effect yet another robust feature of graphene.

The development of commercial graphene-based nanoelectronics will encounter a number of technological challenges. First and foremost, is it possible to produce high-quality graphene wafers in sufficient quantities? Options include dissolving graphite and depositing it as a monolayer on a substrate in a bottom-up approach, or burning off silicon in the top layer of silicon carbide crystals in a top-down approach.

Another problem in the transistors made so far is that there is a noticeable leakage current, even when the device is meant to switched off. This is related to the unstoppable nature of the electrons in graphene (see Box 1) and can only be remedied by creating a bandgap. One way to solve this problem is to use bilayer graphene, because, according to theory, a voltage difference between the two layers will generate a bandgap. However, making bilayer graphene on a large scale is probably even more difficult than making single-layer graphene. SETs could circumvent the problems with leakage currents, but again the large-scale manufacture of such devices with reliable characteristics will be a challenge.

The use of graphene 'nanoribbons' could be another solution because the electronic properties of the ribbon depend on the type of edge it has: simple theoretical considerations suggest that all ribbons with so-called zigzag edges are metallic, whereas those with 'armchair' structures can be semiconductors (with a bandgap) or metals, depending on their width. However, some theorists have recently suggested that all graphene ribbons are semiconducting[7]. At present the edges are naturally passivated by hydrogen atoms, but they could be functionalized by attaching different chemical groups, providing potential for sensor applications. Preliminary reports on graphene ribbons are appearing[8,9], but the challenge of routinely cutting and pasting graphene with the required level of precision will require the very best tools from nanotechnology.

Although graphene research is still in its infancy, the number of experimental breakthroughs in the past three years has been stunning: the observation of the quantum Hall effect at room temperature, the first graphene-based SET, and the bipolar superconducting transistor are just a few of many highlights. Moreover, the development of graphene-based nanoelectronics looks possible, if difficult. The main obstacles concern large-scale manufacturing and the challenge of patterning graphene at the atomic level. However, it took 50 years for silicon technology to reach maturity, so the parents of today would not be irresponsible if they told their kids that when they grow up, they might well find themselves using devices made from carbon pancakes just one atom thick.

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NANOPARTICLES

A very versatile nanocapsule

Numerous copies of a pumpkin-shaped molecule can be linked together to form a nanocapsule shell that can trap compounds inside. The outer surface of this capsule can be decorated with other species by plugging them into the cavities of the hollowed-out pumpkins.

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In the past half-century, scientists have made enormous strides towards creating nanoscale structures and devices. Often these efforts are inspired by biology, not least because nature has been making functional nanosystems using the 'bottom-up' approach for millennia. Scientists have, with varying degrees of success, been attempting to mimic the basic capsid architecture of viruses in order to create nanoscale capsules for applications ranging from targeted drug delivery to functional materials development[1]. Now, writing in the international edition of *Angewandte Chemie*, Kimoon Kim and colleagues at Pohang University of Science and Technology in Korea describe an impressively versatile synthesis of polymer nanocapsules with surfaces that can be easily and reversibly decorated with other molecules[2].

One of the many different strategies for making synthetic nanocapsules takes advantage of self-assembly — the method by which well-ordered architectures are formed spontaneously from small molecules[3] or polymers[4]. For example, convex aromatic compounds can be pieced together along their edges through hydrogen bonds to form hollow spheres that encapsulate small molecules[5]. However, these supramolecular assemblies are held together by relatively weak non-covalent bonds and their stability depends strongly on their environment — under some conditions their presence can be somewhat fleeting, with dissociated components often observed.

One way to enhance the stability of these structures is to covalently link the constituent parts. In general, the crosslinkable groups are attached — either covalently or non-covalently — to a core template. The core is removed by chemical degradation, yielding architectures that will ideally retain the shape of the central template[6]. Such 'core–shell' approaches are now well established[1], as are hybrid construction approaches that use a combination of self-assembly and templating[7]. The new approach taken by Kim and co-workers to make a nanocapsule is fundamentally different from these strategies — the building blocks are simply stitched together using traditional chemical reactions (rather than non-covalent