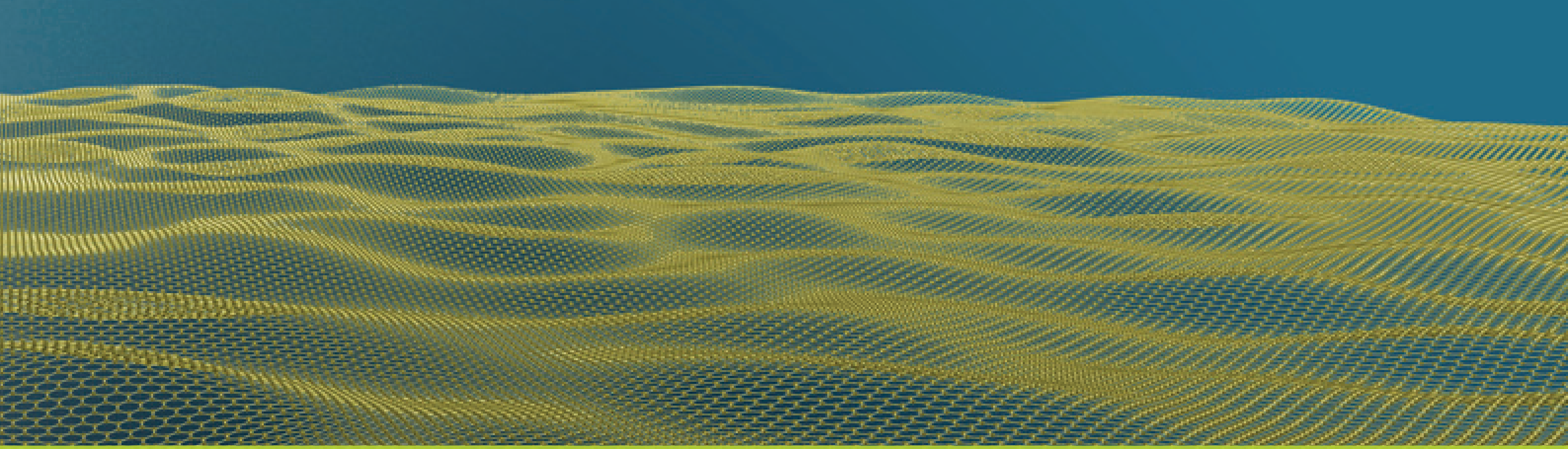
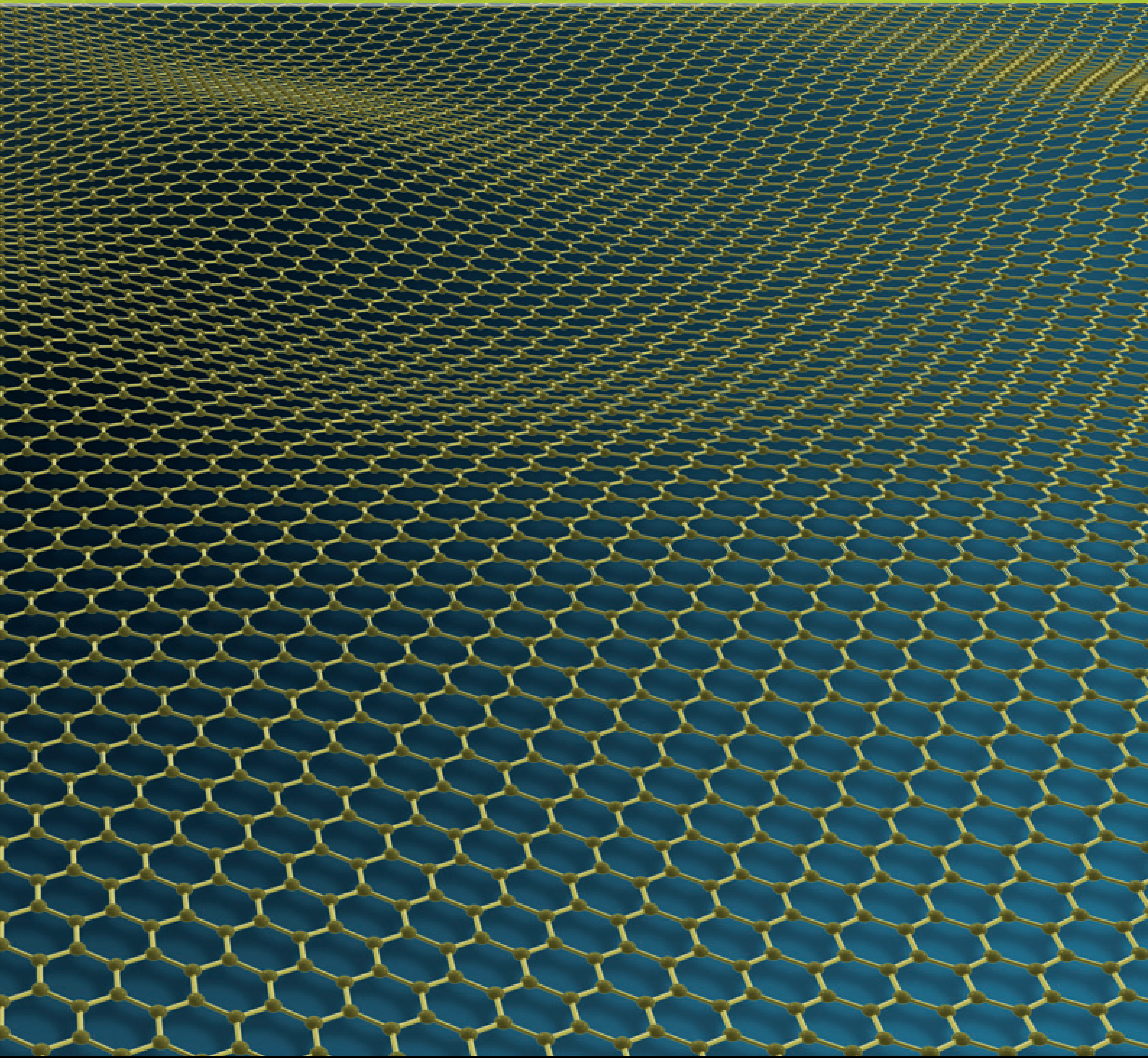


GRAPHENE

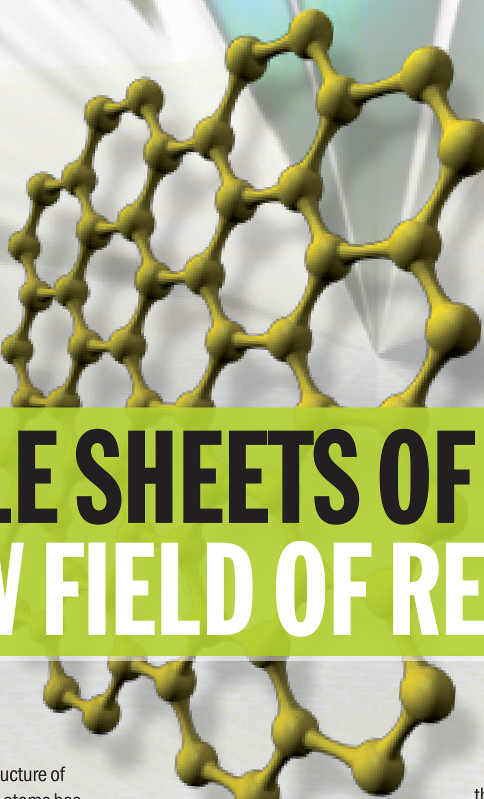
A new form of carbon with scientific impact and technological promise



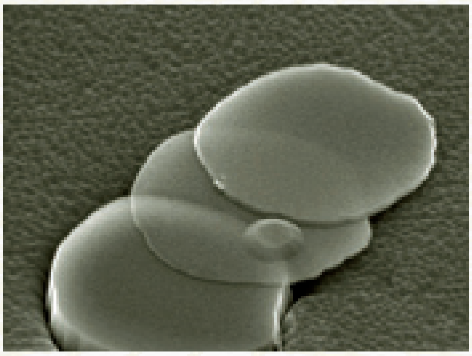
IOP Institute of Physics

In 2010, two physicists, Andre Geim and Konstantin Novoselov, working at the University of Manchester, received the Nobel Prize for Physics for making and studying a new form of carbon – graphene. The material has remarkable physical properties that have entranced both scientists in academia trying to understand the basic behaviour of matter, and those working in industry on the development of advanced technologies considered key to economic progress.

SINGLE SHEETS OF CARBON OPEN UP A NEW FIELD OF RESEARCH



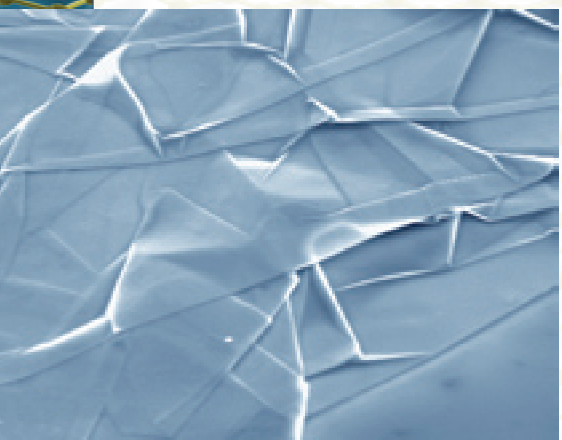
Graphene's single-layered structure of hexagonally arranged carbon atoms has remarkable properties



Flakes of graphite, 30 nm thick, from which graphene layers were isolated

WHAT IS GRAPHENE?

Carbon is chemically versatile, readily binding with other elements to form a plethora of complex molecular structures. Carbon atoms can link with each other either tetrahedrally to form diamond, or more commonly, in layers with a chicken-wire structure, graphite. The hexagonally arranged carbon–carbon bonds are rich in electrons, making the graphite conduct well along the layers. In recent decades, researchers have made new versions of graphite in which the layers curl round into nanometre-sized balls (fullerenes) or roll up into tubes – carbon nanotubes, which have demonstrated technological promise. Graphene, however, consists of just a single layer of graphite.



GRAPHENE'S PROMISE…

Graphene is the thinnest and strongest material ever isolated, and its electronic properties are quite different from those of graphite, nanotubes and the fullerenes. The electrical charge carriers in graphene move, unimpeded, at speeds 10–100 times faster than in today's silicon chips – and at normal temperatures. Furthermore, graphene is stable in air, transparent and flexible. Being carbon, the source material should be cheap and plentiful. It is not surprising that industry is excited by graphene's technological potential.

…AND CHALLENGES

Graphene offers the seductive prospect of fast, nanoscale electronic devices. However, making and manipulating graphene is a daunting task, and the techniques are not yet in place to fabricate devices commercially. Nevertheless, there are many other potential applications for graphene, which could reach the market over the next few years.

A scanning electron micrograph of a crumpled graphene sheet

THE DISCOVERY

Motivated by the global research interest in carbon nanotubes, Geim decided, in the early 2000s, to look at the flat, 2D version. Theoretically, graphene was not supposed to be stable. However, he and Novoselov found a way of lifting off flakes of material from a graphite surface using sticky tape, and then repeating the process until they obtained ultra-thin layers, a few atoms thick. Using an optical microscope, they were, for the first time, able to identify tiny fragments, a few micrometres across, of perfect single-atom layers, when deposited on a silicon-dioxide surface.

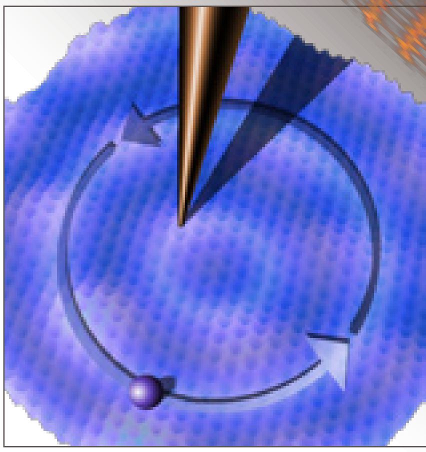
Their research paper in the journal *Science* in 2004 describes the first studies of the electronic properties of graphene. They found that the electrons shoot through graphene ballistically, travelling huge distances without scattering. By making a simple device with an electric field (a gate) to control the electron flow (a field-effect transistor), the electronic properties could be dramatically changed. The field of graphene science was born.

Physicists had speculated on the properties of graphene for more than half a century. Its isolation enabled them to study it experimentally. As in semiconductors, the electrical current is transported by either negative charge carriers (electrons) or the positive "holes" that they leave behind. Unlike conventional electrons and holes in semiconductors, graphene's charge carriers travel over hundreds of nanometres at a speed that is only 300 times slower than that of light.

WHY IS GRAPHENE SPECIAL?

UNIQUE ELECTRONIC PROPERTIES

The charge carriers are clearly a little unusual, and are a result of interactions within graphene's rich, and symmetrical periodic arrangement of electrons spread across its hexagonal lattice, which creates waves of electric charge known as **quasiparticles**. These behave a bit like photons of light – that is, as if they are **massless** – yet retain the quantum character of electrons, carrying quantised charge and spin. What theorists find exciting is that these unique electronic species are subject to the special theory of relativity, which means that they are governed by the version of quantum theory used to describe such relativistic charged particles – **quantum electrodynamics**, or QED. Graphene therefore offers the prospect of testing some aspects of QED, usually requiring large, high-energy particle accelerators, in cheaper table-top experiments.

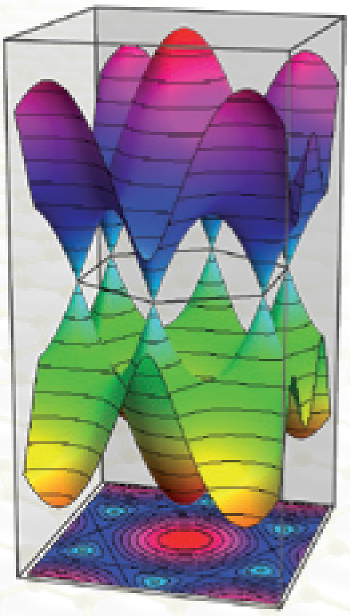


Kubista/Georgia Institute of Technology

A graphic of the electron behaviour of graphene in a magnetic field as mapped with an electron microscope

A QUANTUM PROBE

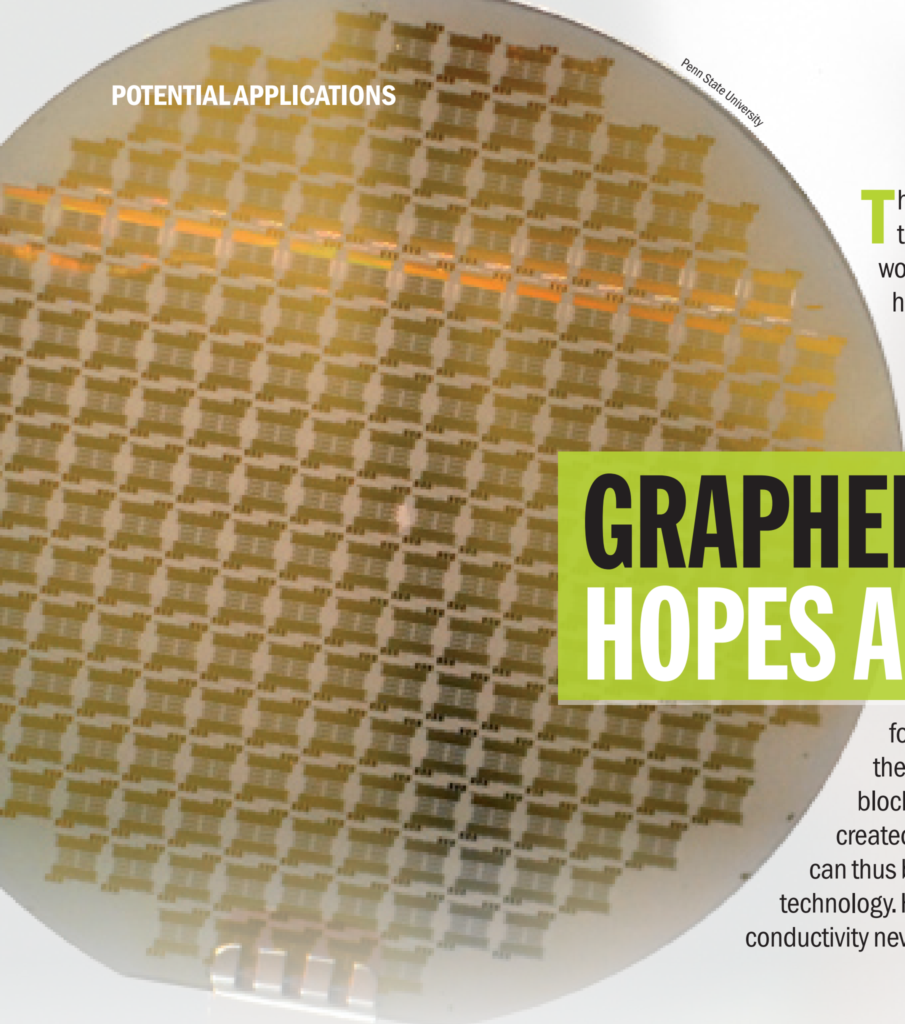
One extraordinary but previously untested QED phenomenon that has recently been demonstrated in graphene is the **Klein paradox**, which predicts that relativistic charged particles can tunnel without hindrance through any energy barrier, no matter how high or wide it is. This happens because, according to QED, such particles generate a "ghost-version" of their corresponding antiparticle that has opposite charge. The antiparticle does not see the barrier and so passes through, creating the normal particle again on the other side. In the case of graphene, the quasiparticles and their holes are the equivalent to pairs of particles and antiparticles such as the electrons and positrons studied in particle-physics experiments.



A visual representation of the unusual energy/momentum relationship of the charge carriers in graphene, which gives rise to its unusual quantum behaviour

Graphene also provides a way of examining quantum phenomena in two dimensions. For example, a magnetic field applied perpendicularly to a current flowing in the plane of a 2D conductor, induces a transverse voltage, that increases in discrete quantum steps – the **quantum Hall effect**. In metals, it appears only at very low temperatures, but in graphene it can be observed under ambient conditions, which indeed confirms its single-layer status. Furthermore, two new types of the quantum Hall effect were observed, which correspond to two different kinds of quasiparticles, one found in graphene and one in a bilayer of graphene.

Graphene continues to excite physicists, not only as a "toy model" to explore fundamental quantum behaviour, but also in stimulating further study of novel effects in ultra-thin layers and surfaces of materials, with potential technological value.



The discovery of graphene's special properties has triggered a huge amount of research activity around the world into how they could be exploited. The possibility of harnessing ultra-fast electrons in atomically thin carbon films immediately suggested a new generation of nano-sized electronic devices that would overcome the scaling and speed limits of silicon. The global market for electronics is worth more than £1 trillion annually, so the rewards would indeed be huge. There is a stumbling block, however. In standard semiconductors, a barrier can be created that can either stop or let electrons through. The current can thus be switched on and off, as required by today's digital technology. However, because of the Klein paradox, graphene's conductivity never completely switches off.

GRAPHENE HOPES AND FUTURES

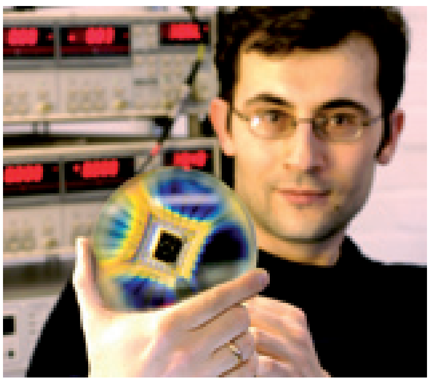
A graphene wafer containing thousands of device structures

CAN GRAPHENE BEHAVE LIKE SILICON?

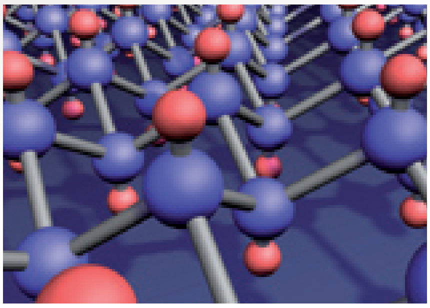
Nevertheless, researchers have been investigating how to manipulate graphene's electronic prowess. **Bilayer graphene** behaves a little differently and its conductivity can be switched on and off using a gate electrode. Another approach, first demonstrated by Novoselov, Geim and colleagues, is reversible chemical modification: **hydrogen** readily binds to graphene, reducing the conductivity to one-millionth of its previous value. Graphene can also be carved into **ribbons** a few nanometres across, with edges structured to confer insulating properties. The Manchester researchers fabricated a **single-electron transistor** from graphene ribbons configured to make a **quantum dot** – a nano-sized structure in which electrons are confined at given energies. Although the many model systems made so far demonstrate the possibility of fabricating integrated circuits, how it would be done on a commercial scale in a controllable way is less clear.

GOING WITH THE FLOW

A more realistic prospect is to take advantage of the ballistic behaviour to make rapidly oscillating analogue devices that depend on a varying conductivity. These could be used in transmitters and receivers for **broadband communications** operating at hundreds of gigahertz or even in the much desired **terahertz** range (1 trillion cycles per second). IBM and Samsung have already demonstrated a prototype processor made from transistors, etched on a 2-inch wafer, that operates at above 100 GHz.

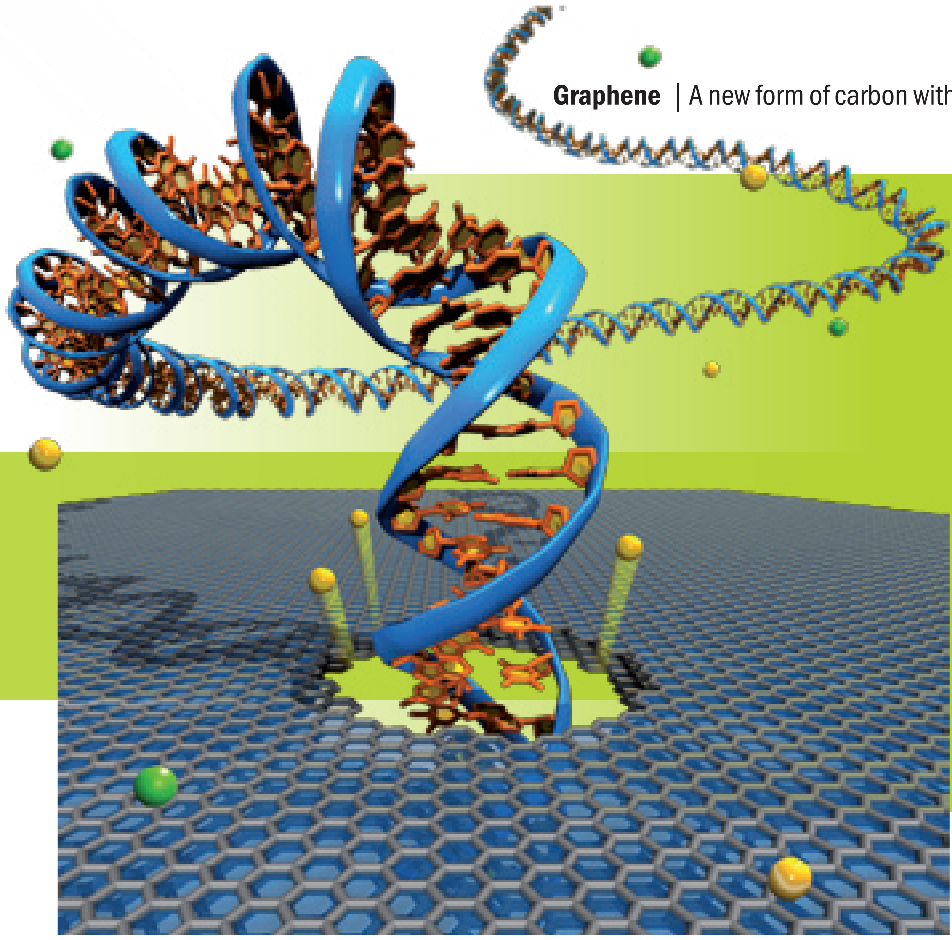


Graphene quantum dots on a chip



The Manchester researchers have added fluorine atoms to graphene to make highly insulating fluorographene, which could be used as a barrier material in microelectronics

Graphene's electronic properties could be exploited in several niche areas: as interconnects in integrated circuits and as conductive sheets to **dissipate heat** (graphene has a thermal conductivity that is higher than copper); or combined with polymers to make **lightweight conductive bulk materials**. Graphene scaffolds are already being employed to support samples for studies using electron or scanning probe microscopes (which require conducting substrates). Researchers are also already exploring whether graphene's large surface area and high conductivity would improve the performance of **battery electrodes** or **supercapacitors** for **energy storage**.



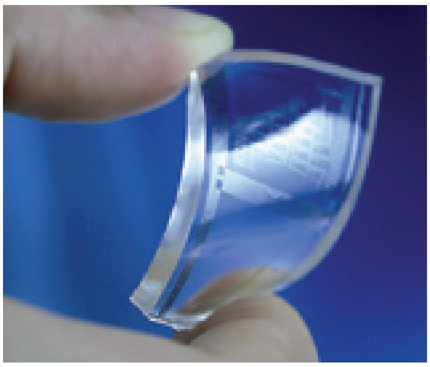
University of Pennsylvania

BIODEVICES

The most sophisticated use of graphene yet is as an artificial membrane in which nanosized pores have been drilled with an electron beam, which are just big enough to allow biomolecules such as DNA to enter. When the membrane is bathed in an electrolyte and a voltage is applied, a DNA molecule is drawn through. The conductivity of the membrane is then altered depending on the exact DNA configuration. The researchers who recently carried out this work suggest that graphene membranes could be employed to carry out **on-the-spot DNA sequencing**.

SEE-THROUGH ELECTRONICS

Because graphene is transparent, it has useful **electro-optical applications**. Electronics companies are desperately looking for a cheap and plentiful material as a **transparent electrode** replacement for expensive and brittle indium tin oxide, employed, for example, in **liquid crystal displays (LCDs)**.



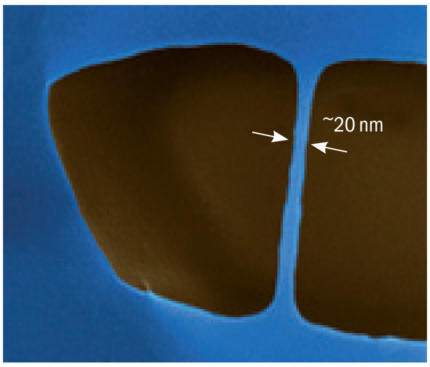
Ji Hye Hong

Graphene electrodes could be incorporated in transparent, flexible devices

Graphene might also find use as a flexible electrode material in **organic light-emitting diode (OLED)** devices, used in lighting and displays, and incorporated into **photovoltaic cells**, which convert sunlight into electricity. Transparent electrodes are also key to the latest **touchscreen** devices.

STRONG AND STRETCHY

Graphene is the strongest material ever measured, being 200 times stronger than steel, and might be a replacement for carbon fibres to be employed as **ultra-lightweight structural components** in fuel-efficient vehicles and planes. The thin layers of graphene can be stretched by 20%, which alters



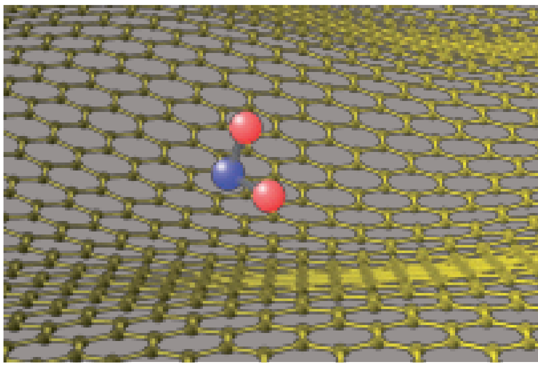
Jarillo-Herrero Group/MIT

Nanostructures etched from suspended graphene flakes could be used as mechanical resonators

the electron mobility, and thus conductivity. Inducing such strain via bending or vibrations, for example, could be employed in **nano-electromechanical devices**, used as sensors and transducers.

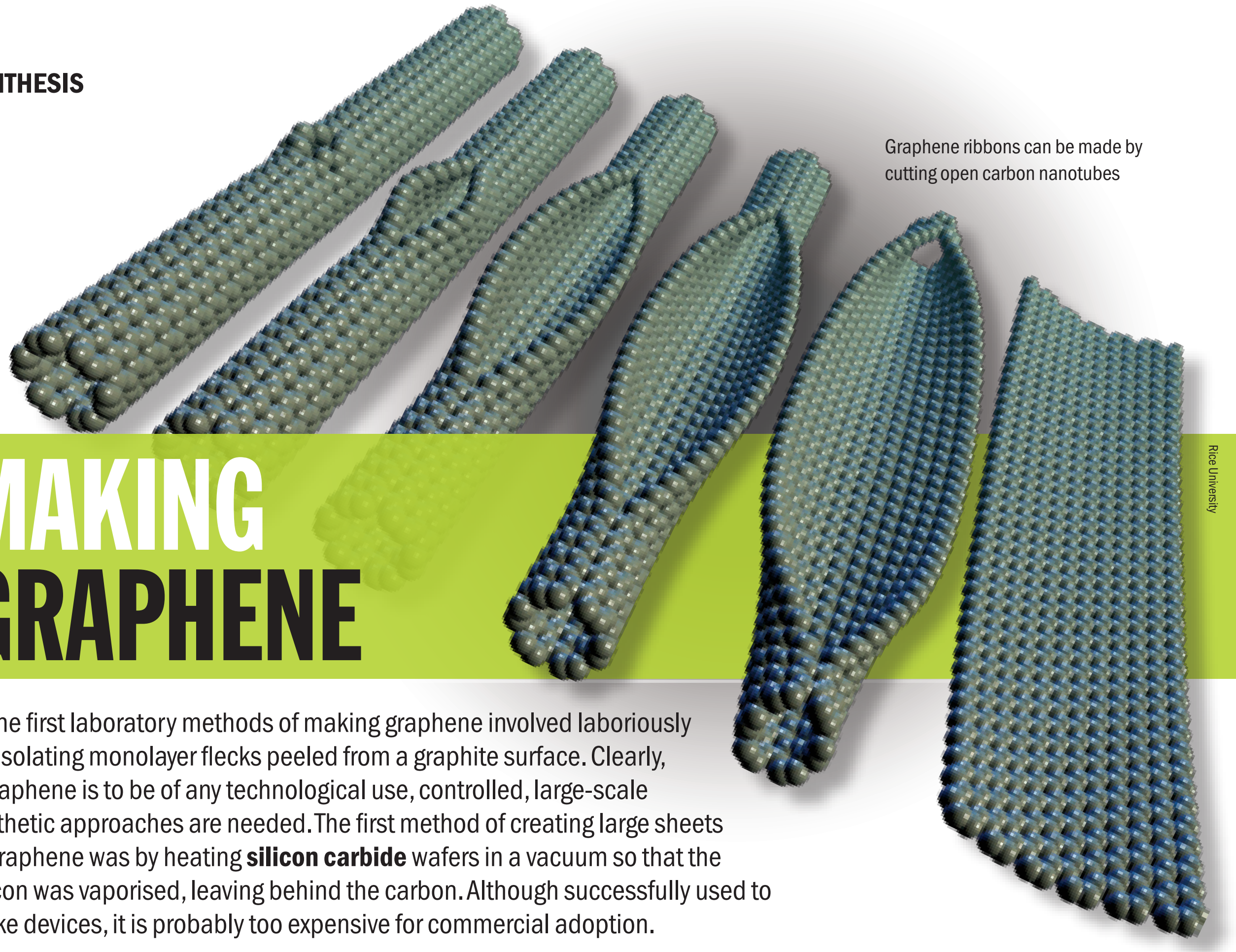
MOLECULAR REWARDS

Chemists are well aware of the complex reactions that electron-rich carbon rings can undergo (aromatic chemistry). They are key to many biochemical processes. Graphene, especially if chemically modified, offers the potential for carrying out surface reactions such as **industrial catalysis** that rely on carbon-based substrates. Researchers have also shown that the conductivity of graphene is altered when particular



A single molecule of nitrogen dioxide can be detected when adsorbed onto graphene

molecules are adsorbed onto its surface. For example, single molecules of the toxic gases carbon monoxide and nitrogen dioxide can been detected, creating the ultimate **chemical sensor**. Graphene could also act as a **chemical filter**. A graphene–magnetite composite was recently shown to remove arsenic from drinking water.

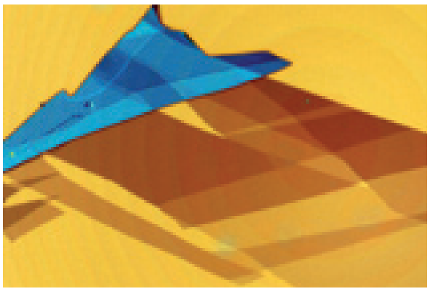


Graphene ribbons can be made by cutting open carbon nanotubes

Rice University

MAKING GRAPHENE

The first laboratory methods of making graphene involved laboriously isolating monolayer flecks peeled from a graphite surface. Clearly, if graphene is to be of any technological use, controlled, large-scale synthetic approaches are needed. The first method of creating large sheets of graphene was by heating **silicon carbide** wafers in a vacuum so that the silicon was vaporised, leaving behind the carbon. Although successfully used to make devices, it is probably too expensive for commercial adoption.



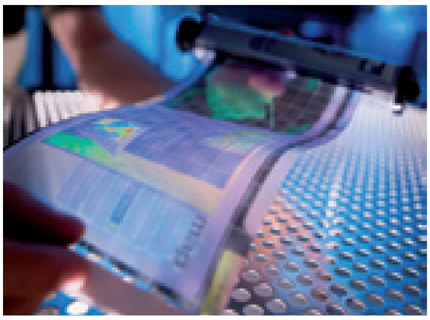
Graphene flakes of different thickness

MASS PRODUCTION

An alternative approach is to employ the established industrial process of **chemical vapour deposition** in which graphene is grown by decomposing hot hydrocarbon gases on a reactive metal surface. A plastic film is stamped on top, and the metal etched away with acid. The plastic-coated graphene can then be transferred to a variety of substrates. The first metal used was nickel, but later copper was found to give finer quality graphene films. Using an industrial roll-to-roll process, in which graphene is grown on copper foil, researchers in South Korea have since made large-area, highly conducting transparent graphene films suitable for displays, touch sensors and solar cells. Samsung currently estimates that graphene could be grown in this manner for as little as $50/m^2.

CHEMICAL EXFOLIATION

Meanwhile chemical methods can produce bulk quantities of small-area graphene sheets for use as structural composites, chemical filters or battery components. Graphite is readily oxidised with acid to form sheets of insulating **graphene oxide**, which separate in water. They can then be cast onto a surface and the oxygen removed with a reducing agent such as hydrazine. Unfortunately, this method produces rather porous films. Several research groups have demonstrated alternative methods of directly exfoliating graphite in solution using **ultrasound** or highly specialised solvents such as **ionic liquids** (salts that are liquid at room temperature).



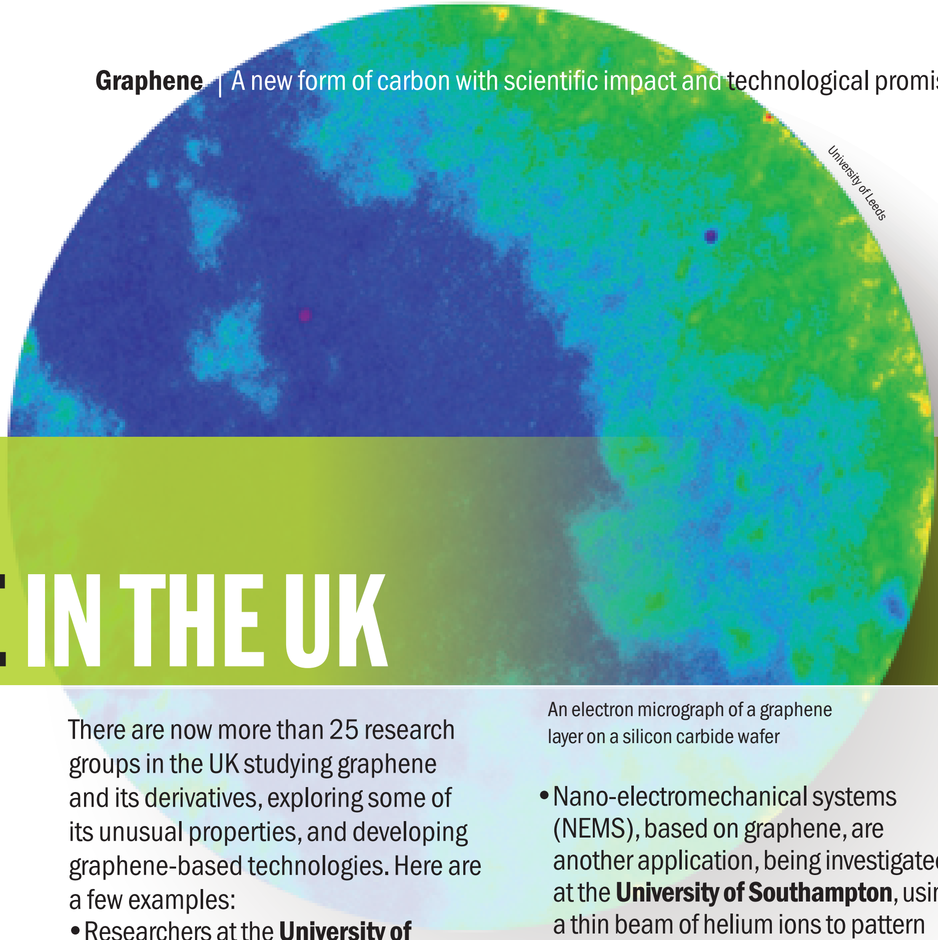
South Korean researchers have produced large areas of graphene using a roll-to-roll process

GRAPHENE PATTERNING FOR ELECTRONICS

Structuring graphene at the nanoscale for devices remains challenging, particularly making nanoribbons with smooth-edge structures that have reproducible properties. Nano-patterning instruments such as the atomic force microscope can be used to cut channels in insulating graphene oxide but such methods are not practicable outside the laboratory. Researchers have also fabricated nanoribbons using the lithographic techniques described above. One interesting approach is to unzip carbon nanotubes. Such methods have tended to be uncontrollable; however, chemists are already looking at alternative methods of fabricating ribbons with smooth edges. One way of enabling the detailed study of the complex properties of graphene is to start from the basic molecular precursors and link them chemically into model devices with precisely structured features. In the meantime, most scientists think that commercial integrated circuits based on graphene are still a long way off.

The Manchester research group remains the leading team in the world working on graphene, having initiated many of the ideas and techniques taken up by others.

GRAPHENE IN THE UK

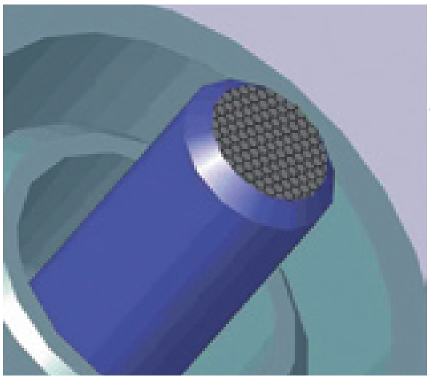


University of Leeds

An electron micrograph of a graphene layer on a silicon carbide wafer

In the UK, researchers at the **universities of Lancaster and Cambridge** have been working with Manchester from the start.

- Theorists at Lancaster pioneered the research in bilayer graphene by predicting its unusual electronic properties and how to control them. They are now studying electronic transport in disordered and chemically modified graphene.
- The Cambridge group carries out a major experimental programme on all aspects of graphene. Recently, the group has been exploring graphene's electro-optical properties.

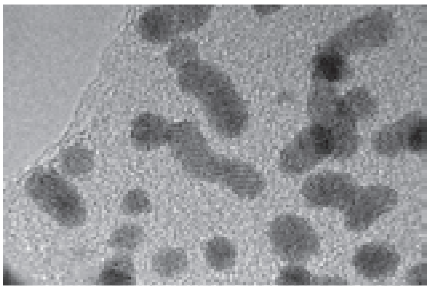


University of Cambridge

Researchers have fabricated an ultra-fast laser based on graphene

There are now more than 25 research groups in the UK studying graphene and its derivatives, exploring some of its unusual properties, and developing graphene-based technologies. Here are a few examples:

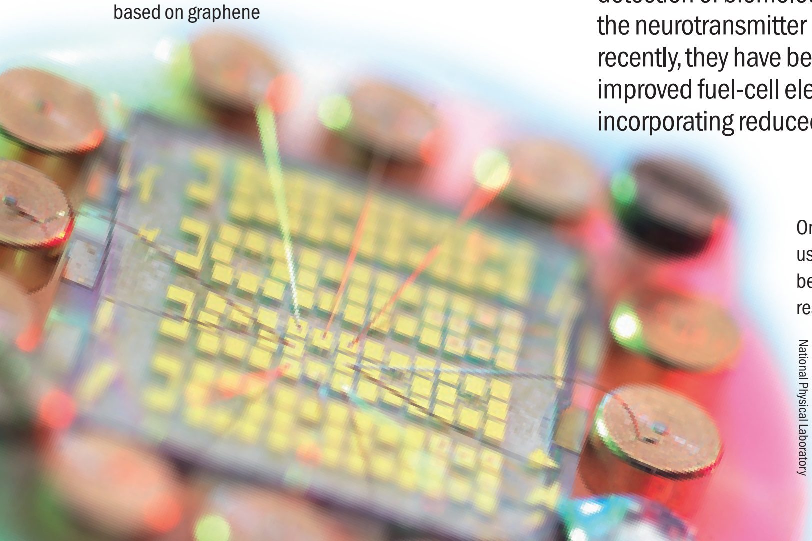
- Researchers at the **University of Leeds** are studying the growth of graphene layers at the wafer scale and developing techniques to investigate the use of graphene in spintronic and superconducting devices with potential for quantum information processing.



University of Ulster

Platinum nanocrystals on reduced graphene oxide, used as an electrocatalyst in improved fuel cells

- At the **University of Ulster**, researchers have been exploiting vertically integrated graphene sheets for the sensitive electrochemical detection of biomolecules such as the neurotransmitter dopamine. More recently, they have been working on improved fuel-cell electrocatalysts incorporating reduced graphene oxide.



One of the first practical uses of graphene will be as an electrical resistance standard

National Physical Laboratory

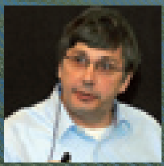
- Nano-electromechanical systems (NEMS), based on graphene, are another application, being investigated at the **University of Southampton**, using a thin beam of helium ions to pattern nanostructures on a graphene bilayer.
- Graphene could be the basis of the quantum resistance standard, based on the quantum Hall effect. Recently, an EU-funded collaboration, including the **National Physical Laboratory** and the theorists at Lancaster, demonstrated such a possibility using large-area graphene films.

UK SUPPORT

The importance of graphene research has been recognised through the Engineering and Physical Sciences Research Council (EPSRC) Science and Innovation Award scheme, with **Manchester** and **Lancaster** being jointly awarded about £6 m to advance the science and pursue applications.

The **universities of Exeter** and **Bath** have also jointly received grants totalling around £5 m from EPSRC to set up a **Centre for Graphene Science** to investigate applications in the areas of photonics, nano-electronics and biosciences. Research covers graphene production, and the fabrication of nanoscale devices including electronic and optical devices, and mechanical, chemical and biological sensors.

A **Lancaster/Cambridge/Exeter collaboration**, researching into non-equilibrium phenomena in graphene-based devices, is supported by a £1.2 m grant from EPSRC.



Andre Geim was born in Russia, having obtained his PhD in 1987 from the Institute of Solid State Physics in Chernogolovka. After working at various European universities, including the universities of Nottingham and Bath, he moved to the University of Manchester in 2001 to take up a chair of physics. He was appointed director of the Manchester Centre for Mesoscience and Nanotechnology in 2002 and Langworthy Professor in 2007, and is now Royal Society 2010 Anniversary Research Professor.

Konstantin Novoselov, also born in Russia, studied for his doctorate with Geim when he was tenured at the University of Nijmegen in the Netherlands, before moving to the University of Manchester in 2001 with his doctoral supervisor. He was awarded his PhD in 2004 and became a professor in early 2010 within the same research group.

Researchers who helped with this booklet:
Andre Geim (University of Manchester)
William Barnes (University of Exeter)
Andrea Ferrari (University of Cambridge)
Vladimir Falko (Lancaster University)
Christopher Marrows (University of Leeds)
Zakaria Moktadir (University of Southampton)
Pagona Papakonstantinou (University of Ulster)
Alexander Tzalenchuk (National Physical Laboratory)

Futher information

General and specialist information on the University of Manchester website: http://onnes.ph.man.ac.uk/nano

The Nobel Prize: http://static.nobelprize.org/nobel_prizes/physics/laureates/2010/sciback_phy_10.pdf

***Graphene Weeks* – a series of topical conferences focusing on the physics and chemistry of graphene and graphene-based electronics, organised by Lancaster University:**
www.esf.org/activities/esf-conferences/details/2011/confdetail350.html?conf=350&year=2011

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