Introduction. Carbon-based electronics: fundamentals and device applications

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Carbon-based materials offer a number of exciting possibilities for both new science and applications. Many of these are based on the novel band structure of graphene, by which solids mimic the properties of relativistic fermions and which offers the potential for high speed nanoscale electronics. When sheets of graphene are rolled up to make carbon nanotubes, further interesting properties are found; for example, both semiconducting and metallic nanotubes able to be produced. The novel properties of these new materials, together with the already remarkable properties of diamond itself, are discussed by a series of experts who came together in May 2007 to discuss and debate the potential for future development.

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For over 50 years, silicon has dominated the electronics industry, with progress inexorably following the prophetic statement from Gordon Moore, the co-founder of Intel, that the number of transistors on a silicon chip would grow exponentially with time, doubling every 2 years (Moore's law). This growth cannot be maintained forever and so the search is on to find and use new materials which may be able to produce higher performance and better functionality. A good candidate is carbon, which comes in a variety of fascinating forms with dramatic physical and electronic properties. Whereas the physical properties of graphite and diamond have been investigated for many years, the potential for electronic applications of other allotropes of carbon has only been appreciated relatively recently. Since the pioneering work of Iijima (1991) on single-wall carbon nanotubes (CNTs), there has been rapid progress in our understanding of their remarkable properties. The recent discovery of graphene, a single atomic monolayer of carbon, and its fabrication into a field-effect transistor in 2004 by Geim and colleagues in Manchester (Novoselov et al. 2004), has opened up a new field of fundamental physics and offers exciting prospects for new electronic devices. This discussion meeting examines some of the latest developments in the science and technology of CNTs and graphene. There are also four papers in this issue on diamond, which has much to offer as an electronic material.

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One contribution of 11 to a Discussion Meeting Issue ‘Carbon-based electronics: fundamentals and device applications’.
Graphene consists of a single sheet of carbon atoms bonded in the sp² configuration of a hexagonal lattice structure. This was studied theoretically 60 years ago by Wallace (1947) as the first approximation to understand the electronic properties of graphite. His work showed that graphene has a unique band structure in which the conduction and valence bands just touch each other, forming an exactly zero-band gap semiconductor (also known as a semi-metal). The energy dispersion relation of the two bands is therefore linear in wave vector, \( k \), and they cross at the \( K \) points of the two-dimensional Brillouin zone. This property, in combination with the hexagonal crystal lattice symmetry, makes the electrons behave as if they were massless fermions, governed by Dirac’s equation, with a relativistic limiting velocity of approximately 1/300th of the speed of light. The point where the dispersion relations cross is known as the Dirac point. These properties are, however, markedly changed when just one extra layer is bonded to the first one. This is due to the coupling of the two layers, which fundamentally alters the symmetry for moving electrons. Crystals with as few as 10 graphene layers behave like bulk graphite, whose properties are fairly well established. The big step forward in studying and understanding graphene was made by the Manchester group in 2004 when they showed that it was possible to deposit a single layer of carbon onto an oxidized silicon wafer. By using this to construct a field-effect transistor, they were able to reveal clearly the unique electronic properties of graphene. The electrons, which behave as massless fermions, show a new form of the quantum Hall effect and have a maximum resistivity related to the conductance quantum when the applied gate voltage tunes the chemical potential to the Dirac point. The work of the Manchester group has led to a surge of interest in graphene, not least because the high electron velocity means that it might become the material of choice for the electronic circuitry of the future (Novoselov & Geim 2007).

Andre Geim’s talk began the meeting with a review of the properties of graphene, followed by an account of the hotly debated processes that scatter electrons (Katsnelson & Geim 2008). The very significant changes in the electronic band structure, which occur when the graphene forms a bilayer structure, and the appearance of a new type of quasi-particle (massive Dirac fermions) were described by Vladimir Fal’ko (Fal’ko 2008). Alberto Morpurgo discussed how both superconducting proximity effects and a novel type of weak localization can now be observed in graphene.

As well as being a fascinating material in its own right, the graphene band structure also helps to explain the behaviour of CNTs. These can be thought of as a small strip of the graphene sheet which has been rolled up to form a perfect single-walled nanocylinder—effectively a one-dimensional quantum wire. As a result, one component of the electron \( k \)-vector is quantized and the majority of single-walled CNTs develop an energy band gap that is directly proportional to this quantized value, which in turn is given by the inverse of the tube diameter. Typical 1 nm diameter tubes have a band gap of approximately 1 eV, which is close to that of Si. For one-third of the nanotubes, the resulting folding of the Brillouin zone means that the Dirac point is reflected back on itself and the nanotube becomes semi-metallic in the same way as in flat graphene layers. Thus by using CNTs, it is possible to generate both the semiconducting band gap essential for the optoelectronic applications and to have a one-dimensional analogue of the graphene Dirac point. As a result, CNTs also have great potential

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for novel electronic components, with the added advantage that they can be easily functionalized using a variety of chemical techniques, making them particularly important for applications such as sensors.

Opening the discussions on CNTs, Sumio Iijima described some of the remarkable advances being made in the growth and imaging of CNTs including the observation of single local atomic defects. The theory of the fascinating electrical conduction properties arising from the one-dimensional nature of metallic single- and double-wall nanotubes was described by Tsuneya Ando (Ando 2008), and Christian Schoenenberger described how some of these could be observed by attaching superconducting and ferromagnetic contacts to CNTs. Michael Strano described the observation of electronically selective chemical reactions and their use in chemical sensing and nanotube purification.

Phaedon Avouris presented the major advances being made in the development of practical devices using CNTs. They have already been used to fabricate light-emitting diodes, ambipolar field-effect transistors and a variety of sensing devices (Avouris et al. 2007).

The discussions following Avouris’s talk were particularly wide ranging and looked at the industrial perspectives of device research. In response to a question about the relative merits of graphene and carbon nanotube field effect transistors (FETs), he pointed out that FET channels made from CNTs are characterized by either ballistic or very high mobility transport, high transconductance and on/off ratios of typically $10^6$. Graphene also has high transport mobility, but being a zero-band gap semiconductor, graphene cannot be turned off completely. The conductance can be varied by, at most, one order of magnitude. A confinement gap can be opened up in graphene nanoribbons. However, the ribbon width must be approximately 1 nm wide to allow room temperature FET operation. Currently, there are no technologies allowing reproducible fabrication at such a small scale. Further complications arise from the edges of the narrow ribbon, where significant electron scattering can occur. In an answer to a question about what needs to be done to fully exploit the approximately 900 GHz switching speed of a CNT FET, Avouris argued that one would need to minimize the parasitic capacitance of the devices and of the associated wiring. For example, a typical CNT FET has a capacitance of approximately 10 aF. The contact wires have a typical capacitance of approximately $0.2 \text{ aF nm}^{-1}$. Therefore, it only takes approximately 50 nm of wiring to match the capacitance of the tube. He emphasized the need to improve all aspects of device design and fabrication to achieve the full potential provided by the CNTs.

The focus of the discussion moved on to Avouris’s brief survey of the present state-of-the-art MOS devices. In particular, in the last 18 months there has been no improvement in the frequency operation for silicon devices, due to length limits imposed by tunnelling and scattering. It was suggested that it may be easier to make much shorter devices with nanotubes. In Avouris’s view, the outstanding ballistic transport properties of CNTs would allow superior frequency operation without the need for extremely short devices as required for silicon. These transport characteristics, coupled with wrap-around gates and high-$k$ dielectric insulators could enhance the performance, thus avoiding the problems associated with traditional short channels.

Avouris then clarified the difference between the operational configurations of CNTs for electronic and optical applications. In general, logic applications require high speed and density; therefore, shorter channel lengths are desirable for CNT FETs. In photonics, on the other hand, longer tubes absorb and emit more light.
The energies of the optical resonances depend on the CNT diameter. Decreasing the diameter increases the absorption/emission wavelength. The current, however, decreases with decreasing diameter, so larger diameter CNTs are preferred in electronics. Higher applied voltages are also required in photonics.

The potential of nanotubes filled with species such as fullerenes entered the discussion. Avouris pointed out that they could in principle fluoresce, provided that the species introduced into the tube are weakly perturbing, and do not have lower energy levels than the nanotube, so that energy transfer to the nanotubes can take place. Exciton localization and enhancement of the non-radiative decay are also probable at the sites of these species.

When the carbon bonds in an sp³ tetrahedral structure, the wide band gap semiconductor diamond is formed. Although the basic electronic properties of diamond have been understood for many years, surprises in its basic physics are still emerging, such as the experimental observation that it is a superconductor when heavily doped with boron (Ekimov et al. 2004). Etienne Bustarret discussed this phenomenon and measurements of the variation of the transition temperature as a function of increasing boron concentration (Bustarret et al. 2004, 2008).

Interest in diamond is now strongly focused on its potential applications. As Steve Coe explained, it has many of the properties which make it the ideal semiconductor for high-temperature, high-power applications, but it is only recently that the quality of the material has been good enough for this potential to be realized. Control of the growth using chemical vapour deposition (CVD) on well-prepared diamond substrates is now excellent, and the quality of single crystals grown by this method is far superior to natural crystals or samples synthesized at high pressure and high temperature (HPHT). For example, the hole mobility of the best natural or HPHT samples is 2000 cm² V⁻¹ s⁻¹, but in the CVD single crystals, this increases to 3800 cm² V⁻¹ s⁻¹ (Isberg et al. 2002) and it is not clear whether this could be further improved.

In the quest to improve the quality of the material, studies of the growth at an atomic level by Jim Butler and others have allowed us to understand the nucleation of dislocations and the incorporation of impurities (Butler & Oleynik 2008). However, it is difficult to dope diamond; the boron acceptor is very deep in semiconductor terms (0.37 eV). Coe showed how intrinsic diamond can be used to make high-power switches and how unipolar structures can be used to construct high frequency metal-semiconductor field effect transistors by using delta B-doped layers (Balmer et al. 2008). A different solution to the doping problem in diamond is to exploit the surface conductivity of the hydrogenated surface. Martin Stutzmann explained the design of ion sensors and the activation of the surface by the attachment of biological molecules, leading to highly specific biochemical sensors. Another extraordinary property of diamond is its negative electron affinity and James Davidson showed how this could be exploited in the production of vacuum emission devices (Davidson et al. 2008). Here, of course, CNTs excel in having a similar negative electron affinity but superior conductivity, and triodes based on these materials show great promise.

The discussion meeting brought together over a hundred active researchers, many of them young, with interests in carbon-based materials, along with the discoverers of nanotubes and graphene, Iijima and Geim, and the discoverer of the quantum Hall effect, Klaus von Klitzing. Von Klitzing reviewed recent studies of the electrical properties of graphene that he has carried out with colleagues in Stuttgart. Professor Mildred Dresselhaus, who described the band structure of graphite in the first ever volume of the journal Carbon over 40 years ago (Dresselhaus & Mavroides 1964), and...
who has done so much to promote the study of carbon materials, concluded the meeting with some deep insights into how the subject has developed. This issue is concluded with a short paper by Dresselhaus et al. (2008) on Raman studies of graphene and CNTs. In addition to the invited talks (some of which are followed by brief transcripts of their question and answer sessions), a number of posters were presented which generated very animated discussions. Brief reports by groups from Exeter (Horsell et al. 2008) and Oxford (Chuang et al. 2008) are also presented in this issue.

References


