

## GRAPHENE

## Calling all chemists

Graphene has potentially useful electronic properties but it is difficult to produce and process on large scales. Working with chemically modified forms of graphene — such as graphene oxide — may provide an alternative.

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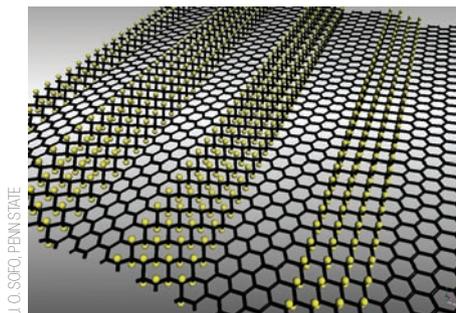
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There has been an explosion of interest in the physics of graphene — individual layers of graphite in which each carbon atom is bonded to three other carbon atoms — since it was first deposited by mechanical exfoliation in 2004<sup>1,2</sup>. In this approach, which has spawned a cottage industry of ‘peeling and rubbing’ in labs around the world, the large majority of platelets are actually too thick to be of use in fundamental physics experiments, so well-trained eyes are needed to find the relatively few monolayer flakes that are produced.

The results of experiments in which these flakes are ‘wired up’ by electron-beam lithography and then studied under a variety of conditions, including high magnetic fields and ultralow temperatures, suggest that graphene-based devices might perform well enough at room temperature to have a future in commercial-scale nanoelectronics<sup>3</sup>. The large mobility of the carriers in graphene is also noteworthy because speed is often central to device performance. If it were possible to uniformly ‘coat’ 300-mm silicon wafers with a monolayer or perhaps bilayer<sup>4</sup> of graphene, standard semiconductor processing techniques could, perhaps, pattern graphene into ‘nanoribbons’ for commercial devices.

The remarkable ‘flatness’ of graphene (when it is deposited on really flat substrates) also suggests that it might eventually be possible to fabricate devices containing multiple layers of graphene and other materials (as long as the processing conditions for the subsequent layers do not harm the graphene layers underneath). In addition to the possibility of low-power, high-density and high-speed switches and logic elements, graphene-based devices may also find other applications — as atom-thick membranes



**Figure 1** Schematic diagram of a graphene sheet that has been chemically modified by hydrogenating the carbon atoms in well-defined regions to define ‘ribbons’ of graphene. Simulations of the electronic properties of chemically modified graphene will be a useful guide to experimenters. For example, how wide do the hydrogenated regions (yellow) need to be to define high-mobility graphene pathways? Does the orientation of the ribbon with respect to the graphene lattice (such as along the ‘armchair’ or ‘zigzag’ directions) influence the electronic properties? See, for example, simulations for a fully hydrogenated graphene sheet (called graphane because it is an alkane) by Jorge Sofo and co-workers<sup>14</sup> at Pennsylvania State University.

for sensing pressure, as components in nanoelectromechanical systems, or in chemical sensing owing to their high surface area.

Direct growth or deposition on industrial-scale silicon wafers should be targeted for nanoelectronics, but significant progress has also been made in the epitaxial growth of graphene layers on single-crystal 4-inch silicon carbide wafers under high temperature and ultrahigh-vacuum conditions<sup>5</sup>. However, the combination of high cost and small wafer size might limit the widespread application of this approach.

So, in the absence of a reliable and cost-effective technique for coating 300-mm silicon wafers, what other alternatives might be considered? One possibility might be to exfoliate bulk

graphite into individual layers. Other layered materials, such as various clays and micas, have been readily dispersed in water to supply individual layers but, perhaps surprisingly, this has never been achieved for graphite in any solvent. Another alternative might seem to be ‘expandable graphite’, an intercalation compound that can expand in volume by a factor of up to 1,000 upon rapid heating<sup>6</sup>. However, the platelets in such expanded graphites are roughly 50 nm thick and contain hundreds of stacked graphene layers.

So, given the limits of existing ‘physical’ approaches, does the remarkably versatile chemistry of carbon offer promising alternatives? For example, could chemical tuning be used to alter the physical properties of graphene sheets? Indeed, could nanoelectronic devices be made from chemically functionalized graphene? Rather than etching a hypothetical graphene coating on a 300-mm silicon wafer to create a pattern of highly conducting graphene nanoribbons, would it be better to chemically functionalize selected regions so that the carbon atoms in these regions were bonded to four other atoms, rather than three? In this approach the tetravalently bonded atoms would jealously hold on to their charge carriers, rather than sharing them openly like the trivalently bonded atoms, thereby defining the desired pattern of graphene nanoribbons (see Fig. 1). Input from theorists about the likely performance of different devices made using this approach will be valuable<sup>7</sup>.

We have talked so far about possibilities, but what progress has already been made with respect to developing chemically modified graphene (CMG)? One approach taken by my group has been to use colloidal suspensions of graphite oxide, which has led to the possibility of distributing CMG in polymer matrices<sup>8</sup> or in thin layers of silica glass<sup>9</sup>, and of layering CMG to achieve a paper-like material with interesting mechanical properties<sup>10</sup>. In separate experiments we have used the deposition and dry-down of droplets from

aqueous suspensions of graphene oxide (which is one type of CMG) to produce relatively large platelets on substrates, and then mapped their optical properties before and after heat treatment<sup>11</sup>. A compelling reason for interest in such colloidal suspensions is that all the graphene oxide platelets in the suspension seem to be individual layers. Alas, this heavily oxidized form of graphene is electrically insulating, but the platelets can be made electrically conductive by exposing them to chemical reductants or heat.

The 'chemistry part' of the graphene story has only just begun and because of the extraordinary number of levers that chemistry affords, there will be a growing dialogue between chemists and researchers in other fields (such as physics, materials and processing) who, otherwise, might only have worked with graphene in its pristine form. As an example of a first step, teams led by Richard Kaner of UCLA<sup>12</sup>, Klaus Kern of the Max Planck Institute in Stuttgart and the EPFL<sup>13</sup>, and myself (I. Jung, D. Dikin, R. Piner & R.S.R, manuscript in preparation) have recently deposited graphene oxide platelets onto

substrates and then converted them to electrically conductive CMG that allowed for voltage gating. Individual platelets were identified by light microscopy, and their electrical properties were studied as a function of temperature or prior exposure to hydrazine or hydrogen plasma.

This work is still at an early stage and some questions remain to be answered. In converting graphite to graphene oxide, have significant defects been introduced into the individual layers? Are unwanted defects introduced when making the aqueous suspension of graphene oxide platelets? If one is able to keep the basic carbon skeleton intact without too many defects, will it be possible to manipulate the surface chemistry, and perhaps even 'return' to pristine graphene, albeit by a rather circuitous route?

Although it should be possible to position the larger CMG platelets<sup>11</sup> where needed on a silicon wafer for further processing, and to perhaps create 'striped' graphene platelets (see Fig. 1) that could also be assembled on silicon wafers through appropriate patterning, it is not yet clear if this approach will be of

interest to the nanoelectronics industry. Nevertheless, whatever happens, graphene and chemically modified graphene will remain of interest for fundamental research. It may be that pristine graphene is essential for applications in nanoelectronics. However, it could be that some degree of chemical functionalization may be tolerated, or perhaps even found to be beneficial.

#### References

1. Novoselov, K. S. *et al. Science* **306**, 666–669 (2004).
2. Lu, X. K., Yu, M. F., Huang, H. & Ruoff, R. S. *Nanotechnology* **10**, 269–272 (1999).
3. Geim, A. K. & MacDonald, A. H. *Physics Today* **60**, 35–41 (August 2007).
4. Min, H. K., Sahu, B., Banerjee, S. K. & MacDonald A. H. *Phys. Rev. B* **75**, 155115 (2007).
5. Berger, C. *et al. Science* **312**, 1191–1196 (2006).
6. Celzard, A., Mareche, J. F. & Furdin, G. *Prog. Mater. Sci.* **50**, 93–179 (2005).
7. Chernozatonskii, L. A., Sorokin, P. B. & Brünig J. W. *Appl. Phys. Lett.* **91**, 183103 (2007).
8. Stankovich, S. *et al. Nature* **442**, 282–285 (2006).
9. Watcharotone, S. *et al. Nano Lett.* **7**, 1888–1892 (2007).
10. Dikin, D. A. *et al. Nature* **448**, 457–460 (2007).
11. Jung, I. *et al. Nano Lett.* **7**, 3569–3575 (2007).
12. Gilje, S., Han, S., Wang, M., Wang, K. L. & Kaner, R. B. *Nano Lett.* **7**, 3394–3398 (2007).
13. Gómez-Navarro, C. *et al. Nano Lett.*, **7**, 3499–3503 (2007).
14. Sofo, J. O., Chaudhari, A. S. & Barber, G. B. *Phys. Rev. B* **75**, 153401 (2007).

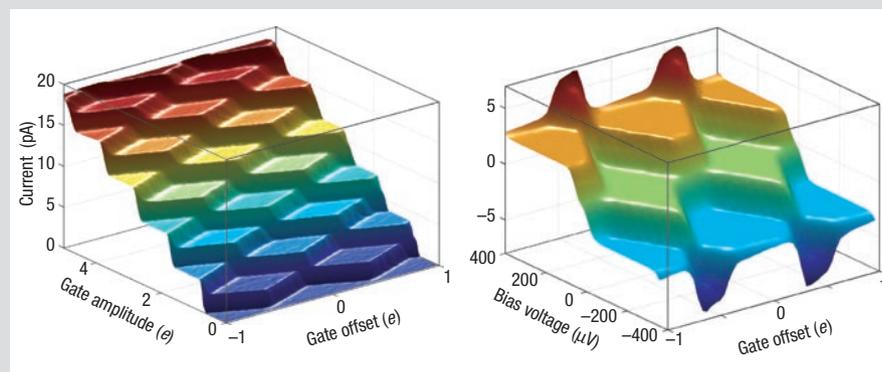
## NANOMETROLOGY

### Island hopping

Developing new measurement standards that are based on the fundamental physical constants, such as Planck's constant and the mass of the electron, is a top priority in metrology laboratories around the world. However, the unit of electrical current, the Ampere, is still defined in terms of the forces acting on wires carrying currents, which is why a number of groups are working on alternative standards.

A central element in some of these approaches is a 'turnstile' that opens and closes at a well-defined frequency,  $f$ , allowing a well-defined number of electrons,  $N$ , to pass through the turnstile every time it opens, leading to a current  $I = Nef$ , where  $e$  is the charge of the electron. Writing in *Nature Physics*, Jukka Pekola and co-workers at the Helsinki University of Technology and Stony Brook University report a new type of turnstile based on a hybrid single-electron transistor (*Nature Phys.* doi:10.1038/nphys808; 2007).

The hybrid device consists of an island of superconducting aluminium that is separated from copper source and drain electrodes by aluminium oxide



tunnel barriers. The electrons must tunnel through these barriers to enter or leave the island. The device is controlled by a d.c. voltage across the source and drain, and a combination of a.c. and d.c. voltages that are applied to a metal gate electrode.

Pekola and co-workers measure the current through the turnstile as these voltages are varied, with the plateaus in the data (left) demonstrating that they are able to control  $N$ . In both figures the vertical axis is the current and the horizontal axes are different components of the voltages. The figure on the far

left, which was recorded at a frequency of 12.5 MHz, shows  $N$  increasing from zero up to ten. The plateaus in the other image, which was recorded at 20 MHz, correspond to  $N=1, 0$  and  $-1$  (that is, a current flowing in the opposite direction).

A quantum standard for current would bring it into line with the standards for resistance and voltage, which are based on the quantum Hall effect and the Josephson effect respectively, thus completing a metrological triangle for electrical units based on Ohm's law.

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