

atomic scale, their results can be compared to the predictions of density functional theory. Not surprisingly, these calculations suggest that the clusters deform when the tip makes contact with them, and that certain arrangements of the metal clusters are unstable — in agreement with the experimental observations. In particular, the researchers find that the contact conductance of the tip–molecule–metal structure gets larger as the number of copper atoms in the cluster increases from one to five. Whereas this result is expected, they also show that the normalized conductance (the conductance divided by the number of atoms in the cluster) reaches a maximum for clusters that contain five atoms. The same trend is found in quantum transport calculations and is illustrated by the extent of the electron wave function across the interface between the cluster and the  $C_{60}$  molecule (see Fig. 4 of ref. 5).

Hence a cluster of fewer than five copper atoms is a ‘bad’ contact: that is, the contact resistance depends on the number of atoms in the cluster and the measured contact conductance is a mix of the conductance of the contact and the molecule. However, for clusters containing more than five atoms, the measured conductance is more intrinsic to the molecule because it has a weak dependence on the number of atoms in the cluster. Schull and co-workers refer to such a contact as a ‘good’ contact.

There are several aspects that make this work truly noteworthy beyond the demonstration of this utmost precision in the contact formation. First, when the cluster contains five or so copper atoms, the conductance through the entire device is comparable to the quantum of conductance ( $G_0 = 2e^2/h$  where  $e$  is the charge on the electron and  $h$  is Planck’s constant), which suggests that a  $C_{60}$  molecule is indeed a good electrical conductor owing to its delocalized

electron system. Second, it has been suggested that  $C_{60}$  molecules could be used to connect metal electrodes to the large organic molecules that are of interest for applications in molecular electronics<sup>6</sup>. Finally, extending the distinction between ‘good’ and ‘bad’ to the atomic scale might prove to be the most salient feature of this work. □

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## NANOELECTRONICS

# Graphene gets a better gap

Graphene nanoribbons with low defect densities and large energy gaps can be fabricated by chemically unzipping carbon nanotubes and annealing the result.

Stephan Roche

**D**espite its impressive electronic properties, large-area graphene is not well suited to controlling electric currents because it is a semimetal, rather than a semiconductor. Therefore there is no energy gap separating the conduction and valence bands<sup>1</sup>, and this makes graphene field-effect transistors difficult to turn off<sup>2</sup>. A partial solution has been to use electron beam lithography and oxygen plasma etching techniques to produce graphene nanoribbons with widths as narrow as 10 nm (ref. 3), or various chemical approaches to make even narrower nanoribbons with widths of just a few nanometres<sup>4</sup>. These techniques can, in theory, introduce an energy gap with a well-defined size as a result of quantum confinement, but in practice they also introduce large numbers of defects that interfere with this control. Writing in *Nature Nanotechnology*, Junji Haruyama, James Tour and co-workers at Aoyama Gakuin University and AIST in Japan, and Rice University in the United States, describe a method for making relatively defect-free nanoribbons with large energy gaps<sup>5</sup>.

Although the nature and origin of the defects in lithographically derived or etched nanoribbons remain elusive (edge defects, ripples, adsorbed impurities and charges trapped in the underlying oxide may all be involved), their impact is considerable. They significantly reduce charge carrier mobility, to several hundred centimetres squared per volt second, and obscure the correlation between the energy gap and the electrical behaviour of the nanoribbon<sup>6</sup>.

For example, a key signature of an energy gap is the so-called transport gap. If an energy gap exists, the current between source and drain electrodes in a graphene transistor will fall to zero for certain values of the gate voltage, creating a ‘gap’ in its electrical characteristics. The reverse, however, is not necessarily true: the presence of a transport gap does not require there to be an energy gap. In fact, the transport gaps measured in nanoribbons have been attributed to effects such as Anderson localization<sup>7</sup> and Coulomb blockade<sup>8</sup>, and not simply to confinement-induced energy gaps<sup>9,10</sup>.

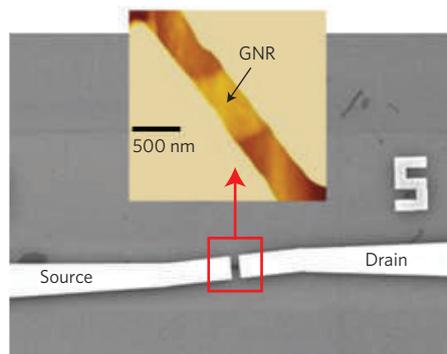
Localization and blockade are not as useful for devices as an intrinsic energy gap. They also interfere with the control over the energy gap that the narrow nanoribbon width is supposed to provide. The situation is made worse by large device-to-device fluctuations caused by the intrinsically disordered nature of the defects that cause these phenomena in the first place. These fluctuations become worse as the width of the nanoribbon decreases.

The main finding reported by Haruyama, Tour and co-workers is that nanoribbons derived by unzipping carbon nanotubes and then annealing the result are remarkably clean, and have transport gaps that result mostly from the intrinsic energy gaps of the nanoribbons, rather than from defects. The Japan–US team produced graphene nanoribbons by suspending multiwalled carbon nanotubes in concentrated sulphuric acid, followed by treatment with  $KMnO_4$ , which led to the oxidation and unzipping of the nanotubes<sup>11</sup>. Images from high-resolution transmission electron microscopes and atomic force microscopes confirmed

the high crystalline purity of these nanoribbons, and showed that the edges are predominantly 'armchair' (the edge atoms describe a repeated armchair-like pattern) and contain few defects. Several successive annealing treatments removed most of the remaining oxygen molecules adsorbed on the nanoribbon surfaces, as confirmed by Raman spectroscopy.

Field-effect transistors were made with both single-layer and bilayer nanoribbons of various widths (from 75 nm to 310 nm), and the electron properties were measured as a function of temperature and gate voltage (Fig. 1). Transport gaps on the order of 1 V were observed around the charge neutrality point (where the gate voltage induces no doping into the channel). Analysis showed that these gaps are close to the energy gaps predicted from quantum confinement effects owing to the nanoribbon width, suggesting a weak contribution of defects to the measured gap. By comparison, the measured transport gaps in lithographically formed nanoribbons<sup>3</sup> are much farther away from values predicted from quantum confinement alone.

The hypothesis that quantum confinement is the primary origin of the transport gap is reinforced by measurements of the temperature-dependent conductance, which shows no sign of variable-range hopping (an effect associated with localization) or single-electron charging effects (associated with Coulomb blockade) at low temperature<sup>4</sup>. The experimental estimate of an intrinsic energy gap of ~50 meV



**Figure 1** | Electron microscope images of a graphene nanoribbon (GNR) that is derived by unzipping carbon nanotubes, and then connected to gold/titanium source and drain electrodes for testing in a field-effect transistor configuration. The inset shows that the nanoribbon ends are completely bonded to the electrodes. Adapted from ref. 5.

for a ~100-nm-wide nanoribbon clearly shows that the unzipping-plus-annealing fabrication process results in much cleaner graphene nanoribbons than lithography or etching. In fact, the transport gap for a perfectly clean nanoribbon of such lateral size is calculated to be approximately 45 meV (with 20 meV contributed from electronic confinement and 25 meV from electron–electron interactions)<sup>10</sup>.

The measured current–voltage characteristics also shed light on the effects of edge disorder in nanoribbons. Calculations<sup>11</sup> have predicted that edge disorder can lead to sharp modulations of

the transport type (p-type versus n-type) as well as conductance suppression features<sup>12</sup>. Haruyama and co-workers observe large variations in device characteristics at high source–drain voltages (high voltages tend to increase the effect of edge structure on transport). These variations lend support to the thesis that edge structure can have a marked effect on charge transport, but only weakly affect the intrinsic energy gap.

The work by the Japan–US team paves the way towards viable graphene electronics. By combining chemical unzipping of carbon nanotubes with high-temperature annealing, ultraclean graphene nanoribbons that are useful for transistors can be fabricated. □

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## QUANTUM COMPUTING

# Solid-state spins survive

Quantum-control pulse sequences can suppress errors and significantly extend the lifetimes of spin-based quantum bits in solid-state devices.

Michael J. Biercuk and David J. Reilly

Any technological exploitation of quantum mechanical effects first requires a suitable physical representation of quantum information. Although approaches based on trapped atoms (and ions) and the manipulation of photons have been extensively pursued, solid-state devices are perhaps the most attractive in the long term for both scientific and pragmatic reasons, particularly the desire to leverage decades of expertise derived from the

semiconductor industry. Controlling individual quantum systems in nanoscale semiconductor devices has therefore attracted tremendous attention. Unfortunately, quantum systems in the solid state are typically short-lived, and are difficult to control with high precision. Primary research goals have therefore related to improving the fidelity of quantum control in solid-state spin quantum bits (or spin 'qubits') and extending their coherent lifetimes. Four recent, independent

experiments have now demonstrated that manipulating spins with high-speed control pulses, in a technique known as dynamical decoupling, allows for high-fidelity control and substantially improved lifetimes in integrated quantum devices<sup>1–4</sup>.

These experiments focused on two distinct physical implementations of qubits. The first is a single pair of confined electrons in a nanopatterned semiconductor heterostructure<sup>5</sup>, which in 2005 successfully demonstrated coherent