

(ohmic contact)^{8,9}. This phenomenon, known as the ‘conductivity mismatch’ problem, can be alleviated by the insertion of a tunnel barrier in the junction region¹⁰. If the tunnel-transmission probability is different for spin-up and spin-down electrons, the barrier enables spin injection while its resistivity prevents the reservoir from annihilating the spin polarization of the semiconductor (Fig. 1). However, to achieve a robust spin injection into the semiconductor, there should be a balance between the needs for resistive tunnel barriers and large spin-injection signal (the more resistive the barrier, the more difficult it is for electrons to tunnel through). The optimum is reached by spin-impedance-matching between the tunnel barrier and the semiconductor¹¹. Quantitatively, it can be described by $G_{\text{tb}} \approx \sigma_{\text{sc}}/L_s$, where G_{tb} is the electrical conductance of the tunnel barrier (in units of $\Omega^{-1} \text{cm}^{-2}$), σ_{sc} is the electrical conductivity of the semiconductor ($\Omega^{-1} \text{cm}^{-1}$), and L_s is the characteristic length-scale that an electron diffuses in the semiconductor prior to losing its injected spin information. The conductance of the tunnel barrier is controlled by its height and thickness, the conductivity of the semiconductor channel by the doping, and the spin-diffusion length by the crystal symmetry and mass density. Usually, the more symmetric the crystal and the lighter its atoms, the longer it takes to lose spin information.

Almost all previous electrical spin-injection experiments in semiconductors have employed over-resistive barriers outside the ballpark of spin-impedance-matching (that is, in the regime

$G_{\text{tb}} \ll \sigma_{\text{sc}}/L_s$). To solve this problem, Van ‘t Erve and co-workers placed single-layer graphene between a ferromagnetic film made of an iron–nickel alloy and an n-type silicon channel⁷. They showed that graphene behaves as a tunnel barrier with much better spin-impedance-matching conditions. The researchers performed donor density and temperature-dependent measurements, from which they inferred that the injected spins reach the bulk region of the silicon channel. Importantly, these measurements showed a robust spin signal that persists up to room temperature.

In spite of being as thin as possible, a graphene layer is impervious to migration of ions from one side of the membrane to the other. This property stems from strong in-plane bonding between carbon atoms in the hexagonal lattice mesh. Preventing metallic ions from migrating to the semiconductor region increases the longevity of devices. Moreover, the carbon atoms hardly interact with atoms outside the plane. A consequence of this chemical inertness is that fewer charge-traps tend to stick on a graphene flake, and the dynamical response to spin injection becomes free of charging-time delays. It is therefore expected that the use of graphene tunnel barriers in semiconductor spintronic devices will produce both fast and stable operation.

There are several possible near-term research efforts that may stem from the fundamental demonstration by Van ‘t Erve and colleagues. One such is to realize a ferromagnet–graphene–silicon device in which the spins are detected after diffusing outside the region of injection.

Such a demonstration can be made with four-terminal devices¹², and will provide unambiguous proof of point-to-point spin propagation within the transport channel. A second effort is to implement an inhomogeneous doping profile such that spin-polarized electrons drift to a region where they are not swamped by a large bath of spin-unpolarized electrons. Silicon spintronics operates best in low-doping environments where spin information can be kept for very long timescales^{13,14}. With monoatomic tunnel barriers becoming a reality, hybrid ferromagnet–graphene–silicon systems are off to the races. □

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GRAPHENE

Conductivity measurements pick up

The conductivity of a single graphene nanoribbon can be measured by lifting the nanoribbon off a surface with the tip of a scanning tunnelling microscope.

Saw Wai Hla

Graphene — a single sheet of carbon atoms arranged in a honeycomb lattice — has generated a frenzy of research activity in recent years^{1–3} and in turn considerable speculation on its potential applications^{1–3}. For applications in nanoelectronics, a form of graphene known as graphene nanoribbons^{4,5}, which are long, narrow strips of the material, are of particular interest. However, if devices

based on graphene nanoribbons are to be built, it will be important to know how they conduct, and such measurements have so far proved challenging. Writing in *Nature Nanotechnology*, Leonhard Grill and colleagues at the Fritz-Haber-Institute of the Max-Planck-Society, the Institute of Materials Research and Engineering in Singapore and CEMES-CNRS in Toulouse have now shown the conductivity of a

single graphene nanoribbon can be directly measured using a scanning tunnelling microscope (STM)⁶.

One of the reasons why graphene has attracted such interest is the simplicity with which it can be made: the material can be cleaved from bulk graphite using only duct tape¹. Producing graphene nanoribbons is, however, more demanding and requires innovative strategies such as

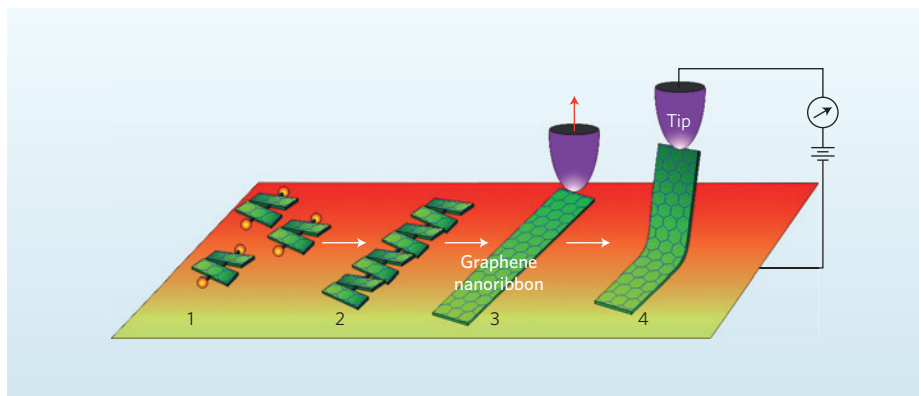


Figure 1 | Measuring the conductivity of a single graphene nanoribbon. The nanoribbons are made from 10,10'-dibromo-9,9'-bianthryl molecules (1), which are composed of two groups of three fused benzene rings (green) connected in the middle by a single C–C bond. A bromine atom is also attached at either end of the molecule (orange). The molecules are deposited on a Au(111) surface that is held at 200 °C. On adsorption, the bromine dissociates and the molecules undergo an on-surface polymerization reaction to form long, non-planar molecular chains (2). Annealing the surface to 400 °C leads to cyclodehydrogenation and the formation of graphene nanoribbons (3). The tip of a STM is then used to lift up one end of the nanoribbon (4). By applying a voltage between the tip and the surface, the conductivity of the nanoribbon can be directly measured.

cutting open carbon nanotubes or the use of lithographic patterning^{4,5}. To produce nanoribbons with atomically well-defined edges is more challenging still, but a technique to assemble atomically precise nanoribbons from basic molecular building blocks on a surface has recently been developed⁷. Grill and colleagues used a similar method and starting molecules to assemble their graphene nanoribbons on a gold surface (Fig. 1). They first deposit the precursor molecules on the surface that is held at 200 °C. The molecules undergo a polymerization reaction that links them together to form long molecular chains. Subsequent heating to 400 °C leads to the formation of graphene nanoribbons with atomically well-defined edges.

Measuring the conductivity of a macroscopic wire is simple: attach two electrodes at opposite ends of the wire and then apply a voltage across it. Because of the challenges associated with manipulating and probing wires with minuscule dimensions, conductivity measurements at the nanoscale are inevitably not as straightforward. To perform these measurements, Grill and colleagues used the tip of the STM to lift one end of the nanoribbon off the surface while the other end remains attached (Fig. 1). In this geometry, the STM tip and the gold surface act as the two electrodes. Then by applying different voltages across the nanoribbon, the researchers can directly measure its conductivity.

Graphene nanoribbons can have two types of edges, which are termed 'armchair' and 'zig-zag' because of their

shapes^{3–5,7–9}. The zig-zag edge has a special electronic structure known as the Tamm state, which originates from non-bonding molecular orbitals near the Fermi level⁸. The existence of the Tamm state was theoretically predicted over a decade ago⁸ but was only recently experimentally observed⁹. The graphene nanoribbons assembled by Grill and colleagues have armchair edges along the long axis of the ribbon and zig-zag edges along the short axis. Nevertheless, the Tamm states of these narrow ends are clearly evident in the STM images, where they appear as protrusions (lobes). The electronic structures of the nanoribbons derived from the STM images are also confirmed by theoretical simulations.

From the measurements, the researchers show that the conductivity of a nanoribbon depends critically on its electronic states such as the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO). It also depends on the distance between the electrodes. In the experiments, the conductivity of the nanoribbon is measured by pulling it off different distances from the surface. At small tip-to-surface distances, the conductivity is dominated by electron tunnelling but at higher tip heights — that is, at larger distances between electrodes — the conductivity decreases exponentially, as expected.

A key finding in these measurements is that the conductivity of the nanoribbon rapidly increases when the voltage applied across the electrodes matches the energies

of the molecular orbitals, that is, the HOMO and LUMO of the nanoribbon. Although this behaviour was also expected, the measurements on individual nanoribbons unambiguously prove that the conductivity is directly related to the electronic states. Because the orbital energies or electronic states of the nanoribbon can be tuned by varying the shape and size of it, this finding highlights an important way to tailor its conductivity. Furthermore, the geometry of the nanoribbon is also shown to play a role. In particular, a bent nanoribbon exhibits an exponential decay in conductivity, whereas pseudo-ballistic transport would be expected for a flat graphene nanoribbon. This geometric effect could be used, for example, to vary the conductivity of the nanoribbon between two states like a switch. Moreover, it might be possible to tune the current passing through the nanoribbon by varying the degree of bending. It could then be used as a gated field-effect transistor.

The atomically precise assembly of graphene on a surface offers a potential route to graphene nanoribbons with tailored shapes and sizes⁷. The technique developed by Grill and colleagues now provides a means to measure the conductivity of these assembled nanoribbons with atomic precision⁶. The fabrication of nanoelectronic devices will of course require more than this. Reliable and reproducible nanoribbon–electrode junctions will, for example, have to be developed. Moreover, a reliable strategy to assemble these nanoribbons into device geometries is still required. Nevertheless, conductivity measurements of single graphene nanoribbons are an important step on the way to functional nanoelectronic devices. □

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