Electrons in carbon country

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For almost all performance measures, there is some carbon-based material that performs better than silicon. Yet it has proved tough to exploit these carbons in electronics, apart from niche applications. Could hybrid carbon-based materials be more successful?

Only in the 1950s did silicon become the semiconductor of choice, for the founders of semiconductor science spent far more time on those from Ge and II–VI semiconductors. Silicon's electronic properties are good, rather than phenomenal. One winning feature was its oxide, which passivates the surface, acts as an impressive dielectric, and enables high-resolution lithography. Silicon then achieved almost unbeatable status through know-how and control. The incredible degree of control of dislocations and dopants, and the wide experience underlying the many steps of semiconductor processing mean silicon is unique. Semiconductors like Si/Ge and the III–Vs can outperform silicon in important ways, and the bandgap engineering of III–Vs makes them formidable photonic materials. Yet III-Vs would be merely niche materials if silicon could be used in new ways that were even modestly competitive. Yet this situation might change. Silicon does not stand alone. Fabrication needs lithography optics and resists, and processing at the anticipated smaller scales is likely to exploit new electronic excitation methods. Alternative dielectric and interconnect materials create new compatibility issues. Auxilliary devices lead to constraints, such as from displays, spintronic components, electron emitters or transparent conductors.

Demands for greater miniaturization, higher speed, lower power use, and heat dissipation are becoming hard to meet with silicon. Despite variants like porous silicon, silicon-based displays are unlikely to be leaders. Silicon may not be the material of choice for some new opportunities, like electronic books. It is not the natural choice where inorganics meet biological systems, nor when the environment is hostile, whether through higher temperatures or electrochemical conditions. Silicon know-how is valuable for microscale machines, but gives only a modest lead over materials with more desirable properties. For quantum information processing, silicon technology will surely prove a significant part, but may not provide all the key ingredients.

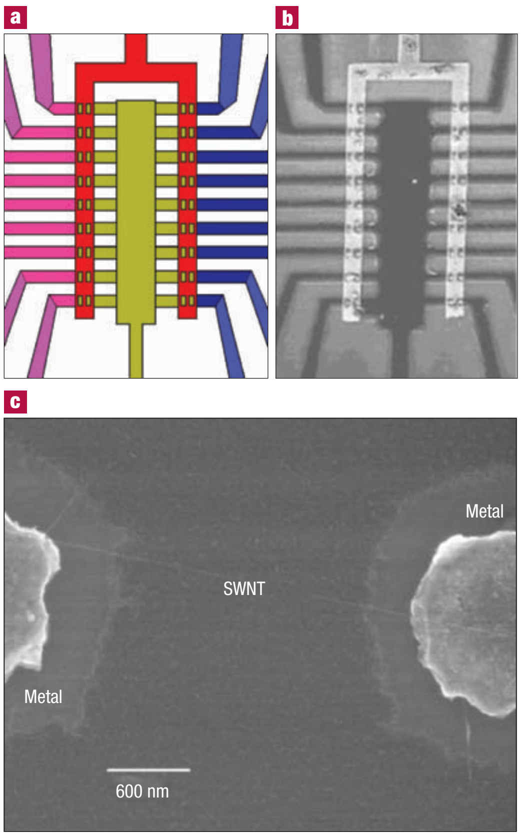

Figure 1 **Nanotube-based logic devices are being made with increasing sophistication; that shown here contains single-wall nanotubes (SWNTs) grown between contacts. a, A schematic and b, a scanning electron microscope image of a field-effect transistor. The nanotube is not visible as it is buried under the gate oxide and gate metal. c, A scanning electron microscope image of a single-wall nanotube linking two metal catalyst particles.**

Figures courtesy of W. Milne and K. Teo (Cambridge); see http://www-g.eng.cam.ac.uk/cnt/ for further information.

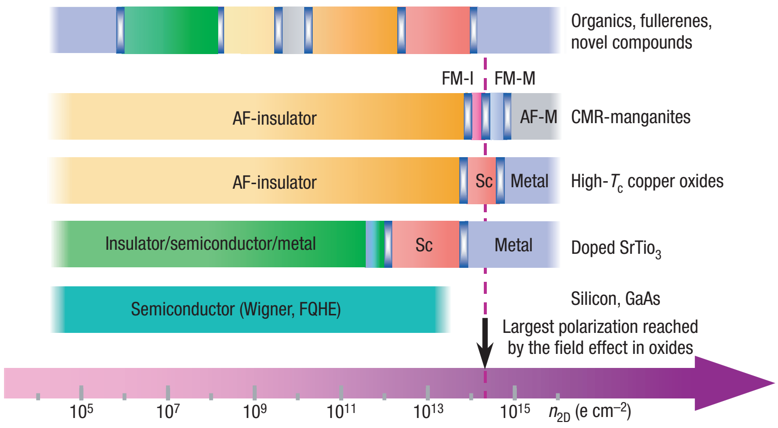

Figure 2 **Wide-ranging behaviours of correlated systems as a function of sheet charge density, n_{2D}. The data summarize results for many carbon-based systems and oxides at absolute zero temperature[1]. AM, antiferromagnetic; FM, ferromagnetic; I, insulator; M, metal; SC, superconductor; CMR, colossal magnetoresistive; FQHE, fractional quantum Hall effect.**

Could carbon-based electronics be viable? The diversity of carbons is striking: diamond, graphites, buckeyballs and nanotubes, amorphous carbons, and nanodiamond. Add hydrogen, and one finds a range of diamond-like carbons and a wealth of organics. The full range of these carbon-based materials includes small molecules and polymers: impressive insulators, semiconducting and conducting polymers, switchable forms, superconducting and magnetic forms, and intercalates with better conductivity for a given weight than copper. Their photochemistry enables novel processing methods. Water-based processing is often possible. Costs are remarkably well controlled, with even diamond film (so-called carbon ceramic) acceptably cheap for commercial applications. Indeed, silicon processing already uses carbon-based resists, and may exploit ingenious ways to use carbons, such as molecular self-organisation to influence dopant positions in a surface layer.

A major strength of conventional semiconductor technology is the opportunity to exploit bandgap engineering. The combination of alloying and stress allow control over bandgaps and mobilities. For organics, any simple band picture may mislead. Yet there is scope for control by molecular design and choices of terminations. Blends can make n-type (electron transporting) and p-type (hole transporting) coexist. There is the opportunity to control texture and optimize mesostructures. The best carbons have impressive, sometimes supreme, performance: the mobility and optical properties of diamond, spin-conserving transport in nanotubes, and electron emission. Despite these virtues, carbon-based electronics is not in the same league as established silicon technology. Maybe it never will be a serious challenger. But why should carbon electronics compete with silicon in those areas where silicon is supreme? Why think of these carbons as yet another 'semiconductor' with different dielectric constant, effective mass or other standard properties?

An alternative view is that carbon electronics should mean the judicious combining of carbons and organics. The combination, one hopes, will take the very best properties, yet avoid those performance measures that are unimpressive. The very best properties are not just electronic or photonic, of course, but include mechanical and thermal behaviour. Diamond is robust electrochemically and very rigid, indeed superhard; graphite and diamond-like carbons have exceptional tribological properties and highly controllable mechanical properties, from the viscoelastic to highly rigid. There is certainly a basis for niche applications with diverse needs, for example, combinations of good mechanical and optical behaviour with resistance to corrosion or radiation, or ingenious micromachines.

For carbon-based electronics to prove more than a niche success, something more is needed. Polymeric electrical insulators are standard in everyday life, even if there is probably scope for science-based improvement. Semiconducting and conducting polymers, as well as devices — such as field-effect transistors and optoelectronics —based on small organic molecules, already perform with real promise. Designer organics with controlled electronic and ionic processes are already the basis of battery and allied systems. But usually the electron is being used in a fairly mundane way. Are there more sophisticated ways that carbon-based systems can offer?

I would identify five promising basic ideas. First, interface engineering promises effective control of electron transfer between different (perhaps carbon-based) media. Diamond shows good cold cathode behaviour, and it is certainly possible to do clever things with nanotubes (Fig 1), including their use as effective electron emitters. For some applications, an underlying problem is reproducibility: if you manage to find the ideal nanotube, it could take a very long time to find another like it. Second, there is plenty of scope to construct mesostructures, possibly to form photonic structures, whether by texturing, blending, self-organisation, or some combination of crosslinking or scission. Third, there must be new ideas for field-effect devices. One might use one carbon to supply fields, or a different carbon to supply carriers to another — an especially powerful approach for highly correlated systems (Fig 2, ref. 1). Fourth, we tend to think of wires to carry power (interconnects being a special case) and optical fibres to carry signals, but we may lose sight of how efficiently the α-helix in protein transfers energy, whether this is really by solitons or otherwise. Mimics of such biological performance might offer value. Fifth, carbons offer optical properties that (apart from laser action, which is often elusive) can be superb, not just for conventional devices. Indeed, several proposed quantum computer gates are based on diamond.

The use of carbon-based materials in combination is not new, although systematic work has been limited, apart perhaps from polymer blends[2]. Light-emitting diodes based on conjugated polymers already have separate layers for electron injection and electron transport, corresponding layers for holes, and a recombination layer. At the molecular scale, these devices can be enhanced by adding structural elements to minimize interference between electronically important molecules[3]. There might be advantages in adding quantum dots with relatively large dielectric constants, possibly oxides, to such as LEDs or photovoltaics to create amphoteric traps by the image interaction at which electrons and holes can recombine. For solar cells, there is advantage in separating the initial light-absorption step from those of carrier separation and transport to electrodes, otherwise the electrons and holes may recombine to form heat, or could only provide electricity if they reached the electrodes. It is standard to have carbon-based additives in insulating polymers to reduce damage following optical or electrical excitation.

The texture of materials is tricky to control, and can have counter-intuitive consequences for electron transport. For example, the combination of discrete space charge and topology can lead to trapping of carriers even when there are no traps in the usual sense[4]. This suggests advantages in incorporating electronically inert molecules into a blend as an aid in optimizing an effective texture. We know that biological systems achieve miracles of self-organisation, well beyond the modest and somewhat inaccurate efforts based on elasticity or on a fast-forming instability, so there is surely an opportunity to optimize texture here.

Nanodiamond is emerging as a composite of interest: nanometre-scale diamond sp^3 structures separated by what one should call interparticle carbon. Charge transport takes place mainly within this interparticle carbon, and can be n-type or p-type. Whether it could be the basis of wide-ranging electronics is less clear: the mobility observed in nanodiamond suggests it is modest and increases with temperature, possibly by carrier hopping between localized states introduced by the inhomogeneity, with the Coulomb blockade playing a role. Single-crystal diamond has high carrier mobility, countered by the major disadvantage of difficult n-type doping, and the far from ideal properties of known donors and acceptors.

Field-effect devices based on nanotubes have been described. But it should be possible to create a variety of field-effect systems. Perhaps they will need to be more varied than for silicon. Any such devices wanting to exploit the outstanding mobilities in diamond, for instance, will first have to generate higher concentrations of mobile carriers, owing to the inherent difficulties in doping it. Devices based on diamond might exploit optical excitation, surface acoustic waves, surface-terminating species, or the many adsorbed small molecules with their own particular virtues[5] (Fig 3). I have not mentioned some of the more exotic aspects of carbon-based electronic systems: local ferri- or ferromagnetism, superconductivity, or the carbon-based species that switch reversibly between structures.

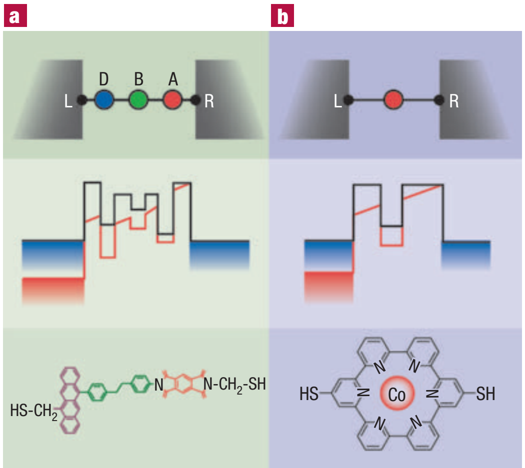

Figure 3 **Examples indicating the range of possible device structures based on small organic molecules[5]. The top panels depict molecules with various localized, low-energy molecular orbitals (coloured dots) bridging two electrodes L (left) and R (right). In the middle panels, the black lines are unperturbed electronic energy levels; the red lines indicate energy levels under an applied field. The bottom panels depict representative molecular structures. a, Donor-bridge-acceptor (DBA) molecule. b, Molecular quantum dot. The transport is dominated by the single metal atom contained in the molecule.**

There is no doubt that it will continue to be cheaper and faster to let silicon do the things silicon already does well. There is no doubt that any carbon-based electronics will have silicon electronics alongside it for some functions. But there are plenty of new demands that silicon cannot always meet. Some will come from exotic new areas, such as quantum information technology. Some will mimic nature's designs from biology; whether the integration of man-made devices and living biological systems goes beyond science fiction remains to be seen. Still others will make use of the design rules and the cheap and fast preparation methods of organic chemistry. A key guideline is the separation of function: let each material component do what it is best at. If followed when combining carbons in their many forms, carbon-based electronics may have a thriving future.

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