

RTT TECHNOLOGY TOPIC November 2013

The Second Age of the Atom?

On the 17th October 1956 the Queen switched on the world's first full scale nuclear power reactor at Calder Hall in Cumberland. Calder Hall was a gas cooled graphite moderated reactor using the nuclear reaction in uranium rods to generate power. http://news.bbc.co.uk/onthisday/hi/dates/stories/october/17/newsid 3147000/3147145.stm

Fifty five years later it looks as though we may be getting another nuclear power station built by EDF Energy, a nationalised French utility, with the support of Chinese investment and expertise. This possibly represents the start of a second age of nuclear power, more effective, efficient and less likely to explode.

Alternatively rather than splitting the atom we might find we can deliver improved energy efficiency by building structures at the atomic level. The net energy efficiency and carbon footprint gain might be greater and less financially and environmentally risky. Our February 2012 technology topic, <u>The New Carbon Economy</u>, reviewed the long (30,000 year) history of graphite (a form of carbon) and short (seven year) history of graphene.

http://www.rttonline.com/tt/TT2012_002.pdf

Graphene is a monolayer, hexagonal arrangement of carbon atoms. When assembled as a multilayer structure it could provide the building blocks for ultra-fast transistors and fast efficient data and energy storage including high density light weight fast recharge batteries.

Graphene has the ability to conduct heat more efficiently than copper and when stacked, doped, chemically reduced or electrically/magnetically biased can be an efficient (low resistance) conductor of electricity. Graphene also has excellent mechanical and gas barrier properties.

In the telecoms industry it could provide the basis for more efficient routers including highly optimised low cost optical devices. It could also improve the RF performance of smart phones initially by improving EMI shielding and thermal management.

In this month's technology topic we review progress with production techniques over the past eighteen months and how different forms of graphene produced from these processes produce different material properties with distinct RF smart phone applications.

Graphene – a family of materials

Graphene is in practice not one material but a family of materials with each material being a product of the manufacturing process used. This in turn determines the properties and performance of the material.

Graphene can be produced by **physical exfoliation**. Applying adhesive tape to a piece of graphite and pulling it off will isolate multi-layer graphene on the tape. By applying a fresh adhesive tape and repeating the process it will eventually produce few layer and monolayer graphene. The isolated sample can be then be deposited on to a substrate such as a quartz or silicon wafer; however the result is neither scalable nor consistent.

Alternatively graphite can be **broken into flakes, for example by ultra sound and shaken and stabilised in a liquid suspension** to produce a range of graphite inks of varying flake size. These can be used to dip or spray substrates. These are relatively low cost to produce but do not

have the performance or consistency of graphene produced from more direct production processes. The process is also subject to changes in the cost of graphite.

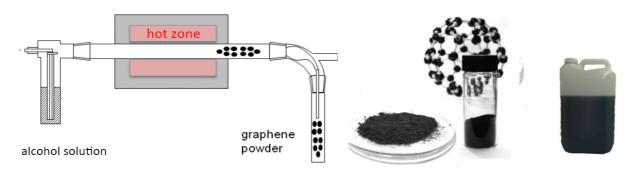
Similar constraints apply to **reduction techniques** producing graphene oxide from graphite oxide. Graphite oxide is a compound of carbon, hydrogen and oxygen molecules produced by treating graphite with a strong oxidiser or combination of oxidisers, for example sulphuric acid, sodium nitrate, potassium permanganate or phosphoric acid. Graphene oxide is a by-product of this reduction and oxidation process. Problematically the oxidation process compromises the quality of the graphene. Research is on-going to find a process that is fast but effective and efficient, probably some combination of electrochemical process, preferably avoiding toxic waste.

More direct processes are essentially various forms of **chemical vapour deposition** which involve disassociating carbon atoms from a suitable gas, for example methane, acetylene or carbon dioxide using heat in a furnace to transfer the atoms directly on to a substrate. This disconnects the process from the direct material cost of mined graphite.

The challenge is to ensure the carbon atoms do not cluster together (forming soot). Creating the right carbon structure requires high levels of heat of the order of more than a 1000 degrees Celsius. Typically a catalyst will be used to reduce but this introduces additional compounds into the combustion chamber and can result in unwanted reactions, for example the carbon atoms dissolving into nickel.

Getting the graphene on to a suitable substrate is also complex. Copper is one substrate option. A mix of copper and mechanically and chemically weak copper oxide allows the graphene to be recovered and the copper to be reused. Other options include the use of **polymers to facilitate the transfer process, for example Polymethyl methacrylate (PMMA)**. The ideal end result is a uniform layer of graphene but this can be frustrated by the convection and turbulence of the carrier gas. The fluid dynamics of the gas can mean that the reactants are depleted before the gas reaches the further end of the substrate.

Another option is synthesised graphene powder.



With thanks to Applied Graphene Materials http://www.appliedgraphenematerials.com

In this example, the source of carbon is alcohol. This is sprayed into a furnace and converted into graphene platelets one to two microns in size with a thickness of typically less than five nm. The powder can be added to a suspension or added to other composite materials to improve electrical and heat conductivity.

The advantage with this process is that it can be scaled to several tonnes per year and should produce polymer composites that have less defects and cracks than polymers using exfoliated or reduced graphene, which may contain graphite lumps.

An alternative is to heat silicon carbide (SiC) to a high temperature (>1100 degrees Celsius) at low pressure. The output is epitaxial graphene with dimensions that are dependent on the size of

the silicon carbide substrate. This determines the thickness, mobility and carrier density of the graphene. Epitaxial graphene has been used by IBM to build a microwave GFET mixer.

http://www.sciencemag.org/content/332/6035/1294.abstract

The role of graphene in next generation smart phones?

One of the potentially useful benefits of graphene transistors is that they overcome the Si short channel effects that occur as Si is scaled down. This should result in higher Ft devices. Graphene transistors have their own set of problems which include lack of saturation (cannot set bias to get maximum Ft) and lack of power gain (very low Fmax) as well as unusual ambipolar transfer characteristics but silicon will have potentially similar issues as and when it hits the 10nm node, forecast as being around 2020.

In the meantime there may be directly useful applications in passive applications including antennas, shielding, interconnects, metamaterials, absorbers and thermal management.

Improved thermal management on FR4?

In 1982 when Motorola started production of first generation cellular phones, one of the challenges was to source low cost FR4 printed circuit board material with sufficient quality and consistency to realise stable RF designs at 850 MHz.

Thirty years later we take good quality FR4 for granted as the default material used for standard printed circuit board layouts at cellular RF frequencies. But this is not to say that circuit board laminate materials would not benefit from improved performance particularly if cost is the same or less.

The limitations of FR4 are the batch to batch consistency of the dielectric constant, impedance stability over frequency, signal loss and thermal conductivity when supporting active devices providing high linearity. Minimal temperature expansion is also important. More highly specified FR4 will have lower loss but higher cost.

Whether graphene (as a semi metal) can be directly useful has yet to be proven though improving thermal management might in itself be useful.

http://ipruw.com/publications/2010/presentations/AipingYu.pdf

While it is true to say that integration levels have increased it is also true to say that the number of discrete active and passive devices has either stayed the same or increased, at least in higher end smart phones. Mixes of materials that provide improved conductivity and improved isolation, for example keeping digital noise out of front end receive paths, would be particularly useful. CVD graphene for example potentially provides significantly higher isolation than gold film and monolayer graphene could potentially shield as much as 97.8% of EMI

http://iopscience.iop.org/0957-4484/23/45/455704/pdf/0957-4484_23_45_455704.pdf

Other 2D Materials

Although graphene has enjoyed the most attention (and a Nobel Prize) it is not the only 2D material.

Reducing silicon to an atom thick, popularly described as **silicene** produces a honeycomb

structure not dissimilar to graphene and like graphene allows electrons to move as if they were massless which means they move very quickly. It could also be used as a transistor in its natural form. It has however only recently been synthesised and is presently harder to manufacture than graphene and is unstable under ambient atmospheric conditions.

http://arxiv-web3.library.cornell.edu/pdf/1310.6820v1.pdf

Reducing germanium, the original transistor material from the 1940's to a single layer of atoms produces **germanane**. This conducts electrons five times faster than germanium and ten times faster than silicon and might be more compatible with existing scale production processes than present graphene manufacturing techniques. As with silicene, germanane has stability problems that presently limit its usability.

http://pubs.acs.org/doi/pdf/10.1021/nn4009406

Molybdenum disulphide is a 3D structure similar to graphite but can be restructured as a single atomic layer sandwiched between two sulphur atoms producing a natural form that could function as a higher efficiency transistor.

http://www.nature.com/nnano/journal/v6/n3/pdf/nnano.2010.279.pdf

It is of course not impossible to consider some combination of all of these materials to produce composites that could act as optimised conductors, semiconductors or insulators.

The behaviour of 2D materials in general remains relatively unexplored and sometimes unexplainable with observed behaviour not always consistent with existing quantum theory. The behaviour of combinations of these materials is presently even more arcane.

Summary - Fifty years is not a long time

In the short (ten to twenty year) term 2D materials could produce useful ubiquitous alternatives to existing composite materials – applications include smart windows and smart wings on aeroplanes, electric car batteries and a whole range of flexible conductive and transparent substrates.

Improved interconnectivity and EMI management in smart phones is more prosaic but could be potentially just as valuable.

In the longer term (twenty to fifty year) term, atomic level devices might yield a step function improvement in processor, memory and energy and data storage efficiency – **the second age of the atom?**

Resources and References

Centre for Advanced Photonics and Electronics – Cambridge University http://www-cape.eng.cam.ac.uk/

http://www.graphene.cam.ac.uk/about-1

http://carbon.chem.wisc.edu/Files/MechanicalExfoliation.pdf

http://www.intechopen.com/books/physics-and-applications-of-grapheneexperiments/chemical-vapor-deposition-of-graphene) http://www.sciencemag.org/content/332/6035/1294.abstract

Graphene synthesis http://www.appliedgraphenematerials.com Alternative production techniques http://www.graphenea.com/

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http://www.rttonline.com/tt/TT1998 008.pdf

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