Realistic applications of CNTs

by John Robertson

Carbon nanotubes (CNTs) are a fascinating subject for curiosity-driven research. But will they give rise to commercially viable applications? CNTs are rolled up sheets of sp^2 bonded graphite with no surface broken bonds. Their possible applications[1,2] arise from the remarkable properties of single-walled nanotubes (SWNTs) such as the highest Young's modulus, highest thermal conductivity, ballistic electron transport, and high aspect ratio structure. To date, development of nanotube-based products has been delayed by a lack of availability of quantities of material and lack of control of their growth. Supplies of multi-walled nanotubes (MWNTs) or nanofibers have been available from Hyperion Catalysis International, but under constraint and only as preformed composites. The supply situation is now improving with several firms producing on a larger scale, such as CNI, Showa Denko, Thomas Swan, and Nanocyl. Now is, therefore, a good time to look at applications from a more business view.

Engineering Department,
Cambridge University,
Cambridge CB2 1PZ, UK
E-mail: jr@eng.cam.ac.uk

A key point for a new product to find a market is that it should have either a unique function not previously existing, or it should have a high (x10) performance advantage to displace an existing product in its market. A second point is that while SWNTs may be the most interesting form of nanotube, they have limitations, so one should really consider the most appropriate form of sp^2 carbon for the job in question, whether it is SWNTs, MWNTs, nanofibers, or a nanostructured carbon. We shall consider applications in four broad areas; composites, field emission, electronics, and electrochemistry.

Nanotubes are produced by three methods: laser furnace, the arc, and chemical vapor deposition (CVD). Laser methods are not for large-scale production. The problem with arc material is purification. Removal of non-nanotube carbon and metal catalyst material is much more costly than production itself. In addition, there is no simple, routine method to measure purity. Electron microscopy is too costly, Raman spectroscopy sees mainly the nanotubes because of their huge cross-section, so infrared may be the eventual method[3], but no standards have been agreed. CVD is the only truly scalable method, with the advantage that purity can be controlled by careful process control.

Composites

The high aspect ratio (length to radius ratio) and high conductivity of CNTs makes them excellent for conducting composites. A mixture of conducting and insulating phases becomes conducting when the volume fraction of conducting

ISSN:1369 7021 © Elsevier Ltd 2004

phase exceeds a 'percolation threshold' of 16%, the minimum amount to give a continuous path across the whole sample. This threshold is independent of the size and shape of the conducting phase, as long as its particles are equiaxed. When the conducting phase consists of long thin particles, the chance of contact increases, which reduces the percolation threshold so that conduction occurs at much lower loading.

Existing conducting composites are made of carbon black in polymers. This should require about 16% of carbon, but it has been reduced by clever processing. Fig. 1 shows an example of composites of MWNTs in epoxy resin achieving percolation at loadings of 0.01% and even 0.004% with careful processing[4]. These are extremely low loadings. The first use of such composites was by Hyperion for electrostatically applying paint onto car components[1]. Nanotube composites have a much better surface finish than the previous carbon black or carbon fiber composites. Another use of nanotube composites is as antistatic shielding, on airplane wings and fuselages for example. This is a realistic application. A future use is for shielding of electromagnetic interference, a critical application for many industrial sectors. This would require a composite with conductivity of 1 S•cm. This requires that the carbon phase should be highly conducting and is probably only achievable if SWNTs are used as the loading. It is achievable, however, and is a credible application.

A fourth application of conducting composites is as a transparent conductor. There is a huge market for transparent electronic conductors such as indium tin oxide (ITO) in displays. In this field, there is a drive towards flexible displays on plastic substrates. ITO is less good for this situation as it is brittle and has poor adhesion to plastic. Conducting composites of SWNTs can be transparent if thin enough[5]. They have the huge advantage of being truly flexible and compatible with polymer substrates. This is a large potential market with few competitors.

Turning to mechanical properties, SWNTs have the highest Young's modulus of about 1 TPa if normalized to their diameter and, therefore, all types of CNTs have attracted much interest for low weight structural composites. It could be hoped that their performance might eventually exceed that of carbon fiber reinforced composites. However, to date, their performance has been rather disappointing. A simple analysis assuming the rule of mixtures would expect the modulus of a composite to be at least $1000x/3$ GPa, where x is the nanotube content, 1000 GPa is the basic nanotube modulus, and the factor of 1/3 allows for isotropically oriented CNTs, assuming the host has minimal modulus. In practice, much lower values are found. This is because, firstly, SWNTs are usually not dispersed in the matrix but distributed as bundles. Secondly, only small amounts of CNTs are dispersed in the host and, thirdly, there is insufficient bonding across the nanotube/host interface to transfer forces. So far, these composites tend to fail either by fracture at the nanotube/host interface or, for MWNTs, by pull out of different shells of the MWNTs. Stronger bonds between CNTs and host are needed, for example by creating covalent bonds by functionalization along long tubes[6]. A second way would be to use secondary bonds such as hydrogen bonds that, although only 5% as strong as covalent bonds, could bond to more sites.

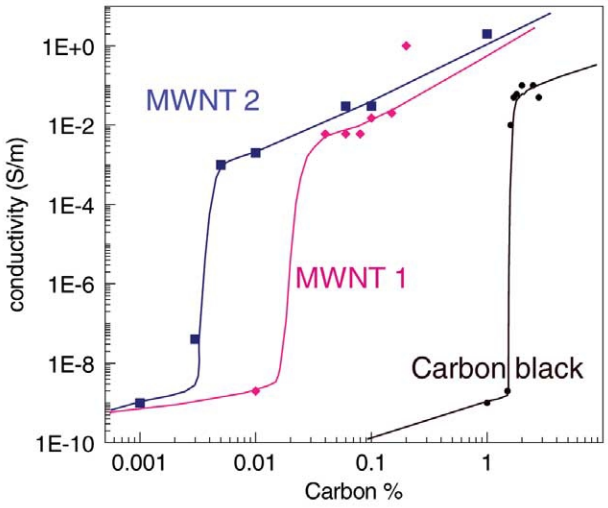

Fig. 1 Conductivity versus carbon content for three different carbon/epoxy composite systems showing the rapid increase in conductivity corresponding to the percolation threshold. Very low threshold values are possible for MWNTs[4].

Many groups are turning to fibers, by aligning CNTs. Vigolo *et al.*[7] drew nanotube/polyvinyl alcohol fibers, a process which has been taken further by Dalton *et al.*[8]. An alternative is to learn lessons from other strong fibers such as Kevlar. Davis *et al.*[9] dispersed SWNTs in 102% sulfuric acid, which possibly protonates the sidewalls, separating individual tubes, and allows fibers to be drawn.

The most novel of these methods is to draw and spin a nanotube fiber directly from a CVD reaction chamber, as done by Li *et al.*[10] and shown schematically in Fig. 2. A typical fiber is shown in Fig. 3. The resulting fiber can then be postimpregnated with epoxy to make a composite. These

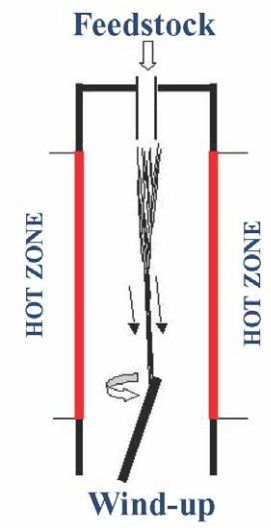

Fig. 2 Schematic of how to wind nanotube fibers directly from a CVD growth chamber. A feedstock of ethanol and thiophene catalyst[10] was used at 1100°C.

fibers presently have failure strengths of up to 1 GPa, compared with an expected ultimate strength of 30-50 GPa for a single nanotube. In fact, fibers made by each method creep before failure, suggesting that a great deal of straightening and aligning is occurring before failure. It also shows that much optimization is needed to share the load better across the many individual CNTs.

Field emission

The high aspect ratio also makes CNTs ideal field-emission (FE) materials. FE is the emission of electrons from a solid under an intense electric field. The simplest way to create such a field is by field enhancement at the tip of a sharp object. Si or W tips were initially used, made by anisotropic etching or deposition. CNTs have an advantage over Si or W tips in that their strong, covalent bonding means they are physically inert to sputtering, chemically inert to poisoning, and can carry a huge current density of 10^9 A/cm^2 before electromigration. In addition, when driven to high currents, their resistivity decreases, so that they do not tend to electric-field-induced sharpening, which causes instabilities in metal tip field emitters[11]. CNTs have better FE performance that other forms of carbon such as diamond and diamond-like carbon.

A clear application of FE from CNTs is as electron guns for next generation scanning electron microscopes (SEMs) and transmission electron microscopes (TEM)[12], Fig. 4. In a low voltage SEM, the largest market, the lateral resolution is limited by chromatic aberration, and an electron source with

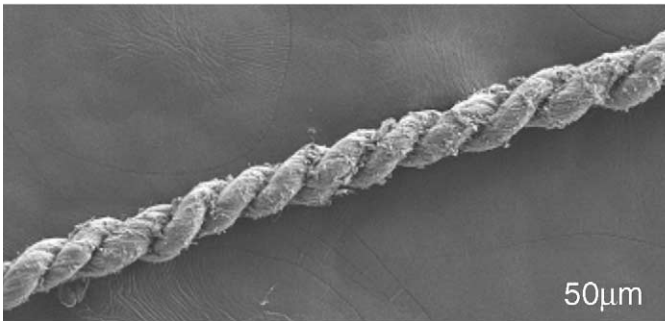

Fig. 3 Scanning electron micrograph of a spun fiber grown directly from a CVD growth chamber. (Reprinted with permission from[10]. © 2004 American Association for the Advancement of Science.)

a small energy spread is needed. A second critical parameter is the reduced brightness of the source, the current density per unit solid angle. The brightness influences the spatial resolution of an electron microscope and the amount of current in a certain probe size. Present day microscopes use Schottky emitters of doped Si or metal FE tips. A single MWNT FE source is found to have a factor of 30 higher brightness than existing electron sources and a small energy width of 0.25 eV. MWNTs are preferred to SWNTs because of their greater mechanical stiffness. The significant performance advantage of CNT electron sources should see them implemented in this high-value niche where cost is not critical.

A second use of CNTs is as FE cathodes in high power microwave amplifiers such as klystrons for base stations[11]. There is still an advantage to using vacuum devices for high-

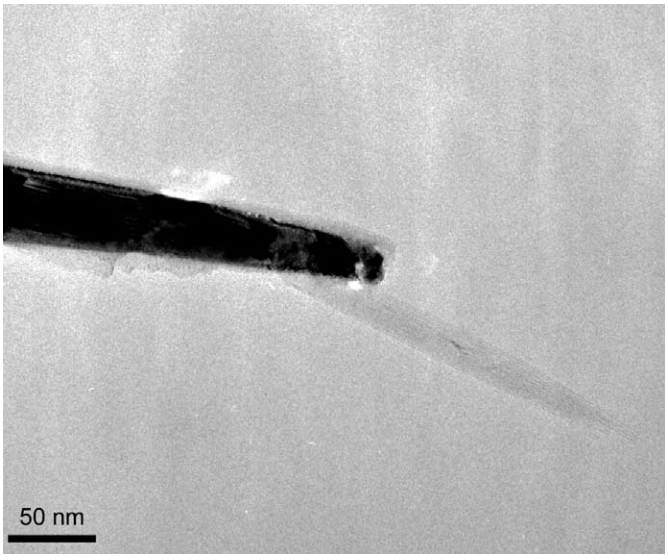

Fig. 4 A MWNT attached to metal tip for use as an FE electron source for the electron gun on a SEM. (Reprinted with permission from[12]. © 2002 Nature Publishing Group.)

frequency, high-power amplifiers because the speed of electrons in vacuum is ~10 000 times higher than in a semiconductor. The figure of merit, P, is given by, $P = E_b^2 v^2 / R\,(2\pi f_T)^2$, where E_b is the breakdown field, v is the electron velocity, f_T is the 3 dB frequency, and R is the wave impedance. A klystron would have a CNT FE cathode with a microwave signal applied to the gate. This configuration is not possible with a conventional thermionic cathode, but the absence of heat from a CNT cold cathode allows a short cathode-gate distance to be used. Otherwise, the microwave signal must be introduced after a grid, as in a traveling wave tube, which makes the device much larger. This is another high-value niche where CNT sources are viable if they reach performance objectives.

A third possible application is as electron sources for miniature X-ray sources[13]. Here an electron beam from a CNT cathode is accelerated to strike a metal target to create X-rays. A small, high-brightness device with a pulsed electron beam allows real-time imaging. This would have to compete against existing X-ray sources and three-dimensional tomographic imaging techniques.

In each of these applications, the CNTs should operate at the highest current density. In microwave and X-ray sources, a multinanotube source is used. Here, CNTs must be spaced apart by at least twice their height, otherwise the field enhancement is reduced by screening from adjacent nanotubes.

A fourth application is in FE displays (FEDs). This application has been a huge attraction because the total display market is $50 billion per annum. The display industry is characterized by a number of very different technologies for rendering an image, unlike, say, the single technology behind Si microelectronics. This means competition can come from unexpected quarters. The display market is dominated

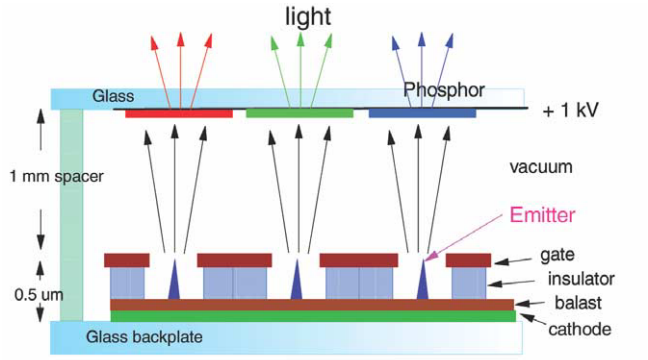

Fig. 5 A schematic of a triode-type FED. The electrons are emitted from the nanotube tips under the field induced by the gate electrode and accelerated by the anode field to strike the phosphor. An image is created as a series of pixels. The gate voltages control each image. The ballast resistors under each emitter limit and share the current between emitters to provide a more uniform image and limit breakdown.

by active matrix liquid crystal displays (AMLCDs), in which an image is formed by varying light transmission through a series of many LCD pixels. The FED is a flat panel display in which the electron beams from many nanotube electron guns are controlled to create an image on a screen of phosphor pixels (Fig. 5). Each 0.1 mm phosphor pixel is served by many electron sources, so there is large redundancy. The advantages of FEDs over LCDs are a higher video rate, higher power efficiency because it is an emissive display, and wider operating temperature range. A previous disadvantage of LCDs of poor viewing angle was corrected five years ago and is no longer an issue.

When CNTs were first pushed for FEDs in 1995-1998, it was envisaged that FEDs would first be used as 5" units in car navigation displays and as seat-back TVs in airplanes. This was a clear market niche (Fig. 6a). However, the development difficulties of FEDs have allowed AMLCDs to move much further. AMLCD technology is now sometimes called the 'silicon of displays' to emphasize its dominant, entrenched status. AMLCDs have captured the small display market (cell

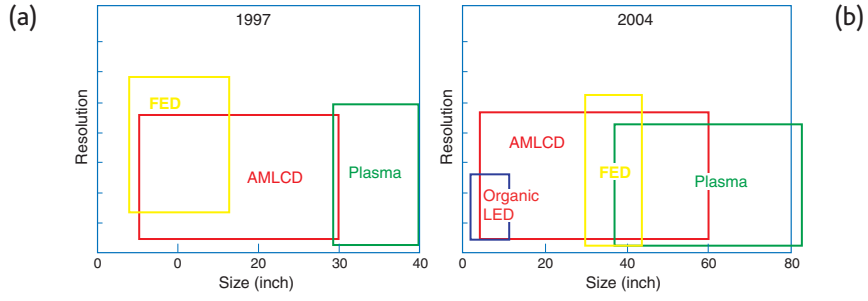

Fig. 6 Schematic showing the dominant areas of display technologies as a function of display size and resolution. In 1997, liquid crystal displays (AMLCDs) already dominated smaller area displays and plasma was set to dominate large areas, with FEDs entering at small areas. In 2004, AMLCDs span small and large area applications, plasma has taken over at larger areas, while organic light emitting diodes (OLEDs) are entering the small area display market. This leaves FEDs as a large area display market around 34".

phones, PDAs, etc.) and, in addition, organic light-emitting diodes (OLEDs) are the likely future technology for sub-5" displays. It was previously thought that AMLCDs were restricted by the conducting lines to the thin film transistors to a maximum size of the order of 30". Thus, a market gap might exist for FEDs in large displays. The development problems of FEDs led most firms to quit the area, leaving mainly Samsung[14] who, seeing the problem of LCDs over 30", redirected its effort to developing a large size 38" version.

However, Fig. 6b shows that this is region is now served by LCDs and plasma display panels (PDPs). It is now possible to make AMLCDs well over 30", and 57" prototypes have been exhibited in 2004. FEDs have a lower ultimate cost base and better power efficiency than PDPs. Nevertheless, the fact that PDPs have been marketed for five years and ever-advancing AMLCDs means that FEDs have a difficult future.

FEDs are a difficult market because there is an entrenched competitor in a commodity market. Other FE applications such as electron sources for light bulbs are equally uncommercial. The FE applications likely to succeed are those where cost is not a key issue, such as electron guns for SEMs.

Electrochemistry

Another area of potential application is electrochemistry. Graphite is well known as a stable electrode material that is not reduced or oxidized over a substantial range of potentials. The large surface area and low resistivity of CNTs makes them of great interest in electrochemistry.

At any electrode in contact with an electrolyte, there exists a dipole layer, the so-called electrochemical double layer (ECDL). Typically ~0.4 nm thick, the ECDL acts as a capacitor if the potential difference across it is less than that needed to dissociate the electrolyte (into hydrogen or oxygen in the case of water). The capacitance is given by $C = \varepsilon A/d$, where ε is the dielectric constant, A is the electrode surface area, and d is the ECDL thickness. This capacitance can be huge for cases such as porous carbon, because of the large A and small d values. This has led to the use of porous carbons such as activated carbon for the electrodes in so-called supercapacitors[15].

Supercapacitors consist of two carbon-based electrodes on a mylar backing, an ion-permeable membrane, and an electrolyte, as shown in Fig. 7. If the electrolyte is water, this restricts the voltage to 1.23 V, but higher voltages of 2.3 V are possible by using a nonaqueous electrolyte such as tetra-

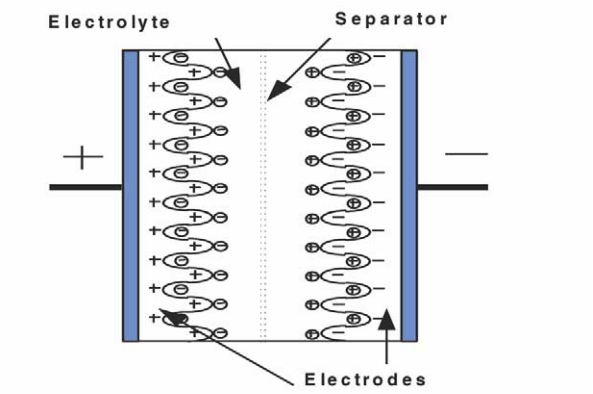

Fig. 7 A schematic of the internal workings of an ECDL supercapacitor. Two large area carbon electrodes are separated by an ion-conducting membrane, with an electrolyte of propylene carbonate, for example.

ethyl ammonium fluoroborate in propylene carbonate. 1000 F supercapacitors are typically 12 cm x 2.5 cm in size and there is already a substantial market in inverters. The electrodes are presently activated carbon, but CNTs are a possible replacement given their large and controllable surface area.

The performance of supercapacitors is judged in terms of their energy density (per unit volume) or $\frac{1}{2}CV^2$ and power density or V^2/R, where R is their series discharge resistance. The performance can be plotted on a 'Ragone plot' (Fig. 8). The energy density of supercapacitors is proportional to C and to the surface area per unit volume of carbon. SWNTs have the largest surface area to volume ratio of any carbon material, 3000 m^2/g, as all their atoms are on the surface, and should make the ultimate electrode material. In fact, the

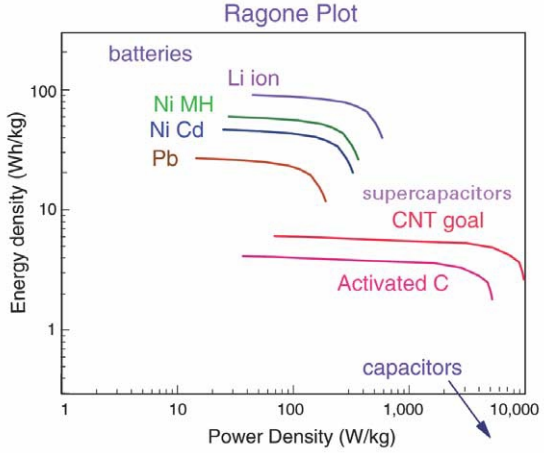

Fig. 8 The power density versus energy density plot distinguishes various electricity storage systems. Batteries are high energy density but low power density, whereas normal capacitors are low energy density but high power density. Li^+ batteries have the highest energy density of any battery. Supercapacitors have a high energy density and high power density, and are intermediate between normal capacitors and batteries.

surface area and energy density of supercapacitors made from activated carbon is already near their theoretical maximum. The advantage of CNTs is that they have a much lower resistance than activated carbon, which could greatly increase their power density. The limiting factor is contacting CNTs to the electrode polymer backing, the ability to do this at low temperatures, and at a low cost, as activated carbon is very cheap.

Li batteries use the transfer of Li^+ between two electrode materials to create the battery with the highest energy density of any existing type. Carbon nanofibers are presently being used to increase the conductivity of porous carbon electrodes and thus improve their power density[16].

The large surface area and tubular structure of CNTs suggest that capillarity effects are important. Thus, CNTs could be very useful for the storage of hydrogen, a key aspect of the clean energy economy. A storage capacity of 10%, if readily cyclable, would be an extremely valuable property compared to other systems. Initial studies suggested a storage capacity of 60% by weight, but more realistic estimates were 8-10 wt% based on extrapolations to 100% nanotube content. However, it turns out that the hydrogen storage capacity of CNTs is less than 1%[17,18]. In order to allow access of hydrogen to the nanotube ends, the samples are subjected to intense ultrasonic treatment to break them up, but this deposits Ti from the sonic horn, and it is the Ti that is absorbing some hydrogen[17]. Thus, the consensus is now that CNTs are not a useful hydrogen storage medium. This applies to all forms of nanostructured carbon.

Traditionally, CNTs are grown by CVD at over 7000°C. Hofmann *et al.*[19] recently showed that low temperature growth of nanotubes and nanofibers on plastic is possible using plasma enhanced CVD. It is also shown that the required catalysts could be delivered to the surface as organo-metallic precursor liquids[20]. This opens up a large range of possibilities for nanotube growth on complex shapes, on unusual low temperature substrates such as polymers, cloths, and foams, and in printable patterns. It may even be possible ultimately to grow CNTs as electrode materials on polymer membranes for fuel cells[21].

Electronics

CNTs can carry the highest current density of any metal, 10^9-10^{10} A/cm^2, over 1000 times that for Cu, before failing as a result of electromigration (self-electrolysis). It is well known that feature sizes in Si integrated circuits are continually reducing. This forces the interconnects between each transistor to carry ever larger current densities. Infineon[22] has recently shown how the vertical interconnects known as vias could be replaced by CNTs and thus satisfy this requirement. This application is relatively easy, particularly as it requires vertical nanotube growth. Multiple CNTs in parallel can be used to lower the overall resistance (of any Schottky barrier). However, the greatest demand is not for vias but for horizontal interconnects. This application is much more difficult to satisfy, as horizontally-directed nanotube growth can be done, but not with high reliability and yield.

CNTs have also been made into field-effect transistors (FETs). The first examples were made by dispersing SWNTs on SiO_2-covered Si wafers and then making contacts. The Si substrate is used as the bottom gate electrode. This is not suitable for a real device, as the gate would be common to all FETs on the wafer. The second generation FET requires a separate 'top gate' over each individual nanotube. Wind *et al.*[23] have achieved FETs with very good performance figures. Javey *et al.*[24] subsequently used a ZrO_2 gate oxide to achieve the best gate turn-on performance of any nanotube device. In comparing nanotube FETs with Si FETs, Wind *et al.*[23] normalized the mutual conductance to the channel width (μS/μm), as is conventional in Si devices, and took the nanotube diameter as the width of the nanotube channel. The resulting figure of merit is 20 times better than existing laboratory complementary metal oxide semiconductor (CMOS) devices. Thus, CNT transistors have extremely good limiting performance over Si. However, this is somewhat misleading. The economics of Si devices is driven by the ability to place ever more transistors on a wafer – as transistors get smaller, so they get cheaper. Higher speed is a nice byproduct. However, a nanotube FET occupies a huge wafer area compared to its diameter because of its connections, so the 'economic' figure of merit is actually quite poor. Nanotube FETs can only be considered when they have an economic device architecture. One possibility, which takes up much less space, is the vertical CNT FET concept of Infineon[22], Fig 9. It is expected that Si CMOS technology will continue in its present form until at least 2016.

A significant problem for electronic applications is that the band gap of a SWNT depends on its chirality. The cohesive energy depends only weakly on diameter and very weakly on

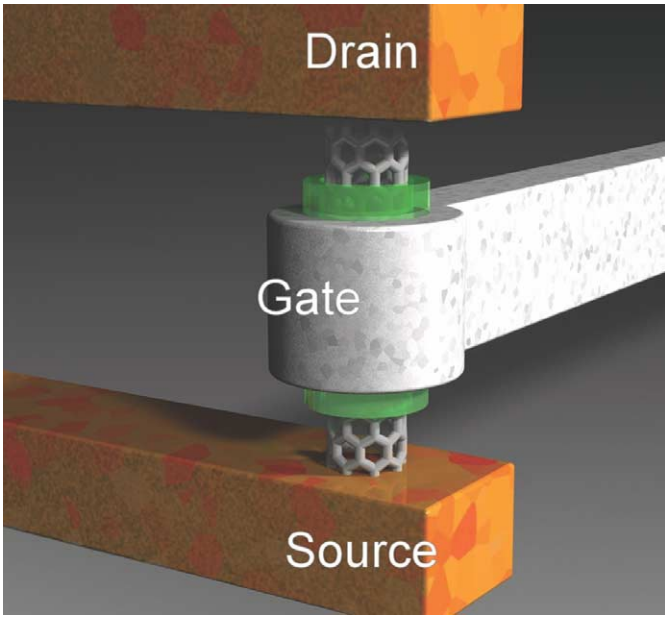

Fig. 9 Infineon's vertical CNT FET concept[22]. A nanotube is grown on the source contact (bottom), a top drain contact is put on, a gate insulator (green) is grown around the CNT by atomic layer deposition, and a wrap-around gate electrode is applied. (Reprinted with permission from[22]. © Elsevier Ltd.)

chirality, so that a mixture will contain both metallic and semiconducting nanotubes. This is a huge disadvantage in electronics. It is necessary to be able to grow a specific type of tube at a defined position in a defined direction with near 100% yield. Control of position and direction is achievable now. It is hoped to be able to gain some control of chirality in the CVD process by the design of the catalyst[25]. At present, in FETs, it is possible to remove metallic tubes by gate biasing all the semiconducting tubes off, and then passing a large current through the remaining metallic CNTs to burn them out. This leaves only the semiconducting tubes in the device. However, the overall process no longer has 100% yield and is not so useful for manufacturing.

CNTs show a large nonlinear absorption of light[26]. This arises because of their one-dimensional band structure with singularities in the electronic density of states. Optical absorption creates electron-hole pairs, but these rapidly fill up the first bands and are then forced to occupy the next bands at higher energy. This creates a nonlinear absorption coefficient. The interesting aspect is that random mixtures of CNTs contain some with band gap singularities covering the whole optical spectrum, so that selection is not necessary. In addition, excited electrons decay rapidly in picoseconds. Thus fast saturable absorber, limiter, and optical switches are possible, without requiring excessive processing of the CNTs.

Conclusion

In summary, the enthusiasm for work in CNTs is justified by their unique properties and richness. But the applications are not as easy as the literature can make out. A number of possible applications are pointed out here, but one of the most quoted, FEDs, will have much difficulty reaching the market. It is suggested that the drive for applications should also encompass less perfect forms of carbon nanofibers as well as the perfect SWNT. MT

Acknowledgments

The author is grateful for conversations with S. Roth and A. H. Windle, and to EPSRC, EC, and CMI for funding.

REFERENCES

1. Baughman, R. H., *et al., Science* (2002) **297**, 787
2. de Heer, W. A., *MRS Bull.* (2004) **29**, 281
3. Haddon, R. C., *et al., MRS Bull.* (2004) **29**, 252
4. Sandler, J. K. W., *et al., Polymer* (2003) **44**, 5893
5. Park, C., *et al., Chem. Phys. Lett.* (2002) **364**, 303; www.eikos.com
6. Cadek, M., *et al., Nano Lett.* (2004) **4**, 353
7. Vigolo, B., *et al., Science* (2000) **290**, 1331
8. Dalton, A. B., *et al., Nature* (2003) **423**, 703
9. Davis, V. A., *et al., Macromolecules* (2004) **37**, 154; Zhou, W., *et al., J. Appl. Phys.* (2004) **95**, 649
10. Li, Y.-L., *et al., Science* (2004) **304**, 276
11. Milne, W. I., *et al., J. Mater. Chem.* (2004) **14**, 933
12. de Jonge, N., *et al., Nature* (2002) **420**, 393
13. Yue, G. Z., *et al., Appl. Phys. Lett.* (2000) **81**, 355; www.xintek.com
14. Choi, W. B., *et al., Appl. Phys. Lett.* (1999) **75**, 3129
15. Emmenegger, Ch., *et al., J. Power Sources* (2003) **124**, 321
16. Endo, M., *et al., Carbon* (2001) **39**, 1287
17. Hirscher, M., *et al., J. Alloys Compd.* (2003) **356-357**, 433
18. Kajiura, H., *et al., Appl. Phys. Lett.* (2003) **82**, 1105
19. Hofmann, S., *et al., Appl. Phys. Lett.* (2003) **83**, 4661
20. Kleinsorge, B., *et al., Chem. Commun.* (2004) (12), 1416
21. Wang, C., *et al., Nano Lett.* (2004) **4**, 345
22. Graham, A. P., *et al., Diamond Relat. Mater.* (2004) **13**, 1296
23. Wind, S. J., *et al., Appl. Phys. Lett.* (2002) **80**, 3817; Avouris, P., *et al., Proc. IEEE* (2003) **91**, 1772
24. Javey, A., *et al., Nat. Mater.* (2002) **1**, 241; *Nano Lett.* (2004) **4**, 447
25. Bachilo, S. M., *et al., J. Am. Chem. Soc.* (2003) **125**, 11186; Li, Y., *et al., Nano Lett.* (2004) **4**, 317
26. Chen, Y. C., *et al., Appl. Phys. Lett.* (2002) **81**, 975