nº 13

September 2008
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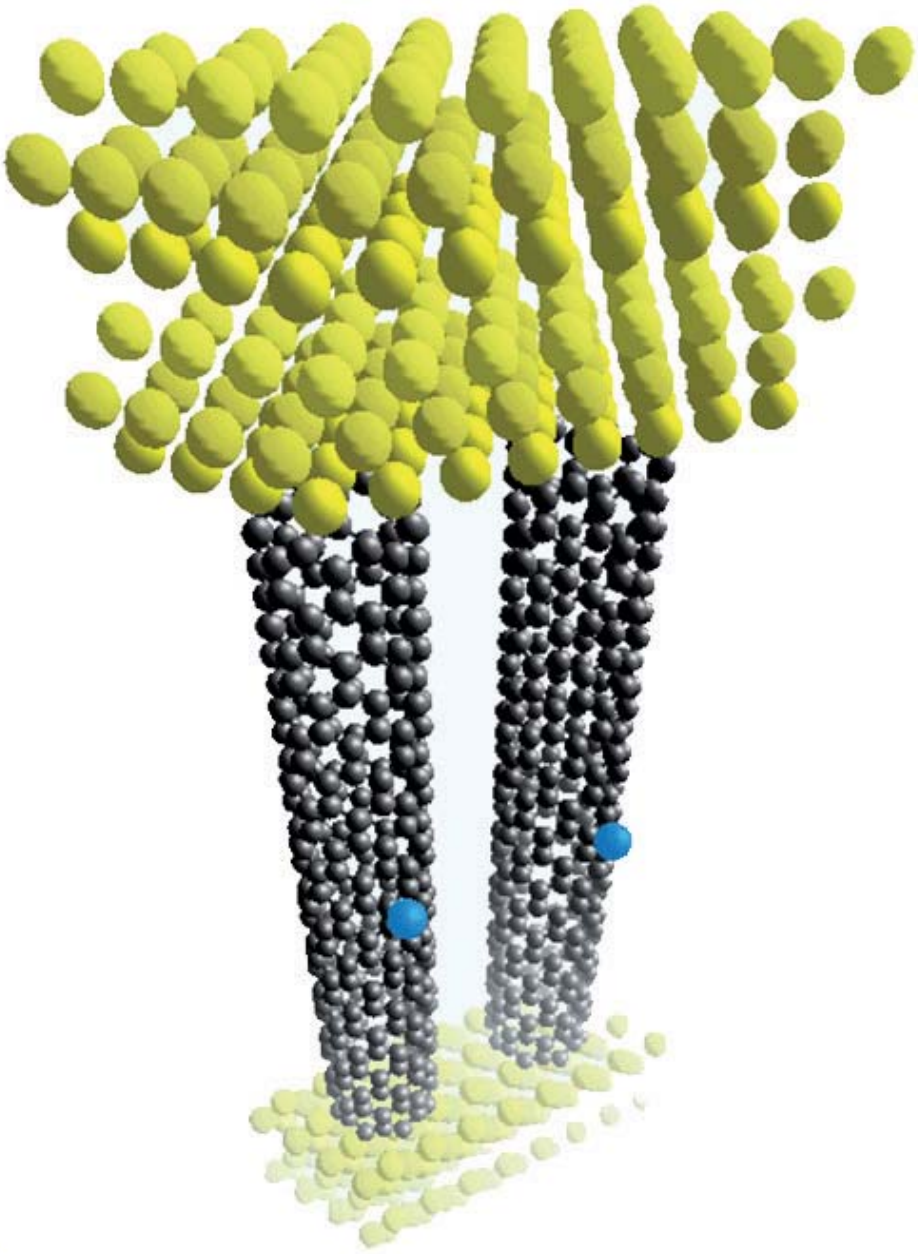
nano newsletter



nanoICT coordination action

NanoICT Position Papers

- **Carbon Nanotubes**
- **Current Status of Modelling for Nanoscale Information Processing and Storage Devices**

CIC nanoGUNE

nanoscience cooperative research center

Nanomagnetism

Nanodevices

Nanooptics

Nanobiotechnology

Self-assembly

Nanoscale imaging

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E nano newsletter

Dear Readers:

This E-Nano newsletter issue contains two position papers from the EU funded nanoICT Coordination Action Working Group coordinators covering the following areas, currently very active worldwide: carbon nanotubes and modelling at the nanoscale.
The first position paper summarizes state-of-the art CNTs dependent on the nature of the desired end-structure but also possible electrical, electronic and photonic applications of carbon nanotubes.
The second position paper provides an analysis of the current status of modelling for nanoscale information processing and storage devices in Europe and a comparison with that in the rest of the world.

Expected impact of initiatives such as these nanoICT contributions to the E-Nano Newsletter is to enhance visibility, communication and networking between specialists in the field, facilitate rapid information flow, look for areas of common ground between different technologies and therefore shape and consolidate the European research community.
In addition, these documents will provide focus and accelerate progress in identified R&D directions and priorities for the "nanoscale ICT devices and systems" FET program (Framework Programmes 7 and 8) and guide public research institutions, keeping Europe at the forefront in research.
NanoICT position papers aim also to be a valid source of guidance for the semiconductor industry (roadmapping), providing the latest developments in the field of emerging nanoelectronic devices that appear promising for future take up by the industry.

We would like to thank all the authors who contributed to this issue as well as the European Commission for the financial support (project nanoICT nº216165).

Dr. Antonio Correia
E nano newsletter Editor
Phantoms Foundation

Cover picture: Scheme of a carbon nanotubes / metal junction. By courtesy of Xavier Blase (CNRS-Institut Néel) and Stephan Roche (CEA, INAC)

Editorial Information

Research - NanoICT Position Papers

EDITORIAL INFORMATION

E nano newsletter nº13 September 2008
Published by **Phantoms Foundation** (Spain)

Editor: Dr. Antonio Correia (Phantoms Foundation)
antonio@phantomsnet.net

Assistant Editors: Jose Luis Roldán and María Teresa Fernández (Phantoms Foundation)

1500 copies of this issue have been printed

Full color newsletter available at:
http://www.phantomsnet.net/Foundation/newsletters.php

For any question please contact the editor at:
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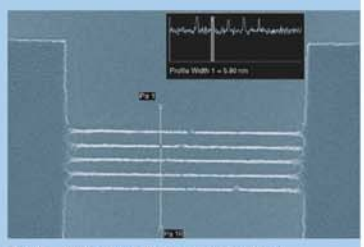
Depósito Legal / Spanish Legal Deposit: M-43078-2005

NANOTECHNOLOGY

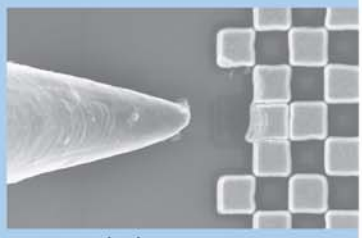
Raith

INNOVATIVE SOLUTIONS FOR NANOFABRICATION AND SEMICONDUCTOR NAVIGATION

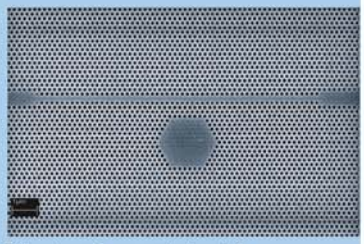


Sub 10 nm lithography

E-beam deposition



Nano Sokoban



Photonic crystal with proximity effect correction

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Carbon Nanotubes

W.I. Milne[1], M. Mann[1], J. Dijon[2], P. Bachmann[3], J. McLaughlin[4], J. Robertson[1], K.B.K. Teo[5], A. Lewalter[3], M. de Souza[6], P. Boggild[7], A Briggs[8], K. Bo Mogensen[7], J.-C. P. Gabriel[9], S. Roche[10] and R. Baptist[11]

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KeyWords
Growth
Carbon nanotubes, multiwall, singlewall, nanofibres (all the words in a and the subtopics), cap structure, catalysts, adhesion, mechanism, modelling
Post-growth modification
Doping & functionalization, dispersion and separation, purification, annealing, cap opening/closing, graphitization
Properties/Characterization
Defects, electron transport, phonons, thermal properties/conductivity, wetting, stiction, friction, mechanical, chemical properties, optical, toxicity, structural properties, contacts
Electronic applications
Field emission (X-ray, Microwave, FEDs, Ionization, Electron microscopy), interconnects, vias, diodes, thin-film transistors, thin-film electrodes, network transistors, single CNT transistors, thermal management, memory
Optical applications
Absorbers, microlenses in LCs, optical antennae, lighting
Electromechanical applications
NEMS (resonators), sensors, nanofluidics, bio-medical
Energy applications
Fuel cells, supercapacitors, batteries, solar cells
Blue sky
Spintronics, quantum computing, SET, ballistic transport

1. Introduction

There has been extensive research into the properties, synthesis and possible applications of carbon nanotubes (CNTs) since they came to prominence following the Iijima paper **[1]** of 1991 **[2]**. Carbon nanotubes are composed of sp^2 covalently-bonded carbon in which graphene walls are rolled up cylindrically to form tubes. The ends can either be left open, which is an unstable configuration due to incomplete bonding, they can be bonded to a secondary surface, not necessarily made of carbon, or they can be capped by a hemisphere of sp^2 carbon, with a fullerene-like structure **[3]**. In terms of electrical properties, single-walled CNTs can be either semiconducting or metallic and this depends upon the way in which they roll up, as illustrated in **Figure 1**.

Multi-walled CNTs are non-semiconducting (i.e. semi-metallic like graphite) in nature. Their diameters range from 2 to 500 nm, and their lengths range from 50 nm to a few mm. Multi-walled CNTs contain several concentric, coaxial graphene cylinders with interlayer spacings of ~0.34 nm **[5]**. This is slightly larger than the single crystal graphite spacing which is 0.335 nm. Studies have shown that the inter-shell spacing can range from 0.34 to 0.39 nm, where the inter-shell spacing decreases with increasing CNT diameter with a pronounced effect in smaller diameter CNTs (such as those smaller than 15 nm) as a result of the high curvature in the graphene sheet **[6,7]**. As each cylinder has a different radius, it is impossible to line the carbon atoms up within the sheets as they do in crystalline graphite. Therefore, multi-walled CNTs tend to exhibit properties of turbostratic graphite in which the layers are uncorrelated. For instance, in highly crystallized multi-walled CNTs, it has been shown that if contacted externally, electric current is generally conducted through only the outermost shell **[8]**, though Fujitsu have been able to contact the inner walls with resistances of 0.7 kΩ per multi-walled CNT **[9]**.

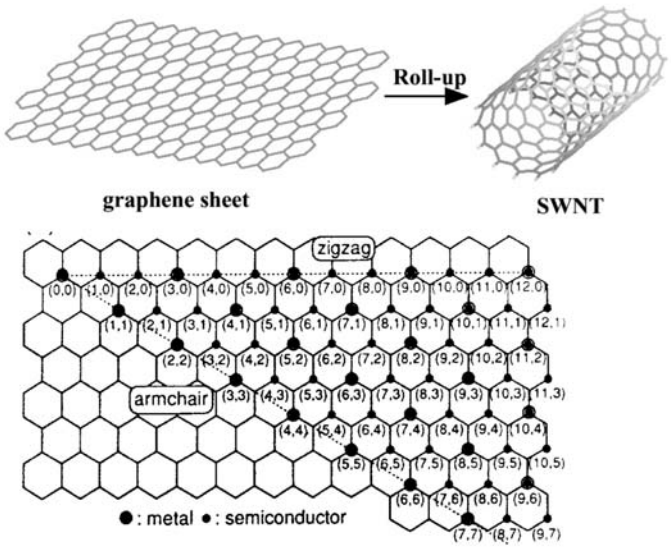

Figure 1: *(top) A graphene sheet rolled up to obtain a single-walled CNT. (bottom) The map shows the different single-walled CNT configurations possible. Were the graphene sheet to roll up in such a way that the atom at (0,0) would also be the atom at (6,6), then the CNT would be metallic. Likewise, if the CNT rolled up so that the atom at (0,0) was also the atom at (6,5), the CNT would be semi-conducting. The small circles denote semiconducting CNTs and the large circles denote non-semiconducting CNTs. Two thirds of CNTs are semi-conducting and one third metallic **[4]**.*

This position paper summarizes state-of-the-art CNTs dependent on the nature of the desired end-structure. It also summarizes possible electrical, electronic and photonic applications of carbon nanotubes (excluding bulk material composite applications).

2. Catalyst preparation

The catalyst metals most commonly used for nanotube growth are Fe, Ni and Co **[10]**. There are several routes to the production of catalyst nanoparticles, the two main methods being the wet catalyst method and the coalescence of thin catalyst films.

The wet catalyst method involves the deposition of metal nitrate/bicarbonate colloids onto a surface (shown in **figure 2a page 6**). On drying, the salt in the solution crystallizes to form small islands of the metal salt. The salt is reduced to a metal oxide by heating or calcinations and

the oxide is then reduced by H_2 and/or thermal decomposition resulting in the formation of metallic catalyst islands from which the CNTs grow **[11,12]**. The wet colloid method produces an uneven distribution of catalyst particles, but does have a significant cost advantage over vacuum techniques such as sputtering and evaporation.
The most commonly used form of catalyst preparation for devices is coalescence (shown in **figure 2c**). A thin film (of thickness typically less than 10 nm) of Fe, Co or Ni is deposited onto a substrate by evaporation, sputter coating or electroplating. Upon heating, the thin film breaks up (known as dewetting) to form nanoislands as a result of increased surface mobility and the strong cohesive forces between the metal atoms **[17,18]**. CNT growth then nucleates from these nanoislands. When grown on silicon and polycrystalline substrates, barrier layers such as ITO, SiO_2 and TiN are required to prevent diffusion of catalyst into the substrate **[19]**.

2(a) Catalyst for SWNT growth

CNT growth is affected by the catalyst and thus different catalysts are required to produce different CNT structures. Metal underlayers also affect resultant CNT growth **[20]**. Typical catalysts favoured for SWNT growth are an Al/Fe/Mo triple layer 10 nm, 1 nm and 0.1 nm thick respectively with the Mo layer on top **[21]**. This produces dense, vertically-aligned, SWNTs grown attached to the substrate. For epitaxial growth on quartz, only a thin layer of Fe is required. Resasco **[22]** uses a Co catalyst in the patented CoMoCat process on a silica substrate with a

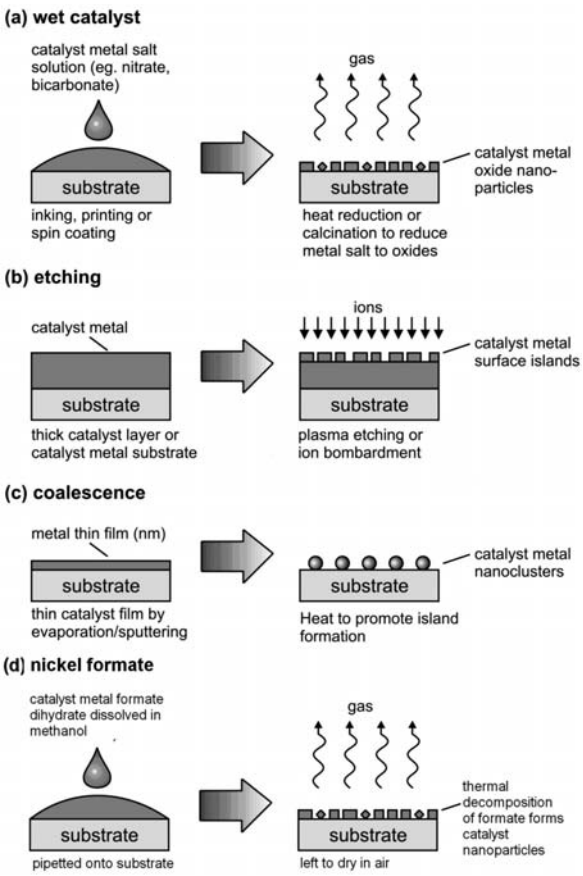

Figure 2**: Methods of producing nano-sized catalysts for nanotube growth **[13-16].

high purity, low diameter distribution of SWNTs as a result. Others use Ni as a SWNT catalyst. The use of ferritin as the catalyst reported by Dai **[23]** and Rogers **[24]**, or of polyoxometallates **[25]** enables tighter control of the catalyst particle size and thus the CNT diameter.

For electronic applications, when the substrate is to play an insulating role, particular attention needs to be paid to the quality of the substrate as well as to the thermal treatment of the wafer in order to minimize the diffusion of catalyst into the substrate and to keep leakage current low. Dubosc et al. **[26]** have demonstrated the use of electrochemical deposition of Ni catalyst with the resultant CNT growth indistinguishable from catalyst deposited by other methods.

2(b) Catalyst for MWNTs

Catalyst thicknesses required for MWNT growth tend to be much greater than that for SWNT growth because catalyst thickness correlates with CNT diameter. Ajayan **[27]** reported the growth of MWNTs using ferrocene and xylene by CVD with the Fe contained within the ferrocene as the catalyst. This produces the best MWNTs if no patterning is required.

For surface-attached growth, Ni, Fe and Co are the most commonly used catalysts, but the quality of the resultant MWNTs depends on the research group and there is little to discriminate between them for CVD processes. However, for plasma-enhanced CVD (PE-CVD), most groups tend to favour Ni catalyst since they produce the straightest MWNTs with the greatest control over growth rate.

2(c) Placement/patterning of catalyst

For device-based applications it is desirable to position the catalyst on the substrate where CNTs are required to grow. The most desirable positioning method is by lithographical means, where optical or electron beam lithography exposes spin-coated resist followed by development, catalyst deposition and lift-off, which leaves behind catalyst deposited on developed areas. CNTs can then be grown in-situ where desired for device fabrication. This has been done most effectively by Teo et al. **[28]**, where single, vertically aligned MWNTs were grown single Ni catalyst dots deposited on silicon (as shown in **figure 3**). Many others have used this process to demonstrate positional growth of CNTs **[29,30]**. Very large scale integration of SWNTs at the 100 mm wafer level were reported in 2001 using deep UV lithography **[31]** and using a more standard available lithography process in 2003 **[32]**. Porous substances such as alumina have been used to grow CNTs with catalyst deposited in the pores. The resultant CNTs grow with the support of the pore walls that act as a template for growth **[34]**. Pores can also either be etched into silicon **[35]** or milled with a focused ion beam **[36]**.

Catalyst can also be positioned by imprinting, where catalyst deposited on templated silicon is pressed onto a substrate **[37]**. Laser interferometry can also be used to position catalyst but only for array-like structures and with a spacing no greater than the size of the dot **[38]**. The use of nanosphere lithography for self-assembly of nanotube arrays have also been demonstrated by Ren et al **[39]**.

European Position: Bernier and Loiseau optimised catalysts for arc production.

The USA with CoMoCat and HipCo as well as Hata in Japan with supergrowth have dominated the optimisation of catalysts for mass production CVD growth. Europe has made significant contributions to low T growth as well as controlled, patterning for multi-walled CNT growth.

3. Growth

The quality of grown carbon nanotubes is subjective, since their quality depends on the structures required. Some applications require high purity and crystallinity; others require tight dimensional control, whilst others might require high packing densities and/or alignment. Consequently, the state of the art depends on the type of structure required. The latest research indicates that, contrary to prior understanding, carbon nanotubes do not follow a vapour liquid solid (VLS) growth model, but rather a vapour solid solid (VSS) model. Hofmann et al. **[40]** have observed growth of both single and multi-walled carbon nanotubes in-situ in an environmental electron microscope. In all cases, the catalyst particle remains solid, with crystalline structure clearly observed. This indicates that growth primarily occurs through surface diffusion rather than the bulk diffusion proposed by Baker **[10]**.

3(a) Single-walled CNTs

(i) State of the art for bulk single-walled growth

The highest quality single-walled CNTs (in terms of defects) are produced by laser ablation, a process developed by Smalley **[41]**, in which the diameter of the grown CNT can be controlled by temperature. A composite graphite target made of Ni and Co produces the best CNTs with a yield of 70%. This is, however, the most expensive common production process.

The highest purity CNTs nucleate from catalysts in a fluidized bed and are currently sold by Thomas Swan **[42]**. The process produces high-quality CNTs, inexpensively in large quantities **[43]**. In Windle's group CNTs are also grown in a continuous flow furnace. The nanotubes are created rapidly by injecting ethanol and ferrocene into a furnace at 1,200 ºC. An aerogel then starts to stick to the cooler wall in the furnace to form fibres. A spindle then winds the aerogel fibres into a thread, at several centimetres per second. The result is an extremely fine, black thread consisting of aligned CNTs **[44]**. Nanocyl also produce purified single-walled nanotubes **[45]** .

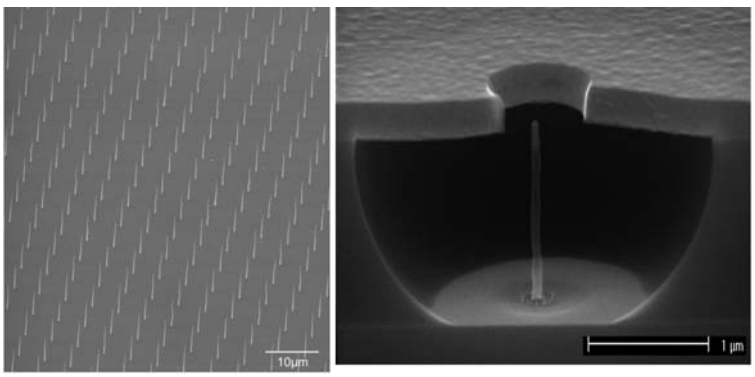

Figure 3: (a) *Array of MWCNTs of height 5 µm and separation 5 µm* ***[28]*** ***(b)*** *Individual MWCNT grown in a micropore etched into SiO_2 using a self alignment method* ***[33]****.*

(ii) Vertically aligned single-walled CNTs

Water/oxygen/ethanol assisted growth provides amongst the longest vertically-aligned CNT mats produced and has been carried out by a number of groups including Maruyama and Dai **[46]**, but it is Hata who can produce the longest CNTs with a carbon purity of 99.98%. The process uses ethylene as the carbon source gas with a small amount of water vapour incorporated into a hydrogen flow process. However, there is little control over growth rate because the mechanism is not clearly understood **[47]**.

(iii) Horizontally aligned single-walled CNTs

Horizontally-aligned SWNTs have been grown on epitaxial surfaces such as sapphire and quartz with varying densities. The growing CNTs follow the crystal planes with a great degree of alignment. The process is standard CVD but the substrate needs to be annealed for surface reconstruction before growth. Among the best, Tsuji's group have grown on sapphire **[48]** and the Rogers group, who have grown on quartz **[24]** (**figure 4**).

Dai et al. have grown horizontally-aligned CNTs with the use of electric fields (figure 4). However, the fields only align metallic CNTs. Semiconducting CNTs are not affected by the field. Gas flows have also been used to control the horizontal alignment of SWNTs, but the flow needs to be very high and the degree of alignment is poor compared with methods mentioned above **[49]**. Most recently Hata has used a vertical alignment and then by dipping in alcohol the tubes get aligned in plane by capillary forces when he pulls up the substrate from the liquid **[50]**.

(iv) Challenges for SWNTs

The key challenges with SWNTs concern control of chirality during growth. For applications such as transistors, all grown CNTs need to be semiconducting (and preferably of identical chirality) whilst for interconnects, all CNTs need to be metallic. Control of diameter is related to this issue.

The possibility of using very long CNTs cut into many pieces has been discussed as a possibility for chirality control in CNT devices, by using the pieces to act as catalysts for identical tubes. However, the chirality of some CNTs has been found to change along long CNTs (being caused by structural defects **[51]**). Returning to interconnects, a higher density (of ~ 10^{13} tubes/cm^{-3}) than that achieved so far is required if it is to replace copper.

The yield of SWNTs grown with templates is very low and must be solved if it is to be seriously considered as a method for growing SWNTs. Also, for SWNT growth to be combined with CMOS, the temperature needs to be reduced to ~ 400 ºC.

To a certain extent the chirality problem has been overcome by using devices based on random network of nanotubes instead. This approach was first brought to light by Snow and co-workers in 2003 **[52]** although it was patented by Nanomix in June 2002 **[53]**.

3(b) Multi-walled CNTs

Though Endo started the injection process, for bulk growth, the best CNTs are again grown by Thomas Swan (as a result of rigorous qualification by Raman and TEM) and Windle's group in Cambridge, though Hyperion **[54]** are the leading suppliers of nanofibres using a similar process to Thomas Swan. So-called Endo-fibres 150 nm in diameter can also be purchased from Showa Denko. Bayer produce narrower "Baytubes" 5-20 nm in diameter **[55]**, but these are impure and need to be purified.

(i) Vertically aligned (including crowding)

There is typically no alignment of CNTs with the CVD process. The grown CNTs are often randomly orientated and resemble spaghetti. However, under certain reaction conditions, even in the absence of a plasma, closely spaced nanotubes will maintain a vertical growth direction resulting in a dense array of tubes resembling a carpet or forest. For this, the ferrocene-catalyzed growth of Ajayan produces MWNTs with the best control over diameter, height and with the greatest degree of alignment **[56]**.

In plasma-enhanced chemical vapour deposition (PECVD), the applied plasma creates a sheath above the substrate in which an electric field perpendicular to the substrate is induced. The deposition gases are broken down by a combination of heat and plasma and vertically aligned CNTs grow following the induced field. For vertically-aligned arrays of single or multiple MWNTs, Teo et al. **[57]** are able to control diameter (σ = ±4.1%) and height (σ = ±6.3%) by placing the catalyst by lithographical means and by positioning the substrate on a driven electrode and within the plasma sheath during a PECVD process.

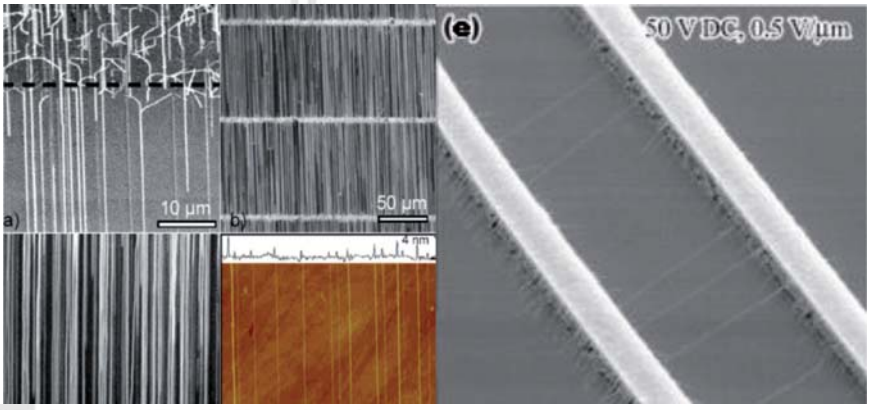

Figure 4: (a-d) *CNTs grown along quartz crystal planes by the Rogers group* ***[24]****. Reprinted with permission from Coskun Kocabas, Moonsub Shim, and John A. Rogers. J. Am. Chem. Soc. 2006, 128, 4540-4541. Copyright (2006) Americal Chemical Society,* ***(e)*** *Horizontally aligned CNTs grown by Dai's group using field to align the CNTs* ***[49]****. Reused with permission from Yuegang Zhang, Applied Physics Letters, 79, 3155 (2001). Copyright 2001, American Institute of Physics.*

Both CVD and PECVD hold a number of advantages over other synthesis methods. For tip growth, nanotube length increases with deposition pressure, and linearly with deposition time up to certain lengths **[58]**. The diameter is controlled by the thickness of the catalyst deposited and the position of the CNTs can be controlled by controlling the catalyst position. For instance, lithographical techniques can be employed to deposit catalyst dots to control the position of grown CNTs that can be employed in field emission devices **[28]**. This results in much more control over the dimensions of the CNTs and removes the need to purify and separate CNTs grown

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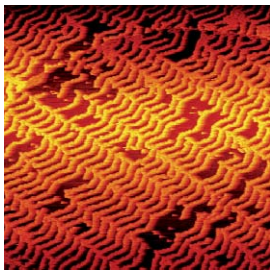
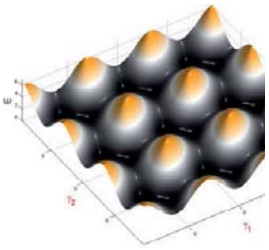
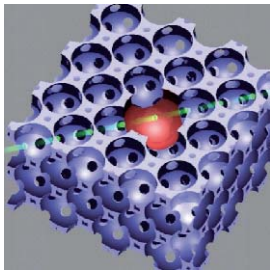
Molecular Nanoscience
Array of PCBM molecules on Au (III)

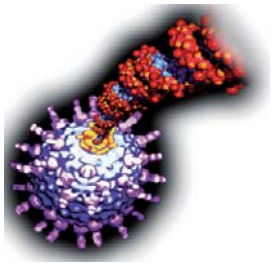




Nanoscience at very low temperatures
Potential landscape of a superconducting qubits

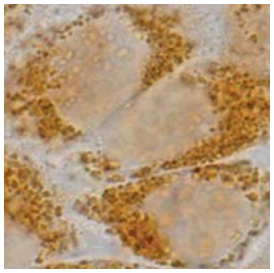
Nanoelectronics Nanophotonics
Photonic crystals

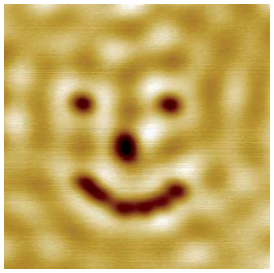




Biomachines and manipulation of biomolecules
Biological molecular motors

Nanomagnetism and the biomedical application of magnetic nanoparticles
Magnetic nanoparticles inside tumoral cells

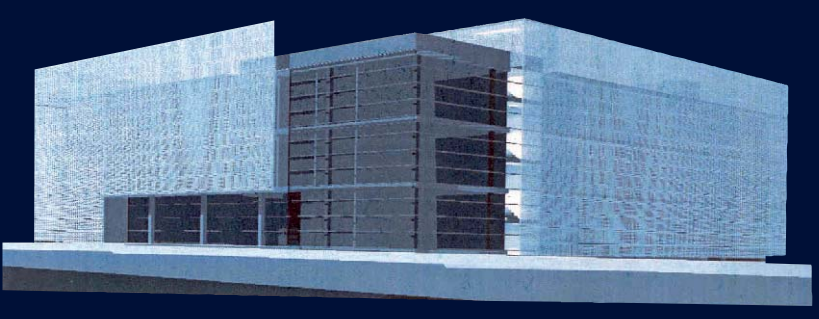




Nanofabrication and advanced instrumentation
Molecular smile assembled with STM

IMDEA- Nanociencia is a private Foundation created by joint initiative of the regional Government of Madrid and the Ministry of Education of the Government of Spain in February 2007 to manage a new research Institute in Nanoscience and Nanotechnology (IMDEA-Nanociencia), which is located in the campus of the Universidad Autónoma de Madrid, 12 km away from Madrid downtown with an excellent communication by public transportation with the Madrid-Barajas airport (25-30 min) and Madrid downtown (15-20 m).

The Institute offers attractive opportunities to develop a career in science at various levels from Ph.D. students to senior staff positions.



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by other methods.

(ii) Challenges for multi-walled CNTs

Some of the challenges for MWNT growth are identical to that of SWNT growth. Growth temperature needs to be reduced if CNTs are to be employed in CMOS. Raman spectra of MWNTs grown by CVD/PECVD at low temperatures show them to be highly defective. Post-annealing processes can increase graphitization, but these are typically at temperatures much higher than circuitry can withstand. There is also the question of contact resistance that is often quite high and variable. This needs to be addressed with still further improvements on dimensional control.

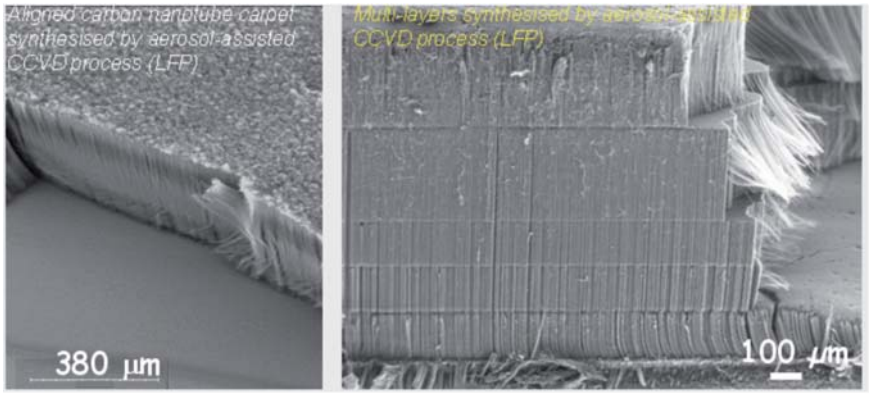

Figure 6: *images showing the growth of CNT carpets grown by an aerosol-assisted process.*

European Position: Europe led the way with research in arc deposition but commercialisation was limited. More recently Nanocyl **[45]**, Thomas Swan **[42]**, and Arkema **[59]** and Bayer **[55]** have made significant contributions to up scaling CVD and recently AIXTRON **[60]** and Oxford Instruments **[61]** have begun to provide large area PECVD capability. The leading universities in Europe will include Cambridge Univ., Dresden and EPFL. Growth of MWNTs on large wafers (200mm) is now routinely done at various locations for microelectronics applications (see for example, images of CVD reactors at CEA-Grenoble in **figure 5**). The aerosol-assisted CCVD process allowing the production of carpets of aligned nanotubes is produced at CEA-Saclay in the group of Martine Mayne (and can be seen in **figure 6**).

4. Post growth modification

CVD generally produces the poorest quality CNTs with the greatest number of defects. When the growth process ends, power is shutdown and the substrate allowed to cool, but this often results in the deposition of amorphous carbon around the CNT. This can be removed either by hydrogen or ammonia plasma, or a rapid thermal annealing process that also increases the graphitization, conductivity and contact of the CNT **[62]**.

For CNTs grown by arc discharge and laser, various techniques have been employed to purify, given the best samples are only 70% pure (using laser ablation), with the remainder made up of amorphous carbon. CNTs are first dispersed by sonification **[63]**. The gas-phase method developed at the NASA Glenn Research Center to purify gramscale quantities of single-wall CNTs uses a modification of a gas-phase purification technique reported by Smalley and others **[64]**, by combining high-temperature oxidations and repeated extractions with nitric and hydrochloric acid. This procedure significantly reduces the amount of impurities such as residual catalyst, and non-nanotube forms of carbon within the CNTs, increasing their stability significantly. Once the CNTs are separated, the use of a centrifuge enables the isolation of certain chiralities of SWNTs, particularly (6,5) and (7,5) as shown by Hersam's group at North Western University **[65]**. This method seems to be the way forward for scalable chirality separation.

European Position: The US lead the way in novel techniques based on density differentiation but in Europe, Krupke, Knappes and co-workers at Karlsruhe pioneered the dielectrophoresis method.

5. Doping

Conventional doping by substitution of external impurity atoms in a semiconductor is unsuited for CNTs, since the presence of an external atom breaks the ideal symmetry properties in the CNT. Theoretically, substitutional doping by nitrogen (n-type) and boron (p-type) has been widely examined **[66-71]**. Adsorption of gases such as H_2, O_2, H_2O, NH_3, NO_2 have been reported in **[72-75]**.

More appropriate doping strategies which conserve the mean free path of the charge carriers involve physisorption of alkali metal atoms **[76-91]**. Alkali-metal atoms located outside or inside the tube act as donor impurities **[92,93]** while halogen atoms, molecules, or chains act as acceptors **[76,84,94,95]**. Fullerenes or metallofullerenes, encapsulated inside CNTs, allow good structural stability and have been used to tune the band gap and/or Fermi level of the host tube **[96-99]**.

"Doping" by physisorption of molecules, lies at the heart of a growing field of chemical sensors, but there are issues with stability.

European Position: In Europe Maurizio Prato's group in Trieste is the most successful in this area.

Figure 5*: Dense forest of Small diameter MWCNT from left to right:* ***a)*** *Patterned layer on a 200mm layer* ***b)*** *50µm high forest on conductive layer of TiN* ***c)*** *close view of the material with individual CNT making bundles of 60nm of diameter (courtesy of CEA-LITEN).*

6. Oxidation/Functionalization

CNTs can be oxidized by various means. Refluxing in acids such as nitric or sulphuric, or with potassium manganate adds functional groups to the CNTs that alter the wetting angle. The caps of CNTs can be opened either by physical means or more commonly, by chemical means, in which the cap is opened by heating CNTs in the presence of a oxidizing

gas such as oxygen or carbon dioxide.
Open-capped CNTs, unless functionalized, are unstable structures because of dangling bonds. Cap closing of open-capped structures often occurs during field emission. De Jonge et al. **[100]** demonstrated this happens for currents as low as 80 nA per tube.
The chemical inertness and low surface energy of the graphitic structure of the CNT is not conducive to functionalization.
Recent progress in solubilisation has facilitated chemical functionalization of SWNTs for various applications such as catalysis, catalysts support, sensors, gas storage, high-performance composites, biological and organic/inorganic compounds **[101-111]**. Most functionalization methods involve strong acid treatment of the CNT producing extensive nanotube breakage. A class of functionalization reactions that does not involve acid treatment is the direct addition to the π-electrons of the CNT **[112,113]**.
The main approaches for functionalization can be grouped into the following categories:
(a) the covalent attachment of chemical groups through reactions onto the π-conjugated skeleton of CNT;
(b) the non-covalent adsorption or wrapping of various functional molecules; and
Within category (a) reports of fluorination **[114,115]**, atomic hydrogen **[116]**, aryl groups **[117]**, nitrenes, carbenes, and radicals **[118]**, COOH **[119,120]**, NH_2 **[121]** *N*-alkylidene amino groups **[122]**, alkyl groups **[123]** and aniline **[124]** amine and amide **[125]** have been reported.
Within category (b) are included grafting of biomolecules such as bovine serum albumine **[126-128]** or horse spleen ferritin **[129]**, poly-Llysine, a polymer that promotes cell adhesion **[130,131]**, Streptavidin **[132]** and biotin at the carboxylic sites of oxidized nanotubes **[133]** and polymers **[134-139]**.
European Position: Haddon and co-workers in the US were early leaders and Carroll and co-workers in Wake Forrest University applied functionalization to devices. In Europe Hirsch in Erlangen has made major contributions and Coleman and co-workers at TCD have furthered our knowledge in this area.

7. Properties/Characterization

CNTs typically have a Young's Modulus ~10 times that of steel **[140]** and an electrical conductivity many times that of copper **[141]**. Some important properties of CNTs are listed in **table 1.**
The properties of CNTs are determined by a number of methods. Electronic properties are determined by adding contacts and the use of probe stations. It should be noted that a drawback to this method is the variability in contact quality that can cause significant variance in measured attributes. Raman spectra are used to characterize defects in the CNTs; the higher the I_d:I_g ratio, the lower the number of defects. Also, radial breathing modes can be used to characterize the diameter distributions of the grown CNTs in a sample **[144,145]**.
The band structures of all single-walled CNTs can be summarized using the Kataura plot **[146]**.

8. Electronic applications

Various applications for CNTs in the ICT field have been touted but in the near term only a few of these seem feasible: their use in field emission applications and their inclusion in the production of transparent conductors and in interconnects and vias seem most probable.

Mechanical Properties	
Young's modulus of multi-walled CNTs	~1-1.2 TPa
Young's modulus of single-walled CNT ropes	~1 TPa
Tensile strength of single-walled nanotube ropes	~60 GPa
Stiction	~10^{-7} N on 5 μm latex beads **[142]**
Hydrophobicity	161° contact angle **[143]**
Thermal Properties at Room Temperature	
Thermal conductivity of single-walled CNTs	1750-5800 WmK
Thermal conductivity of multi-walled CNTs	>3000 WmK
Electrical Properties	
Typical resistivity of single- and multi-walled CNTs	10^{-6} Ωm
Typical maximum current density	10^{7}-10^{9} A cm^{2}
Quantized conductance, theoretical/measured	(6.5 kΩ)$^{-1}$/(12.9 kΩ)$^{-1}$ per channel
Electronic Properties	
Single-walled CNT band gap	
Whose n-m is divisible by 3	0 eV (metallic)
Whose n-m is non-divisible by 3	0.4-0.7 eV (semiconducting)
Multi-walled CNT band gap	~0 eV (non-semiconducting)

Table 1.**: Summary of main properties of CNTs **[19].

8(a) Field emission

Field emission from CNTs can be applied to many technologies because of their high-current-carrying capability, chemical inertness, physical strength and high aspect ratio. The major applications are listed below.

(i) Field emission displays

Motorola in the early/mid 1990's investigated the use of carbon based materials for Field Emission Displays including the use of diamond, DLC and CNTs **[147,148]**. More recently they have reported a CNT based Field Emission HDTV **[149]**. Over the last 10 years or so various companies including Philips, TECO Nanotech, ISE Electronics and especially Samsung (SAIT) **[150]** have worked on the use of CNTs for TV applications. SAIT successfully produced demos of full colour 39"diagonal TVs and this technology was transferred to Samsung SDI for production in the mid 2000s. However, no displays based on this technology are yet on the market.
More work continues on Field Emission displays but the only recent major announcements are on SEDs (Surfaceconduction Electron-emitter Displays). Formerly a collaboration between Toshiba and Canon, the displays

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utilise emission from carbon but not CNTs **[151]**. Legal disputes have prevented this from coming to market thus far. Most recently, Sony have announced a major investment in FEDs based on a Spindt process. Teco Nanotech Co Ltd (a small company based in Taiwan) also market three basic CNT-based FEDs, the largest being 8.9" diagonal **[152]**. CEA (France) continue to fund research in this area, with typical displays produced shown in **figure 7**.

(ii) Microwave generators

High power/frequency amplifiers for higher bandwidth, more channels and microwave links are increasingly using the 30 GHz and above frequency range. In order to satisfy the power (tens of Watts) and bandwidth requirements (30 GHz), satellites are using travelling wave tubes (TWTs) based on thermionic cathodes. Present day TWTs, however, are bulky and heavy, and take up valuable space and weight budget in a satellite, and any miniaturization of the current TWT would give rise to cost savings in a satellite launch and aid the implementation of micro-satellites. Solid state devices are not used in this high frequency regime because the maximum power attained by solid state devices today at 30 GHz is ~1 W. Attempts have been made to replace the thermionic cathode in a TWT with a Spindt tip cathode delivering the dc electron beam. However, the bulk of the TWT device is still there, since it is the tube (in which the electron beam modulation takes place) that is physically large. The most effective way to reduce the size of a TWT is via direct modulation of the e-beam, for example, in a triode configuration using CNTs as the electron source.

Thales, in collaboration with Cambridge University Engineering Department, have successfully demonstrated a Class D (i.e. pulse mode/on-off) operation of a carbon nanotube array cathode at 1.5 GHz, with an average current density of 1.3 A/cm^2 and peak current density of 12 A/cm^2 (see **figure 8**); these are compatible with travelling wave tube amplifier requirements (>1 A/cm^2) **[153]**.

Recently, they have also achieved 32 GHz direct modulation of a carbon nanotube array cathode under Class A (i.e. sine wave) operation, with over 90% modulation depth. This unique ability to directly modulate or generate RF/GHz electron beams from carbon nanotube emitters is especially important for microwave devices as it essentially replaces the hot cathode and its associated modulation

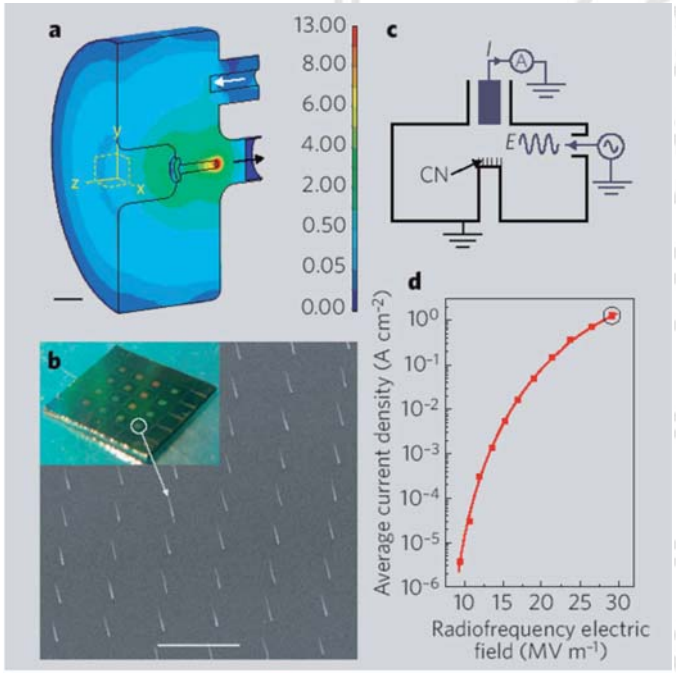


Figure 8: *Simulation of the coaxial resonant cavity (a cross-section is shown) that was used to generate a high electric field (red) at the carbon-nanotube-array cathode from the radiofrequency input; colour scale shows the applied macroscopic electric field in volts (10^5) per metre. White arrow, coaxial radiofrequency input; black arrow, emitted electron beam, collected by an antenna; scale bar 10 mm.* ***b)*** *Electron micrograph of the carbon-nanotube-array cold cathode at a tilt of 45°. The carbon nanotubes have an average diameter of 49 nm, height of 5.5 µm and a spacing of 10 µm; scale bar, 15 µm. Inset, photograph of 16 cathodes.* ***c)*** *Representation of the equivalent electrical circuit, where E is the applied electric field and I is the emitted current; CN, carbon nanotube array.* ***d)*** *Measured average current density plotted against applied radiofrequency electric field using 1.5-GHz sinusoidal input. The circled point corresponds to I=3.2 mA. The cavity-quality factor was 3,160* ***[153]****. Reprinted by permission from Macmillan Publishers Ltd: Nature, K.B.K. Teo, E. Minoux, L. Hudanski, F. Peauger, J.-P. Schnell, L. Gangloff, P. Legagneux, D. Dieumgard, G.A.J. Amaratunga and W.I. Milne. "Microwave Devices: Carbon Nanotubes as Cold Cathodes", Nature 437, 968 (2005), copyright 2005.*

stage **[154]**. Other advantages that carbon nanotube cathodes offer include no heating requirement and the ability to turn on or off instantly (for efficient operation). Because of their small size, and their ability to generate and modulate the beam directly on demand without the need for high temperatures, CNT cathodes could be employed in a new generation of lightweight, efficient and compact microwave devices for telecommunications in satellites or spacecraft.

Xintek have also been working on CNT-based microwave amplifiers for the US Air Force **[155]**.

The main problem at present is the limited modulation bandwidth associated with such devices.

(iii) X-ray Instruments

Oxford Instruments have worked together with NASA on CNT-based X-ray sources

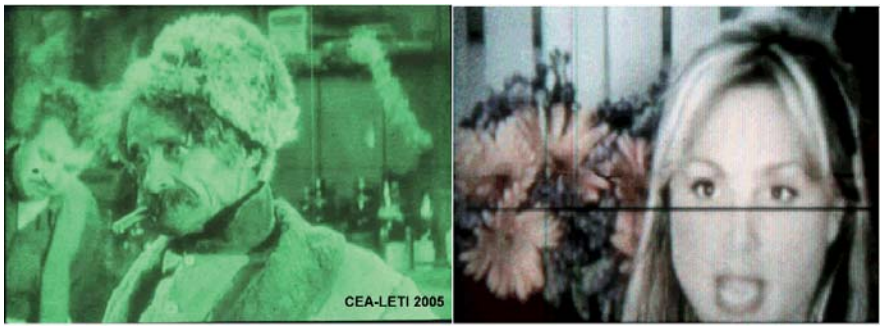


Figure 7: *Two stages of development of CNT FED at CEA. On the left: monochrome display with 350µm pixels, on the right: color video display with 600µm pixels. On these display the non uniformity from pixel to pixel is 5% while it is 3% with LCD displays and 2% for CRT (courtesy of CEA-LITEN).*

that employ field emission as the electron source, rather than thermionic emission, which has much lower power efficiency **[156]**. Their application is targeted towards low-power use for a space mission to Mars (though high power would be more preferable), once again because of their low weight and fast response time. Oxford Instruments have also developed and sold hand-held low power X-ray imagers which can be applied to medicine and for diagnostics in circuit boards **[157]**. Zhou and co-workers at Xintek (see **figure 9**) have developed a fast response, sharp-focus X-ray tube with quick pulsation **[158]**. MoXtek have also produced similar devices **[159]**.

Challenges for these devices are in achieving high power with stability and reproducibility.

(iv) Ionization for propulsion and detection

electric propulsion

Replacing hollow and filament cathodes with field emitter (FE) cathodes could significantly improve the scalability, power, and performance of some meso- and microscale Electric Propulsion (EP) systems. There is considerable interest now in microscale spacecraft to support robotic exploration of the solar system and characterize the near-Earth environment. The challenge is to arrive at a working, miniature electric propulsion system which can operate at much lower power levels than conventional electric propulsion hardware, and meets the unique mass, power, and size requirements of a microscale spacecraft.

Busek Company, Inc. (Natick, MA), has developed field emission cathodes (FECs) based on carbon nanotubes **[160]**. The non-thermionic devices have onset voltages about an order of magnitude lower than devices that rely on diamond or diamond-like carbon films.

Worcester Polytechnic Institute (WPI) falls under the programs headed by Professors Blandino and Gatsonis. Blandino's research is largely focused on the study of colloid thrusters for small satellite propulsion, and in the development of novel, earth-orbiting spacecraft formations **[161]**. The Gatsonis activity also includes modelling of plasma micropropulsion **[162]**.

Groups from the Rutherford Appleton Laboratory **[163]** and Brunel University **[164]** are studying Field emission performance of macroscopically gated multi-walled carbon nanotubes for a spacecraft neutralizer.

Gauges/Sensors

The Physical Metrology Division, Korea Research Institute of Standards and Science are using the field emission effect of a carbon nanotube to characterize a new type of technology for detecting low pressure. The fabricated low pressure sensor is of a triode type, consisting of a cathode (carbon nanotubes field emitter arrays), a grid, and a collector. The gauge has a triode configuration similar to that of a conventional hot cathode ionization gauge but also has a cold emission source. Due to the excellent field emission characteristics of CNT, it is possible to make a cost effective cold cathode type ionization gauge. For an effective CNT cathode they used the screen-printing method and also controlled the collector and the grid potentials in order to obtain a high ionization current. They found that the ratio of the ionization current to the CNT cathode current changes according to the pressure in the chamber **[165]**.

Miniaturised gas ionization sensors using carbon nanotubes

Ajayan et al. from the Rensselaer Polytechnic Institute have developed Ionization sensors work by fingerprinting the ionization characteristics of distinct gases **[166]**. They report the fabrication and successful testing of ionization microsensors featuring the electrical breakdown of a range of gases and gas mixtures at carbon nanotube tips. The sharp tips of nanotubes generate very high electric fields at relatively low voltages, lowering breakdown voltages several-fold in comparison to traditional electrodes, and thereby enabling compact, battery-powered and safe operation of such sensors. The sensors show good sensitivity and selectivity, and are unaffected by extraneous factors such as temperature, humidity, and gas flow. As such, the devices offer several practical advantages over previously reported nanotube sensor systems. The simple, low-cost, sensors described here could be deployed for a variety of applications, such as environmental monitoring, sensing in chemical processing plants, and gas detection for counter-terrorism.

McLaughlin and Maguire **[167]** at University of Ulster report the use of CNT's in order to decrease the turn-on voltage associated with microplasmas and the enhancement of emission spectra associated with gas types. In particular the device focuses on mixed gas types such as breath analysis and environmental monitoring. The ability of low cost CNT structured electrodes is key to improving performances related to higher sensitivity and specificity of gases such as NOx. Catalyst free growth techniques have been reported using thermal CVD routes and the study is also looking at the optimum CNT spacing and height required for short time ionisation or FE applications to gas sensors.

The main driver at present is to improve the efficiency which currently lies at around 1%.

(v) Backlighting

Although their use in full colour TVs is still problematical, the use of CNTs as electron emitters in FE-based backlight units for AMLCDs is still under investigation by various companies worldwide. Major players in the TFT-LCD

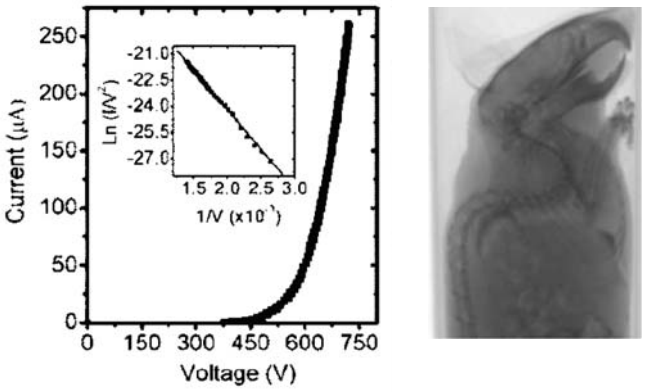


Figure 9: *Left, the x-ray tube current versus the gate voltage measured with the anode voltage fixed at 40 kV. It follows the classic Fowler–Nordheim relation. The distance between the cathode and the gate is 150 μm. Right, X-ray image of a normal mouse carcass (25 g) obtained using a CNT source-based imaging system* ***[158]****. Reprinted with permission from J Zhang, Rev. Sci. Instrum. 76, 094301 (2005). Copyright 2005, American Institute of Physics.*

display industry, such as Samsung, Corning and LG Electronics (LGE), are keen to develop carbon-nanotube (CNT) backlight modules, with Taiwan-based backlight-module makers also interested in following suit **[168]**. In Korea Iljin also have several years of experience in this area **[169]**.

In theory, CNT backlight modules have a lower temperature, consume less power and are less expensive to produce than traditional backlight modules. It is a good candidate to eventually replace CCFL (cold cathode fluorescent lamp) backlighting but has strong competition from LEDs, which could be much cheaper to produce.

The challenges are again to improve the lifetime of the emitters and to reduce cost to be competitive with other technologies.

(vi) Electron microscopy

Electron microscopy demands a bright, stable, low-noise electron source with a low kinetic energy spread to maximise spatial resolution and contrast. Recent research has investigated whether the carbon nanotube can act as an improved electron source for this application and how it compares to the other electron sources available today. Various groups from FEI, CUED, EMPA, El-Mul etc. have researched the optimum way to produce CNTs for use in microscopy. The most detailed analysis was carried out by De Jonge and co-workers and the field emission properties of CNTs collated from all of de Jonge's papers **[170]** for their use in SEM/TEM sources are summarized below:

Reduced Brightness / ($Asr^{-1}m^{-2}V^{-1}$)	10^9
Energy Spread / eV	0.25 - 0.50
Short-term stability %	0.2
Running Temp / K	700-900
Vacuum Level / mBar	< $2x10^{-8}$
Noise Percentage %	0.12
Virtual source size[i] / nm	0.2

[i]*Virtual source size is analogous to the effective emitting area on the surface of the carbon nanotube in which the advantage lies in this area being minimized.*

The CNTs act as a cold cathode source and the standard manufacturing procedure is to add them to the tip of a standard tungsten emitter. Several different methods of attachment/growth have been attempted. Teo et al. used a carbon glue to attach the CNT to the tungsten tip. Growth, rather than attachment is felt to be a better process. Riley et al. **[171]** have shown that a forest of highly defective CNTs can be grown on a tungsten tip by thermal chemical vapour deposition (TCVD), but in order for electron beam equipment to work effectively, there must be only a single source of electrons, hence a single CNT on each tungsten tip. Mann et al. **[172]** therefore used PECVD and describe how such a procedure is scalable with the ability to grow a single CNT on each W tip (shown in **figure 10**). It is also possible to grow many tips simultaneously. El Mul has developed a silicon-based CNT micro-cathode in which the CNT is grown in an etched pore **[173]**.

Though the emission characteristics of the CNT have been found to be extremely promising with the attachment process has been essentially overcome. Progress is also being made in improving stability and reproducibility.

European Position for Field Emission and Applications

From a display viewpoint Europe were very much forerunners but then Samsung provided the more recent display drive. As regards work on sources for electron microscopy in Europe De Jonge and co workers did some excellent work on characterisation of single emitters as did Groning on arrays of emitters. Thales in collaboration with several universities have continued European interest in the design of high frequency CNT based sources. For X-ray sources Oxford Instruments led the way and more recently Xintek in the US and Philips in Europe have expanded the work. In backlighting as in Displays the Far East leads the way. The leaders in the FE based propulsion area are in the US where the Jet Propulsion Laboratory Pasadena, Busek Co., Inc. and the Worcester Polytechnic Institute (WPI) lead the way. In Europe the main groups are from the Rutherford Appleton Laboratory, Brunel University, the University of Groningen, and the University of Ulster.

8(b) Interconnects, vias

In order to achieve the current densities/conductivity needed for applications in vias, dense arrays of CNTs are required. Very dense arrays of nanotubes have been grown by chemical vapour deposition (CVD) by various groups, following Fan et al. **[174]**. They are called forests, mats or vertically-aligned nanotube arrays. They are usually multi-walled and grown from Ni, Co or Fe catalysts. It has been suggested that a nanotube density of at least 10^{13} cm^{-2} was needed in order to produce the required conductivity but recently Fujitsu have indicated that $5x10^{12}$ cm^{-2} would be acceptable **[175]**. However growing such dense arrays in vias of high aspect ratio is not so straightforward. Numerous groups worldwide are trying to optimise the process including CEA but Fujitsu **[176]** (see **figure 11 page 16**) have reported the most significant advances and have recently reported that they have achieved a density of $9x10^{11}$ cm^{-2}. They have also reported a resistivity of 379 μΩcm for a via 2 μm in diameter. A Microwave CVD method was employed to produce CNTs at temperatures compatible with CMOS. However, much improvement is still required before these become a practical proposition.

Figure 10: *Left, electron micrograph of a single CNT grown on a tungsten tip. Note that the growth is aligned with the tungsten axis. Centre, a tungsten tip mounted in a suppressor module. Right, a CNT grown on a tungsten already mounted in the suppressor in situ.*

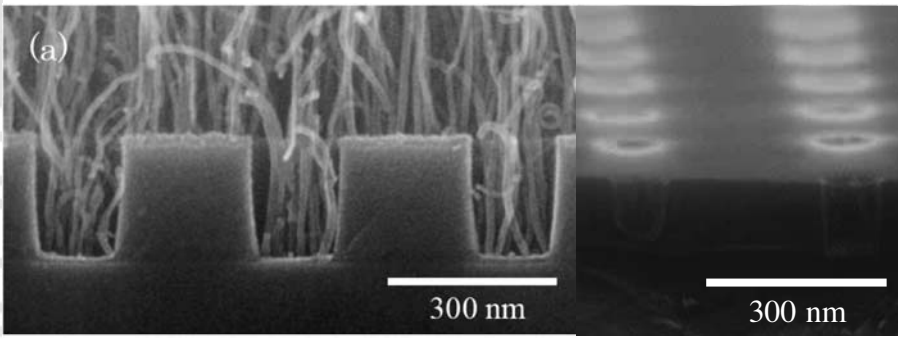


Figure 11: *Left, CNT vias grown in pores etched into silicon* ***[177],*** *© [2007] IEEE. Reprinted, with permission, from M. Nihei et al., "Electrical Properties of Carbon Nanotube Via Interconnects Fabricated by Novel Damascene Process", Proceedings of IEEE/ IITC 2007. Right, CNTs grown in pores in Silicon.*

Problems include choice of catalyst, catalyst deposition, depositing top contacts, increasing the packing density and reducing the overall resistivity. The growth also needs optimization for back-end processing and must be carried out at low enough temperatures so as not to damage CMOS. If SWNTs are to be employed, the packing density of metallic tubes must be high enough to justify replacing metal interconnects. For MWNTs, for a sufficient current density, internal walls must also contribute to conduction. Neither have as yet been achieved.

European Position: Infineon identified Vias as a possible early application of CNTs in electronics, Intel in the US evaluated spun-on CNTs for contacts but more recently Fujitsu. Japan lead the way.

8(c) Transparent, conductive contacts/membranes

As the use of ITO becomes ubiquitous and indium becomes more scarce and thence more expensive there is an ongoing search for alternative transparent conducting contact materials. Initiated at Nanomix **[178]**, various groups worldwide including those of Rinzler, Roth, Chhowalla and Grüner have worked in this area to replace indium tin oxide (ITO) in e.g. LCDs, touch screens, and photovoltaic devices. Nantero Inc. (Boston), Eikos Inc. of Franklin, Massachusetts and Unidym Inc. (recently bought by Arrowhead) of Silicon Valley, California are also developing IP and transparent, electrically conductive films of carbon nanotubes **[179]**. CNT films are substantially more robust than ITO films mechanically, potentially making them ideal for use in displays for computers, cell phones, PDAs and ATMs as well as in other plastic electronic applications. At SID2008, University of Stuttgart and Applied Nanotech presented the world's first 4-inch QVGA colour LCD display using CNT as the transparent conductive film. The CNT were deposited by spray coating **[180]**. There is still a need to increase conductivity whilst maintaining a sufficiently high (~95%) transparency and for some applications, roughness is a problem. Also, most recently it has been pointed out by Fanchini et al. **[181]** that CNT/Polymer films are anisotropic and suffer from birefringent effects which may cause problems in some of its most useful potential application areas such as OLEDs, Displays and PV. Gruner summarizes the work in this area well (**figure 12 page 17**).

European Position: US dominates this area through the work of Eikos Inc, Nanomix Inc., Grüner and co-workers and Rinzler's group in Florida. Chhowalla at Rutgers has now carried on this work and Roth in Stuttgart leads the way in Europe.

8(d) Thermal management

There is also an increasing need to replace indium for thermal interfaces in eg: CPUs, graphic processors and (automotive) power transistors, as price and scarcity increase. Various companies and universities (such as Ajayan's group **[183]**) are working in this area but very little (if anything) has been published. Current problems in using CNTs are insufficient packing density and problems with graphitisation leading to a reduction in conductivity.

European Position : Ajayan is the most notable contributor to this research. Very little work has been published by workers from the EU.

First author	Contact	Architecture	Mobility / cm^2/Vs	On-off ratio	Conductance S/m	Sub-threshold slope / mV/dec
Martel **[184]**, Tans **[185]**	Au	Bottom gate (SiO_2/Si)	20	10^5	0.0017	------
Durkop **[186]**	Cr/Au	Bottom gate (SiO_2/Si)	$>10^5$	------	1.4	100
Wind **[187]**	Ti	Top gate (SiO_2/Al or Ti)	2300	10^6	3.25	130
Rosenblatt **[188]** Minot **[189]**	Au	NaCl and KCl solution top gate (Ag/AgCl probe)	1500	10^5	20	80
MH Yang **[190]**	Pd	Top gate Al	------	10^5	1000	67-70
Javey **[191]**	Mo	ZrO_2 top gate (Metal Ti/Au)	3000	10^4	6	70

Table 2.

8(e) Transistors and diodes for logic

(i) Individual CNT-based transistors

Arguably this has been the electronic application on which most research has focused. As shown in table 2. Martel et al. and Tans et al. first reported a bottom gate individual single walled carbon nanotube field effect transistor (SWNT-FETs) with an on/off ratio of ~10^5 and a mobility of 20 cm^2/Vs in 1998 **[184,185]**. Afterwards, Durkop et al. claimed a mobility for bottom-gate SWNT-FET of >10^5 cm^2/Vs with a subthreshold swing ~100 mV/decade **[186]**.

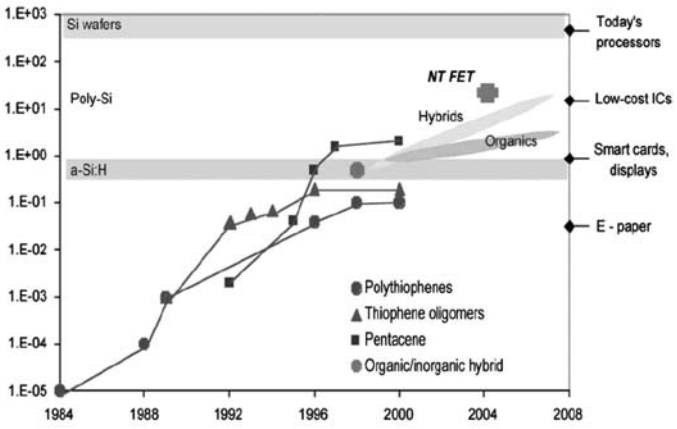


Figure 12: *The evolution of the mobility of the plastic FET devices over the past decades. The mobility of CNTN FETs is indicated by the bold cross towards the top right-hand corner. Some application barriers are also indicated on the right side of the figure* ***[182]****. G Gruner. J. Mater. Chem., 2006, 16, 3533 – 3539 – Reproduced by permission of the Royal Society of Chemistry.*

This mobility is still the highest reported for bottom gate CNT-FETs thus far. Meanwhile, top gate SWNT-FETs were also attracting attention since such a structure can be readily used for logic circuits. In 2002, Wind et al. first demonstrated a top gate SWNT-FET with an on/off ratio of ~10^6, a transconductance of 2300 S/m and a subthreshold swing of 130 mV/decade **[187]**. Rosenblatt et al. and Minot et al. **[188,189]** using NaCl and KCl solutions as the top gate SWNT-FETs showed a mobility of 1500 cm^2/Vs, a subthreshold swing of ~80 mV/decade and an on/off ratio of 10^5. Yang et al. **[190]** showed a very high transconductance of 1000 S/m in a top gate device (shown in **figure 13**, together with a bottom gate device). Javey et al. also demonstrated high performance SWNT-FETs using high-k dielectric ZrO_2 as the top gate insulator. Devices exhibited a mobility of 3,000 cm^2/Vs, a transconductance of 6000 S/m and a subthreshold swing of ~70 mV/decade respectively **[191]**.

Several groups have also investigated vertical CNT-FETs (wrap-around gate). Choi et al. reported the first vertical MWNT-FET with a best conductance of 50 mS in 2003 **[192]** but this only works at low temperatures. Maschmann et al. demonstrate a vertical SWNT-FET in 2006 **[193]**. Their devices exhibited a good ohmic SWNT-metal contact, but the gate effect is not as efficient as either the top gate or bottom gate SWNT-FETs. SWNT-FET always exhibit p-type operation when contacted ohmically, but n-type SWNT-FETs are also needed for fabrication of logic circuits. Derycke et al. claimed both annealing (removal of oxygen) and doping (e.g. potassium) can convert a p-type SWNT-FET into a n-type and a logic inverter was demonstrated **[194,195]**. Javey et al.

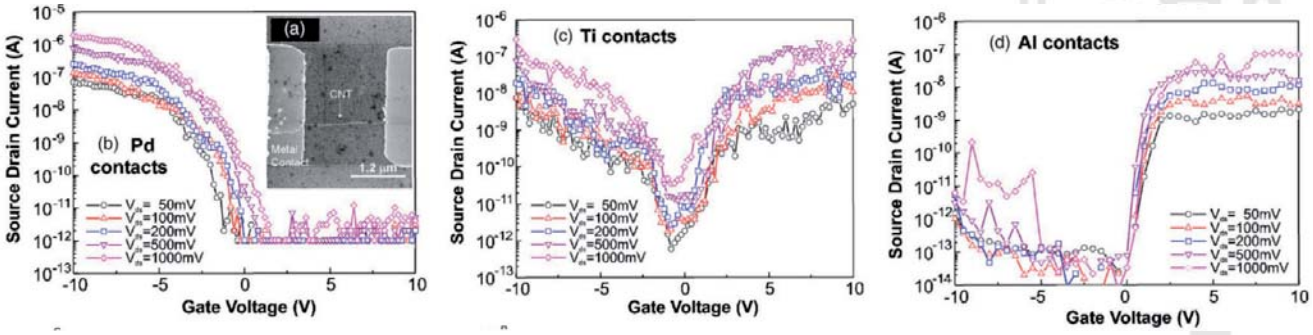


Figure 13: *SWNT-FET transistor characteristics with different contacts. Left, Pd makes and ohmic contact which results in p-type conduction. Centre, Ti contacts result in strong ambipolar behaviour. Right, Al makes a Schottky contact which results in n-type conduction but with a strong leakage current.*

and Chen et al. reported that using different metal electrodes (e.g. Al) they could also obtain n-type SWNT-FETs with a ring oscillator also fabricated **[196,197]**.

Challenges for the future include controlling the chirality, improving the yield of working devices, improving the reproducibility of the contact, ensuring all CNTs are semiconducting, improving the uniformity of the devices, controlling their positioning, and developing a process that can be scaled up to mass-production.

European Position: The state-of-the-art transistors (dependent on characteristics) are those produced by the groups of Avouris at IBM and in Europe , Bourgoin at CEA, Saclay, Ecole Polytechnique and Dekker at Delft University of Technology.

(ii) Network CNTs

In order to overcome the various problems with individual CNT transistors, numerous groups have concentrated on the production of transistors manufactured from CNT networks or even CNT/Polymer mixtures.

In 2002, the first report (a patent) for transistors based on random network of nanotubes and its use in chemical sensors was deposited by Nanomix Inc. **[198]**, followed in 2003 by the disclosure of their integration onto a 100 mm Si wafer **[199]**. First public disclosure was made in 2003 by Snow et al. **[200]** who demonstrated a SWNT thin film transistor with a mobility of >10 cm^2/Vs and a subthreshold swing of 250 mV/decade with an on/off ratio of 10. In 2007, Kang et al. grew highly dense, perfectly aligned SWNT arrays on a quartz substrate which was then transferred to a flexible plastic substrate (PET). The SWNT-FETs were fabricated on the PET substrate and exhibited a mobility of 1000 cm^2/Vs and a transconductance of 3000 S/m **[201]**. The Rogers group has exhibited state-of-the-art network transistors for on-off ratio and mobility (see **figure 14**). Grenoble have also investigated this and have made a small chip of 75 such transistors.

The interest of the networks comes from the fact that if the average nanotube length is small compared to the distance between source and drain, more than one tube is needed to make the connection. Hence the probability of having an electrical path made only of metallic tubes is ~$(1/3)^n$ where n is tne number of tubes needed to make the junction. Secondly, the on/off ratio increases since, even if two tubes are metallic, their contact is not metallic **[202]**. Finally, even a single defect is enough to open a bandgap in a metallic tube, turning it into a semiconductor **[203]**. This means that controlling the number of defects is an important challenge to overcome.

Note that the first transparent CNT based transistor made on a flexible substrate was achieved by transferring a CNT random network and its contact from its initial silicon substrate onto a polyimine polymer **[204]**.

European Position: Rogers in the USA produces the state of the art thin Film transistors and in Europe, apart from some preliminary work in Universities little seems to be happening.

9. Optical applications

9(a) Saturable absorbers

The band gap of semiconducting CNTs depends on their diameter and chirality, i.e. the twist angle along the tube axis **[205]**. Thus, by tuning the nanotube diameter it is easy to provide optical absorption over a broad spectral range **[206]**. Single-walled CNTs exhibit strong saturable absorption nonlinearities, i.e. they become transparent under sufficiently intense light and can be used for various photonic applications e.g in switches, routers and to regene-rate optical signals, or form ultra-short laser pulses **[207-209]**. It is possible to achieve strong saturable absorption with CNTs over a very broad spectral range (between 900 and 3000 nm **[210]**). CNTs also have sub-picosecond relaxation times and are thus ideal for ultrafast photonics **[211,212]**. CNT saturable absorbers can be produced by cheap wet chemistry and can be easily integrated into polymer photonic systems. This makes a CNT-based saturable absorber very attractive when compared to existing technology, which utilises multiple quantum wells (MQW) semiconductor saturable absorbers and requires costly and complicated molecular beam epitaxial growth of multiple quantum wells plus a post-growth ion implantation to reduce relaxation times **[213]**. Additionally, the MQW saturable absorbers can operate only between 800 and 2000 nm, a much narrower absorption bandwidth.

The major laser systems mode-locked by CNT saturable absorbers demonstrated so far (see **figure 15 page 19**) includes fibre lasers, waveguide lasers and solid-state lasers, generating sub-ps pulses in a broad spectral range between 1070 and 1600 nm **[214]**. The shortest pulse of about 68 fs was achieved with a solid state Er^{3+} glass laser by using a CNT-polyimide composite **[215]**.

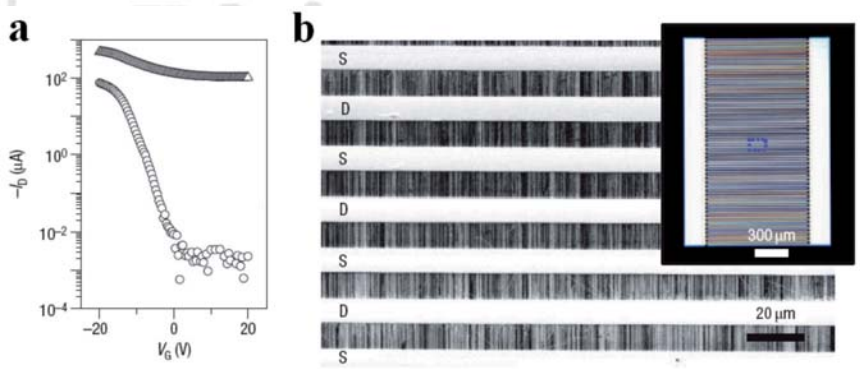
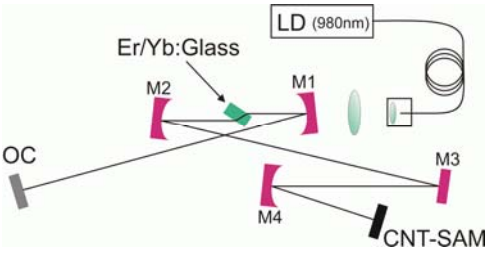


Figure 14: (a) *Transfer curves from a transistor that uses aligned arrays of SWNTs transferred from a quartz growth substrate to a doped silicon substrate with a bilayer dielectric of epoxy (150 nm)/SiO_2 (100 nm). The data correspond to measurements on the device before (open triangles) and after (open circles) an electrical breakdown process that eliminates metallic transport pathways from source to drain. This process improves the on/off ratio by a factor of more than 10,000.* ***(b)*** *Optical (inset) and SEM images of a transistor that uses interdigitated source and drain electrodes, in a bottom gate configuration with a gate dielectric of HfO_2 (10 nm) on a substrate and gate of Si. The width and length of the channel are 93 mm and 10 μm, respectively. The box indicated by the dashed blue lines in the optical image inset delineates the region shown in the SEM image* ***[201]****. Reprinted by permission from Macmillan Publishers Ltd: Nature (London), Seong Jun Kang, Coskun Kocabas, Taner Ozel, Moonsub Shim, Ninad Pimparkar, Muhammad A. Alam, Slava V. Rotkin, John A. Rogers, Nature (London), 2, 230 (2007), copyright 2007.*



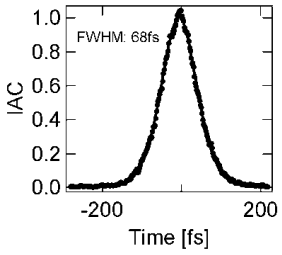


Figure 15: *Left, Experimental setup of the Er/Yb:glass laser. OC: output coupler; M1-M4: standard Bragg-mirrors; CNT-SAM: Saturable absorber mirror based on carbon nanotubes; LD: pigtailed laser diode for pumping the Er/Yb:glass (QX/Er, Kigre Inc., 4.8 mm path-length). Right, background-free autocorrelation. The solid line is a sech2 fit with a corresponding FWHM pulse-duration of 68 fs* ***[215]****.*

Additionally, amplified spontaneous emission noise suppression has been demonstrated with CNT-based saturable absorbers, showing great promise for this technology for multi-channel, all-optical signal regeneration in fibre telecom systems **[216]**.

Challenges include justifying the research to industry due to the limited market potential.

European Position: There are 5 major research groups working on CNT saturable absorber applications around the world: Sakakibara at National Institute for Advanced Industrial science and Technology (AIST), Tsukuba, Japan, Maruyama and Yamashita at Tokyo University & Set in Alnair Labs, and Yoshida at Tohoku University and in Europe. Dr. E. Obraztsova in the Institute for General Physics, Moscow, and Cambridge University Engineering are the major players

9(b) Microlenses in LCs

Microlenses in liquid crystal devices have potential applications in adaptive optical systems (where different focal lengths are required dependent on position), wavefront sensors (which measure the aberrations in an optical wavefront) and optical diffusers (which take a laser beam and redistribute it into any pattern desired). The use of sparse, MWCNT electrode arrays has been used to electrically switch liquid crystals. The nanotubes act as individual electrode sites which produce an electric field profile, dictating the refractive index profile within the liquid crystal cell (see **figure 16**). The refractive index profile then acts to provide a series of graded index profiles which form a simple lens structure. By changing the electric field applied, it is possible to tune the properties of this graded index structure and hence form an electrically reconfigurable micro-optical array **[217]**. The problems for the lenslets come mostly from the alignment of the LC and the limited aperture of the lenslets. More generally, for the kinoform or modal hologram, the problem is to be able to individually address each CNT. Growing them onto a TFT or a VLSI circuit would be ideal (such as an LCOS backplane).

European Position: The Engineering Department in Cambridge as far as we know, are the only group in Europe working in this area.

9(c) Antennae

Ren at Boston College has demonstrated the use of a single multi-walled CNT to act as an optical antenna, whose response is fully consistent with conventional radio antenna theory **[218]**. The antenna has a cylindrically symmetric radiation pattern and is characterized by a multi-lobe pattern, which is most pronounced in the specular direction. Possible applications for optical antennae include optical switching, power conversion and light transmission. One particular application is the “rectenna”, which is the light analogue of the crystal radio in which an antenna is attached to an ultrafast diode. This could lead to a new class of light demodulators for optoelectronic circuits, or to a new generation of highly efficient solar cells.

European Position: Early stages of research in the Dept of Engineering at Cambridge University in collaboration with Queen Mary College, London and ALPS (Electric), Japan.

9(d) Lighting

There is ongoing work on the use of CNTs for low energy lighting applications. The use of CNTs as electron emitters to stimulate phosphors has been reported by various groups and the replacement of metallic filaments with carbon CNTs/Fibres has been investigated by groups mostly in China. Carbon nanotube bulbs made from CNT strands and films have been fabricated and their luminescent properties, including the lighting efficiency, voltage-current relation and thermal stability have been investigated. The results show that a CNT bulb has a comparable spectrum of visible light to a tungsten bulb and its average efficiency is 40% higher than that of a tungsten filament at the same temperature (1400-2300 K). The nanotube filaments show both resistance and thermal stability over a large temperature region. No obvious damage was found on a nanotube bulb held at 2300 K for more than 24 hours in vacuum, but the cost needs to be significantly reduced and the lifetime significantly increased for this to be considered seriously as an option.

European Position: Mostly in the Far East but Bonnard et al at EPFL have worked in this area.

10. Electromechanical and sensor applications

10(a) NEMS

Recently Amaratunaga et al **[219]** demonstrated novel non volatile and volatile memory devices based on vertically aligned MWCNTs (see

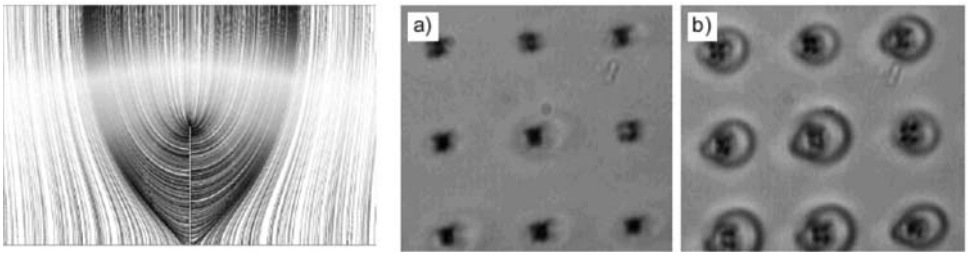


Figure 16: *Left, Simulated electrical field profile surrounding the single carbon nanotube (10 μm high) with an applied field of 1V m^{-1}. Right, Defocus of the nanotube lenslet array at 40x.* ***a)*** *Defocused image of the array at 0 V μm^{-1} applied field.* ***b)*** *Array brought into focus with 2.1 V μm^{-1} applied field* ***[217]****.*

figure 17).

Nanoelectromechanical switches with vertically aligned carbon nanotubes have been produced. However, Nantero are the market leaders in this area and have created multiple prototype devices, including an array of ten billion suspended nanotube junctions on a single silicon wafer **[220]**. Nantero's design for NRAM™ involves the use of suspended nanotube junctions as memory bits, with the "up" position representing bit zero and the "down" position representing bit one. Bits are switched between states through the application of electrical fields.

In theory the NRAM chip would replace two kinds of memory. While cell phones, for example, use both flash chips and SRAM or DRAM chips, NRAM would perform both functions. However the memory market is oversupplied and they frequently have to be sold at a loss, making it difficult for any new technology to break in. In addition, several other major companies are developing their own non-volatile memory technologies with PRAM perhaps the leading contender at present.

PRAM, FRAM, MRAM and RRAM are all large companies. With Nantero's relatively small size, market penetration is a big issue.

European Position: Nantero are the world leaders but in Europe ETH, TU Denmark, Cambridge Univ. Engineering in collaboration with Samsung and Thales plus numerous other groups are making significant contributions.

10(b) Sensors

CNTs for sensing is one of their most interesting electronic applications. Both SWCNTs and MWCNTs, functionalised and unfunctionalised, have been investigated. They have been used as gas, chemical and biological sensors and Nanomix Inc was the first to put on the market an electronic device that integrated carbon nanotubes on a silicon platform (in May 2005 they produced a hydrogen sensor) **[221]**. Since then, Nanomix has taken out various other sensing patents e.g. for carbon dioxide, nitrous oxide, glucose, DNA detection etc **[222]**. The next product to become available should be a breath analyzer detecting NO as a marker of asthma. More recently workers in Cambridge and Warwick University in collaboration with ETRI, South Korea have integrated CNTs onto SOI substrates to produce smart gas sensors (see **figure 18**) **[223]**. The CNTs have been locally grown on microheaters allowing back end deposition at T ~700 °C.

Numerous other groups worldwide continue to investigate CNTs for sensing because of their ease of functionality and high surface area. Dekker and his group are focusing on biosensors and electrochemical sensors using carbon nanotubes.

There are very many problems to overcome in bringing this technology to the market. Reproducibility of the CNT growth, processing as well as variable behaviour once integrated in a sensor can result in poor selectivity and sensitivity. In some devices, defects play a key role, in others, the source/drain metal-nanotube contact is key. Also, both the nanotube-nanotube junction or even amorphous carbon remaining on the nanotube can play a significant role in the detection scheme **[224]**. Indeed, there are many possible sensing mechanisms, hence a fundamental understanding of them is required to enable good optimisation and reproducibility of the sensors.

Although Nanomix has already raised $34 millions they have yet to deliver a significant, high volume product to the market. However, progress in these areas continues to be made globally.

European Groups Many companies and research institutions are carrying out work in this area, with THALES, Dekker (Delft), being the most successful.

10(c) CNT's in biotechnology and medical devices research

Definition: Nanomedicine, for the purpose of this section is defined as the application of nanotechnology to achieve breakthroughs in healthcare. It exploits the improved and often novel physical, chemical and biological properties of

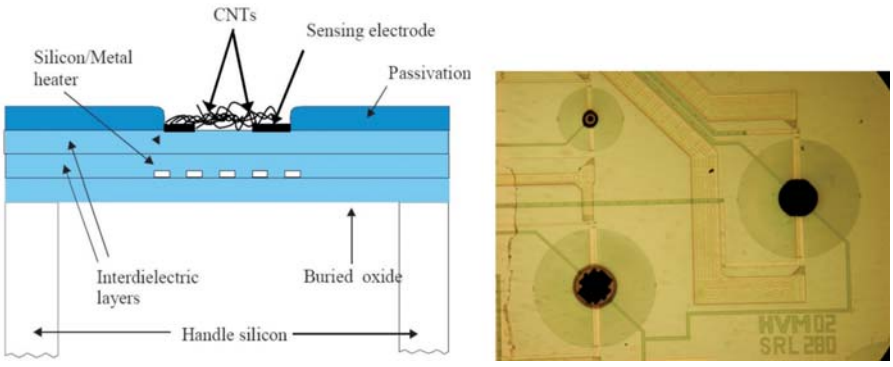


Figure 18: *Left, structural cross-sectional layout of the sensing area of the chip. Right, microscopic images of carbon nanotubes grown locally on ultrathin membranes incorporating a tungsten heater **[223]**. Reprinted by permission from IOP Publishing Ltd. M.S. Haque, K.B.K. Teo, N.L. Rupesinghe, S.Z. Ali, I. Haneef, S. Maeng, J. Park, F. Udrea, and W.I. Milne. "On-chip Deposition of Carbon Nanotubes using CMOS Microhotplates", Nanotechnology 19, 025607 (2007). Author and Publisher are acknowledged.*

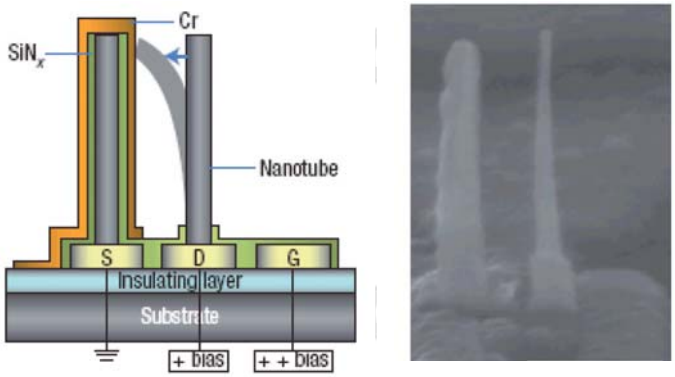


Figure 17: *Left, a schematic diagram showing a cross-section of a switch fabricated by Jang et al.. Both contacts and catalyst were deposited with e-beam lithography. Right, an electron micrograph showing the grown CNTs acting as a switch **[219]**. Reprinted by permission from Macmillan Publishers Ltd: Nature Nanotechnolog , J.E. Jang, S.N. Cha, Y.J. Choi, D.J. Kang, T.P. Butler, D.G. Hasko, J.E. Jung, J.M. Kim and G.A.J. Amaratunga. "Nanoscale Memory Cell Based on a Nanoelectromechanical Switched Capacitor", Nature Nanotechnology 3, 26 - 30 (2008), copyright 2008.*

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Low-field and solid-state NMR applied to food quality control (in collaboration with Dr N. C. Nielsen, iNano University of Aarhus and Aalborg, Denmark).

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materials at the nanometer scale. Nanomedicine has the potential to enable early detection and prevention, and to essentially improve diagnosis treatment and follow-up of diseases. This document addresses the overall roadmaps associated with nanomedicine and in particular identifies the role of CNT's. The key issues associated with CNT's related to nanomedicine is mainly related to the following issues:

- Some of the main challenges are linked to industrialisation. There is no conventional manufacturing method that creates low cost CNTs. Desirable properties are robustness, reproducibility, uniformity and purity.
- Reproducible production relating to surface defects; surface chemistry, size (hight and diameter; morphology; type etc.
- The ability to functionalise the surface with appropriate chemistries.
- The ability to produce arrays; periodicity; catalyst free- or tailored catalyst grown from self-assembly.
- To produce lost cost routes to manufacture in the case of disposable or competitive devices.
- The ability to integrate into microfluidic systems; CMOS circuitry or flexible substrate systems.

A clear set of studies are required to resolve all the issue of biocompatibility and nanotoxicity associated with the use, manufacture and purchase of CNT's of all forms.

In the next ten years, the development of biosensors and importantly, nanotechnology, will allow the design and fabrication of miniaturised clinical laboratory analysers to a degree were it is possible to analyse several laboratory measurements at the bedside with as little as 3µL of whole blood. The use of quantum dots; self-assembly; multifunctional nanoparticles, nano-templates and nano-scale fabrication including nanoimprinting will have a major impact on the design and development of much improved highly sensitive and rapid diagnostics; thus allowing accurate drug delivery integration. Nanoenabled high throughput analysis will also reduce the time it takes to bring a new drug delivery platform to market.

Nanomix is attempting to put such a device on the market in the next 12-18 months, with its NO sensor which is applied to monitoring asthma.

10(d) Nanofluidics

The interest in taking advantage of the unique properties of carbon nanotubes in nanofluidic devices has increased tremendously in the last couple of years. The carbon nanotubes can either be used directly as a nanofluidic channel in order to achieve extremely small and smooth pores with enhanced flow properties **[225]** or be embedded into existing fluidic channels to take advantage of their hydrophobic sorbent properties and high surface-to-volume ratio for improving chemical separation systems **[226,227]**.

By integrating vertically aligned carbon nanotubes into silicon nitride **[228]** and polymer membranes **[229,230]** respectively, it has been possible to study the flow of liquids and gases through the core of carbon nanotubes. The flow rates were enhanced with several orders of magnitude, compared to what would be expected from continuum hydrodynamic theory **[225]**. The reason for this is believed to be due to the hydrophobic nature of the inner carbon nanotube sidewall, together with the high smoothness, which results in a weak interaction with the water molecules, thereby enabling nearly frictionless flow through the core of the tubes. This effect is resemble transport through transmembrane protein pores, such as aquaporins, where water molecules line up in a single file with very little interaction with the sidewall.

This application of carbon nanotubes is envisioned to result in novel ultrafiltration and size-based exclusion separation devices, since the pores size is approaching the size of ion channels in cells **[225]**. The carbon nanotube membranes are, however, fabricated by CVD and this application is therefore suffering from the lack of large scale cost-effective CNT depositing equipment.

In the last couple of years CNTs have also been investigated as a sorbent material for improving both the resolution and sensitivity of chemical separations **[226,227]**. This has been done by incorporating the nanotubes in the stationary phase of mainly gas chromatography columns to take advantage of their high surface-to-volume ratio and better thermal and mechanical stability compared to organic phases, which make them ideal for especially temperature programmed separations **[226,227,231]**. The carbon nanotubes, in the form of powder, is hard to pack directly in the columns due to its marked tendency for aggregation and hence channel blockage **[226,227,232]** so the CNTs have typically either been incorporated in a monolithic column **[233]** immobilized on the inner channel wall **[234]** (or deposited on the surface of beads that subsequently were packed) **[235]**.

A major complication of these methods, beside that they are manual and very labor intensive, is that they rely on the necessity of forming uniform CNT suspensions, which is difficult, since CNTs are insoluble in aqueous solutions and most organic solvents **[226]**. It is therefore typically required to either dynamically or covalently modify the CNTs to avoid aggregation **[227]**. These problems can be overcome by direct growth of the CNTs on a surface, in e.g. microfluidic channels **[236,237,238]** so they are anchored to the channel wall and therefore unable to from aggregates. This also allows a much higher CNT concentration without clogging the fluidic devices. Growing of CNTs in microfluidic systems has the additional benefit that lithography can be used for the pattern definition, which should make it possible to make much more uniform and therefore more efficient columns **[239]**.

A major limitation of this application is also the lack of low cost CNT deposition equipment, since it is necessary to use vertically aligned CNTs that are attached to the surface to avoid aggregation and to benefit from the high uniformity of the nanostructures.

European Position: Montena Components of Switzerland are in competition with Maxwell Technologies in this area.

11. Energy applications

11(a) Fuel cells

Carbon nanotubes can be used to replace the porous carbon in electrode-bipolar plates in proton exchange membrane fuel cells, which are usually made of metal or

graphite/carbon black. The CNTs increase the conductivity and surface area of the electrodes which means that the amount of platinum catalyst required can be reduced **[240]**. The state of the art in this area is the mixing of CNTs and platinum catalyst particles reported by F. Chen et al. of Taiwan.

Whilst CNTs reduce the amount of platinum required, it is only a small percentage, which means that the cost of the fuel cell remains high. Also, CNTs are comparable in price to gold, meaning the saving is minimal.

European Position: The leaders in this area are the Taiwanese groups. The European leaders are linked to S Roth (Max Planck Institute, Stuttgart).

11(b) Supercapacitors

Electric double-layer capacitors, or supercapacitors have energy densities 1000 times greater than typical electrolytic capacitors. This occurs because they use the high surface area of porous carbon or nanotubes, and the narrow thickness of the electrochemical double layer as the capacitor separation. Supercapacitors allow inverters in electric trains to transform between voltages. They allow electric vehicles to have greater acceleration than from simple batteries. They would allow smoothing of power supplies on mobile phones.

Experimental devices replace the activated charcoal required to store the charge with carbon nanotubes, which have a similar charge storage capability to charcoal (which is almost pure carbon) but are mechanically arranged in a much more regular pattern that exposes a much greater suitable surface area. The figures of merit are energy density, related to the capacitance per unit volume of the carbon, and thereby the surface area of the porous carbon, and secondly the power density, related to the series resistance. Activated carbon is close to the theoretical surface area of carbon layers already, so going to nanotubes does not gain so much. But nanotubes have lower electrical resistance than porous carbon, so there is a gain in power density. In order to gain in energy density, development is towards hybrid CNT-polymer supercapacitors, using polypyrrole etc. Ionic displacement within the Ppy acts as a pseudo capacitance/battery.

The weakness of supercapacitors in electric vehicle applications is that they must be priced against conventional batteries which are very low in price.

European Position: Leader in Europe is Beguin et al. **[241]** who have used multi-walled CNTs mixed with polymers to create capacitance values of 100-330 F/g. Europe also has a strong industrial; input in this area with companies such as Maxwell (formerly Montena, Switzerland).

11(c) Batteries

The outstanding mechanical properties and the high surface-to-volume ratio make carbon nanotubes potentially useful as anode materials **[242]** or as additives **[243]** in lithium-ion battery systems. The CNTs give mechanical enhancement to the electrodes, holding the graphite matrix together. They also increase the conductivity and durability of the battery, as well as increasing the area that can react with the electrolyte. Sony produce the best CNT-enhanced lithium-ion batteries. The main problem is the high cost of CNTs.

Recently, a so-called paper battery has been developed, where CNTs are used as electrodes which are attached to cellulose immersed in an electrolyte. The technology is cheap, the batteries are flexible and no harmful chemicals are required **[244]**. The main problem with this is the high production cost of the battery, which needs to be reduced for mass production. The ambition is to print the batteries using a roll-to-roll system.

European Position: Although much of the innovation in this are has been carried out in the US and the Far East, in Europe there are various groups notably in Germany contributing in this area.

11(d) Solar cells

There has been much research into incorporating carbon nanotubes into solar cells. One application is the dispersion of CNTs in the photoactive layer. Amaratunga **[245]** has observed enhancement of the photocurrent by two orders of magnitude with a 1.0% by weight single-walled CNT dispersion. However, the power efficiency of the devices remains low at 0.04% suggesting incomplete exciton dissociation at low CNT concentrations. At higher concentrations, the CNTs short-circuit the device. More recently, a polymer photovoltaic device from C_{60}-modified SWCNTs and P3HT has been fabricated **[246]**. P3HT, a conjugated polymer was added resulting in a power conversion efficiency of 0.57% under simulated solar irradiation (95 mW cm^{-2}). An improved short circuit current density was attributed to the addition of SWCNTs to the composite causing faster electron transport via the network of SWCNTs. Further optimization is required to improve the efficiency still further. Furthermore, photoconversion efficiencies of 1.5% and 1.3% have been achieved with SWCNTs deposited in combination with light harvesting CdS quantum dots and porphyrins, respectively **[247]**.

CNTs have also been developed as a replacement for transparent conductive coatings to replace ITO which is becoming more expensive as supply runs out. Studies have demonstrated SWCNT thin films can be used as conducting, transparent electrodes for hole collection in OPV devices with efficiencies between 1% and 2.5% confirming that they are comparable to devices fabricated using ITO **[248,249]**.

Finally, CNTs have been investigated for application in dye-sensitized solar cells (DSSC). CNT networks can act as a support to anchor light harvesting semiconductor particles. Research efforts along these lines include organizing CdS quantum dots on SWCNTs. Other varieties of semiconductor particles including CdSe and CdTe can induce charge-transfer processes under visible light irradiation when attached to CNTs **[250]**. The SWNTs facilitate electron transport and increase the photoconversion efficiency of DSSCs. Other researchers fabricated DSSCs using the sol-gel method to obtain titanium dioxide coated MWCNTs for use as electrodes **[251]**.

European Position: Although much of the work in this area has been driven by the USA and Japan significant input on both the incorporation of the CNTs as part of the active layer and in transparent contact materials has been made in universities across the European community.

11(e) Hydrogen storage

CNTs have been suggested as potential candidates for hydrogen storage. However, the reported hydrogen uptake varies significantly from group to group, with the mechanism not clearly understood. Current methods involve compressing the CNTs into pellets which are then subjected to hydrogen at high pressure. The target set by the US Department of Energy is 6% by weight hydrogen by 2010. Whilst most groups have found hydrogen uptake to be in the 1-2% region **[252]**, amongst the highest reported are Gundish et al. **[253]** at 3.7% and Dai's group **[254]** at 5.1%. It should be noted that Hirschler and Roth found most values to be false **[255]**, for example due to Ti take up during sonication.

From a more fundamental point of view, since the average adsorption energy of hydrogen on CNTs is not significantly different from its value on amorphous carbon. It is mainly the surface area which plays a crucial role. Hence 5.8% was achieved a long time ago on super-high surface area activated carbon **[256]**.

European Position: Over the last 10 or so years there have been numerous groups worldwide working in this area; especially in the USA, Japan and China. Europe too has made a significant investment, notably through groups in Germany, France, Greece (theoretical work) and the UK but still the DoE 6% target remains elusive.

12. Future/Blue Sky

12(a) Spintronics

Spin transport has been demonstrated over lengths of hundreds of nanometers in CNTs **[257]**, and the limit may be much longer. The Kondo effect has been demonstrated **[258]**, and Fano resonances have been found **[259]**. Spin blockade has been demonstrated in a double dot structure **[260]**.

Problems to overcome include the production of uniform, defect-free SWNTs, free from paramagnetic impurities, and with a single chiral index and fabrication of reproducible devices with uniform contacts.

European Position: Hitachi, Cambridge Laboratory, the Cavendish Lab Charles Smith, in collaboration with Andrew Briggs at Oxford are the leaders in the field; Others include Delft (Leo Kouwenhoven) and the Niels Bohr Institute, Copenhagen.

12(b) Quantum computing

Arrays of qubits have been created in the form of endohedral fullerenes in SWNTs, to make so-called peapod **[261]**. The interactions between the spins have been characterized by electron paramagnetic resonance, showing transitions from exchange narrowing to spin-spin dephasing. Theoretical architectures have been developed for global control of qubits **[262]**. The spin properties of N@C60 have been shown to make it one of the strongest candidates for condensed matter quantum computing **[263]**. Quantum memories have been demonstrated, in which information in the electron spin is transferred to the nuclear spin, and subsequently retrieved. In this system the gate operation times is of order 10 ns, and the storage time is in excess of 50 ms, which clearly needs to be improved.

Problems to overcome include the development of the technology for single spin read out in CNTs and the demonstration of entanglement using peapods.

European Position: Oxford leads the world in peapods for quantum computing, in collaboration with Princeton (Steve Lyon), Nottingham (Andrei Khlobystov), Cambridge (Charles Smith), EPFL (Laszlo Forro), There is also activity in Berlin (Wolfgang Harneit), at L. Néel Institute in Grenoble and at CEMES-CNRS in Toulouse **[264]**.

12(c) Ballistic transport

Owing to their perfect geometry, carbon nanotubes are expected to exhibit ballistic transport for most radii encountered in experimentation **[265]**. However, backscattering due to electron-phonon interactions has been demonstrated in single-wall carbon nanotubes at biases of several volts **[266]**. This scattering is nonetheless only manifested in relatively low-energy electrons in devices of lengths of several hundred nanometers **[267]**. The mean free path for acoustic phonon scattering in CNTs is long (~ 1 micron) and hence its impact on the drain current for a 50 nm channel length is negligible **[268,269]**. The mean free path for optical scattering is about 10 nm and the energy of emission is ~ 0.16 eV **[270]**. The injected hole can be backscattered near the drain, but the likelihood of it scattering back to the source is small on account of the higher Schottky barriers encountered at the drain [6]. Monte Carlo simulations including electron-phonon interactions yield mobility values similar to those under ballistic transport (~ 10^4 cm^2/Vs) in semiconducting tubes of radii up to ~ 2 nm **[271]**. It is worth noting though that onset of ambipolar conduction in CNTFETs has been found to be modified by phonon scattering **[272]**. Monte Carlo simulations have also revealed steady-state velocity saturation due to optical phonon scattering and negative differential mobility at high electric fields **[273]**.

Regarding other scattering mechanisms, by using a k.p approximation, Ando and co-workers provided an elegant proof of the suppression of back scattering for impurities with smooth potential range, much larger than the lattice constant **[274]**. However the nature of disorder in nanotube-based materials and devices is more complex, including topological defects, chemical impurities, vacancies, etc.. The impact of such defects can strongly jeopardize initial good ballistic capability of otherwise clean nanotubes, and its study is therefore genuinely relevant. Several advanced computational scheme based on first principles (see reference **[273]**) allow a realistic description of scattering potentials, with quantitative estimation of associated elastic mean free paths and charge mobilities.

Additionally, even though transport in CNTs can be considered largely ballistic, CNTFETs have been demonstrated to be Schottky barrier FETs **[275]**. Even undoped CNTFETs, with zero-Schottky-barrier contacts are limited by voltage-controlled tunnelling barriers, presented by the body of the CNT, at the source and drain **[276]**. As a result, the current is strongly controlled by the CNT diameter, chirality, contact geometry/type/thickness and oxide thickness, all of which modulate the barriers and present problems such as ambipolar conduction. Both inter and intraband tunnelling needs to be taken into account when modelling the transport. Furthermore, a cor-

rect treatment requires taking into account quantum confinement around the tube circumferential direction, quantum tunnelling through Schottky barriers at the metal/nanotube contacts, quantum tunnelling and reflection at barriers in the nanotube channel.
Limitations in predicting CNTFET transport arise both from theory and experiment. To date there has not been any demonstration of the relationship of the electrical property of a CNTFET to its physical structure. Notwithstanding limitations of experimental techniques, limitations of theory include many-body effects in the atomistic modelling of the CNT and the dependence of transport modelling on "fitting" parameters.
The main remaining challenges is to better understand high-bias transport regimes because of their relevance in device performances (high flow of current densities), as well as the possible control of Schottky-Barrier features by a proper choice of metal contacts/nanotubes characteristics/environment exposure/chemical functionalization, and so forth. Furthermore, the performances of nanotube-based vias also need to be increased by optimised control of tube growth processes.
In that respect, sophisticated computational modelling tools and expertise are clearly essential factors to allow the in-depth exploration of transport properties and device performance optimization.
European Position: In Europe, several groups have brought key contributions **[277]** to the fields of modelling carbon nanotubes physical (and transport) properties, mainly in Belgium (Jean-Christophe Charlier at University of Louvain), France with Xavier Blase (Institut Néel, Grenoble) and Stephan Roche (CEA Grenoble, France), and Spain with Angel Rubio (University of San Sebastian). These scientists are leading the international community in several fields from ab-initio computation of growth processes, electronic and vibrational properties, to the simulation of quantum transport in nanotubes-based materials and devices. Several other European groups are also contributing to the field of device simulation such as Giuseppe Iannaconne in Pisa (Italy), Kosina/Selberherr at TU Vienna, Giovanni Cuniberti at TU-Dresden in Germany, to cite a few. This community expert in theory and simulation is extremely important to sustain experimental efforts and device optimisation.

12(d) Single electron transistors

A single electron transistor (SET) is a device in which a quantum dot (QD) is connected with source and drain contacts through small tunnel junctions. A QD is a small metallic island in which electrons are confined. Therefore, it is sometimes compared with a natural atom, where electrons are confined in the Coulomb potential on a much smaller scale. When the discrete levels and the shell structure are clearly formed, the quantum dot is called an artificial atom. In the SWCNT QD, electrons are confined in the axial direction as well as the circumference direction.
Single electron transistor (SET) operation in single-walled carbon nanotubes (SWNTs) to estimate the length of ballistic conduction in laser-synthesized SWNTs has been investigated. The devices were fabricated by an alternating current-aligned method and the SWNTs were side-contacted to the electrodes. At 5 K, Coulomb oscillation and Coulomb diamonds were observed and the Coulomb island length, i.e., the ballistic conduction length, was calculated to be about 200-300 nm. Whilst many groups have published work in this area, as far as it can be ascertained, this is the only report of a true SET action in CNTs **[278]**.
European Position: Major efforts have been made in Japan including work in various companies such as Toshiba, Hitachi, NEC and NTT. The work in Europe tends to be at the more fundamental/University level.

13. Conclusions

CNTs have many unique and indeed useful properties for applications in the ICT area. Research into CNTs will continue for at least the next several years especially into quantum effects and associated behaviour, as well-characterized, high-quality SWCNTs become more available. Although CNTs are still being touted for various industrial applications, much more investment is necessary for them to reach commercial viability. The USA and Japan lead in this development but Europe has made significant impact in many areas despite the fact that investment in Europe is but a fraction of that in the other major high-tech industrial zones.

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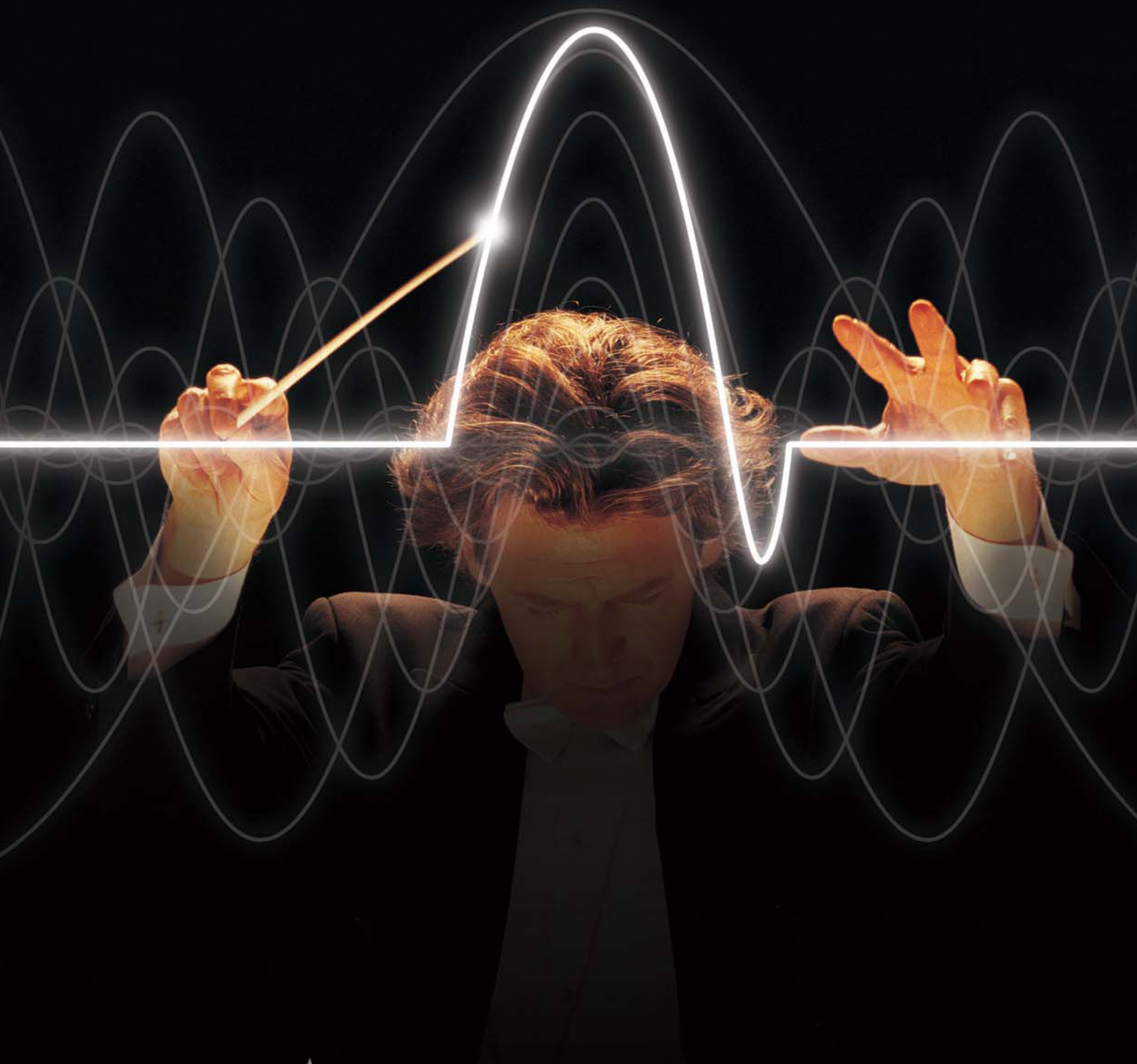

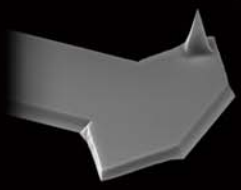

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Current status of modelling for nanoscale information processing and storage devices

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During the meeting of the Theory and Modelling working group, the current status of modelling for nanoscale information processing and storage devices has been discussed and the main issues on which collaboration within the modelling community is needed have been pointed out. An analysis of the current situation in Europe in comparison with that in the rest of the world has been performed, too.

Introduction

We are currently witnessing the final phase of the downscaling of MOS technology and, at the same time, the rise of a multiplicity of novel device concepts based on properties of matter at the nanoscale.

Ultra-scaled MOS devices and nanodevices relying on new physical principles share the reduced dimensionality and, as a result, many of the modelling challenges. In

addition, new materials and process steps are being included into MOS technology at each new node, to be able to achieve the objectives of the Roadmap; these changes make traditional simulation approaches inadequate for reliable predictions. So far, modelling at the nanoscale has been mainly aimed at supporting research and at explaining the origin of observed phenomena.

In order to meet the needs of the MOS industry and to make practical exploitation of new device and solid-state or molecular material concepts possible, a new integrated approach to modelling at the nanoscale is needed, as we will detail in the following. A hierarchy of multi-scale tools must be set up, in analogy with what already exists for microelectronics, although with a more complex structure resulting from the more intricate physical nature of the devices.

A coordinated effort in the field of modelling is apparent in the United States, where significant funding has been awarded to the Network for Computational Nanotechnology, which is coordinating efforts for the development of simulation tools for nanotechnology of interest both for the academia and for the industry.

Although the required integrated platforms need to be developed, the efforts made in the last few years by the modelling community have yielded significant advances in terms of quantitatively reliable simulation and of ab-initio capability, which represent a solid basis on which a true multi-scale, multi-physics hierarchy can be built. The combination of these new advanced software tools and the availability of an unprecedented and easily accessible computational power (in particular considering the recent advances in terms of GPU-based general purpose computing) make the time ripe for a real leap forward in the scope and performance of computational approaches for nanotechnology and nanosciences.

Current status of MOS simulation and industrial needs

The continuous downscaling of MOSFET critical dimensions, such as the gate length and the gate oxide thickness, has been a very successful process in current manufacturing, as testified, e.g., by the ITRS requirements. However, conventional scaling down of MOSFET channel length is declining as the physical and economic limits of such an approach are coming closer. Novel solutions are increasingly being used in MOSFET channel engineering within the industry.

Among the new technological features of very advanced devices, high-k dielectrics, the archetype of which is hafnium oxide, can significantly reduce gate leakage. Mechanical strain applied in the channel and substrate orientation can also significantly improve carrier mobility. Moreover, alternative geometries, such as double-gated devices, in which the channel doping level is relatively low, must be evaluated within the perspective of an industrial integration. In particular, the subsequent effects of the high-k gate dielectric and of the double-gate geometry on channel mobility must be clearly quantified.

Technology Computer-Aided Design (TCAD) refers to the use of computer simulations to develop and optimize semiconductor devices. State-of-the-art commercial TCAD device simulators are currently working using the Drift-Diffusion (DD) approximation of the Boltzmann transport equation. Quantum effects are accounted for using the Density Gradient approximation, that works well for traditional bulk devices, but that can be unreliable for advanced devices such as the double-gated-MOS structure or for new materials. Moreover, emerging materials also significantly challenge the conventional DD-based tools, mostly due to a lack of appropriate models and parameters. It becomes urgent to develop new physically-based models with a view of integrating them into a standardized simulation platform that can be efficiently used in an industrial environment. For this purpose, tight collaborations between world-class universities and research institutions, CAD vendors and industrial partners must be established. Within the framework of these collaborations, there will be the best chances of success, both in terms of academic model development and theoretical achievements, but also in terms of concrete implementations and benchmarks of new models in TCAD tools. Innovative concepts based on nano-materials or molecular devices, new models and simulation tools would provide our ICT industries a competitive advantage for device development and optimization in terms of time-cycle and wafer-costs.

Commercial v.s. academic quantum-transport solvers

In response to the industrial need of new simulation tools, a class of quantum and transport solvers is emerging. These commercial state-of-the-art solvers can be divided into two categories. In the first category, one can find the quantum-transport solvers, such as those based on the Non-Equilibrium Green Function Method, in which carrier transport is treated using the full quantum Green function formalism. In the second category one can include the Monte Carlo Solvers, that model carrier transport via the Boltzmann equation. This equation is solved in a stochastic way, using a classical description of the free fly of the electrons but a quantum description of the interactions. The currently available high-level NEG **[1]** and MC solutions **[2]** are still in the development phase, and no ready-to-use industrial solutions are available so far to meet the requirements of the 32 nm node and beyond.

From the point of view of technology development support, the Monte Carlo simulators should be able to provide reliable electrical results on a regular basis for 32 nm MOS devices. However the need for full-band Monte-Carlo codes together with bandstructure solvers that account for strain and are capable of dealing with new materials must be highlighted. Indeed, some commercial 3D Schroedinger solvers **[1]** combined with NEG solvers start being available. These solvers can be used to model ballistic quantum transport in advanced devices with strong transverse confinement. However, they do not include any inelastic scattering mechanism, and thus are not suitable for the calculation of transport properties in the 32 nm node devices and near-future nodes.

On the other hand, high-level device simulation tools are at an early stage of development in universities and research institutions. These codes generally include advanced physical models, such as strain-dependent bandstructure and scattering mechanism, and should provide accurate predictions in complex nano-systems.

However, such simulation tools are in general difficult to use in an industrial environment, in particular because of a lack of documentation, support and graphical user interface, although an increasing number of academic codes are now including graphic tools **[3,4]**. Taking advantage of these ongoing research projects, it should be possible to integrate such high-level codes into industrial TCAD tools or to use them to obtain calibrated TCAD models useful for the industry. Concerning this latter point, the quantum drift-diffusion-based solution must be "customized," in order to make fast and accurate simulations of advanced devices possible. For instance, the effect of the high-k gate dielectric stack on device performance must be addressed with a particular attention to its impact on carrier transport properties. This is definitely one of the most challenging issues in semiconductor industry at present.

Efficient modelling tools, as well as accurate physics highlights, would certainly bring a significant competitive advantage for the development and the optimization of the 32 nm CMOS technology and for future technologies including molecular devices.

Importance of modelling variability

Near the end of the current edition of the International Technology Roadmap for Semiconductors (ITRS) in 2018, transistors will reach sub-10 nm dimensions **[5]**. In order to maintain a good control of the electrical characteristics, new transistor architectures have to be developed. It is widely recognized that quantum effects and intrinsic fluctuations introduced by the discreteness of electronic charge and atoms will be major factors affecting the scaling and integration of such devices as they approach few-nanometer dimensions **[6-11]**.

For instance, in conventional one-gate nanotransistors, variations in the number and position of dopant atoms in the active and source/drain regions make each nano-transistor microscopically different from its neighbors **[12-16]**. In nanowire MOS transistors the trapping of one single electron in the channel region can change the current by over 90% **[17,18]**. Interface roughness of the order of 1-2 atomic layers introduces variations in gate tunneling, quantum confinement and surface/bulk mobility from device to device. The inclusion of new materials such as SiGe will induce additional sources of fluctuations associated with random variations in the structure, defects, strain and inelastic scattering **[19,20]**. These intrinsic fluctuations will have an important impact on the functionality and reliability of the corresponding circuits at a time when fluctuation margins are shrinking due to continuous reductions in supply voltage and increased transistor count per chip **[7,8]**.

The problem of fluctuations and disorder is actually more general and affects fundamental aspects of information storage and processing as device size is scaled down. The presence of disorder limits the capability of patterning by introducing a spatial variance: when the pattern size approaches the spatial variance, patterns are unavoidably lost. An analogous problem exists as a result of time fluctuations (shot noise) associated with the granularity of charge: as current levels are reduced, the signal power decreases faster (quadratically with current) than the shot noise power (linear with current), leading to a progressive degradation of the signal-to-noise power ratio.

Disorder has demonstrated all of its disruptive power on nanodevices in the case of single-electron transistors: as a result of their extreme charge sensitivity, stray charges, randomly located in the substrate, are sufficient to completely disrupt their operation.

Fluctuations associated with the granularity of charge and spatial disorder are fundamental roadblocks that affect any effort towards handling information on an increasingly small scale.

It is thus of strategic importance to develop device simulation tools that are capable of efficiently exploring the extremely large parameter space induced by such variability and evaluate the actual performance limits of new nanodevices. Strategies to decrease the amount of naturally occurring disorder or to cope with it need to be devised as emerging devices are developed into new technologies aiming at the limits of the downscaling process.

Integration between material and device simulation

Both for decananometric MOSFETs and for most emerging devices, the distinction between material and device simulation is getting increasingly blurred, because at low dimensional scales the properties of the material sharply diverge from those of the bulk or of a thin film and become strongly dependent on the detailed device geometry. Such a convergence should start being reflected also in research funding, because, at the dimensional scale on which research is currently focused, a project cannot possibly take into consideration only one of these two aspects. This was not the case until a few years ago, when a material could be investigated within the field of chemistry or material science and then parameters were passed on to those active in the field of device physics and design, who would include them in their simulation tools.

Fortunately, the nanoelectronics simulation community is not starting from scratch in terms of atomic scale materials computations. Computational physics and quantum chemistry researchers have been developing sophisticated programs, some with on the order of millions of lines of source code, to explicitly calculate the quantum mechanics of solids and molecules from first principles. Since quantum mechanics determines the charge distributions within materials, all electrical, optical, thermal and mechanical properties, in fact any physical or chemical property, can in principle be deduced from these calculations.

However, these programs have not been written with nanoelectronic TCAD needs in mind, and substantial theoretical and computational problems remain before their application in process and device modeling reaches maturity. However, the coupling of electronic structure theory programs to information technology simulations is occurring now, and there is nothing to suggest this trend will not continue unabated.

Quantum electronic structure codes come in essentially two flavors: plane wave and Gaussian expansions. The plane wave codes are suitable for solid state calculations, and Gaussian codes have emerged from molecular applications (there are many programs not fitting this blatant

stereotyping, but there are many more that do). Interestingly, it seems that the requirements of modern device design imply the necessity of plane wave type expansions for electrons injected into devices, yet more localized expansions, such as Gaussian functions, to describe the chemical bonding within material structures. This combined approach was advocated by many in the early days of solid-state calculations, but seems to have fallen by the wayside due mainly to historical reasons. Electronic structure theory represents the lowest level of computation in our simulation hierarchy, and at this level there are many different degrees of rigor and associated errors in the computations. The ability to treat varying length and time scales, within varying degrees of approximation, leads to the requirement for a multi-scale approach to coupled materials/device simulation.

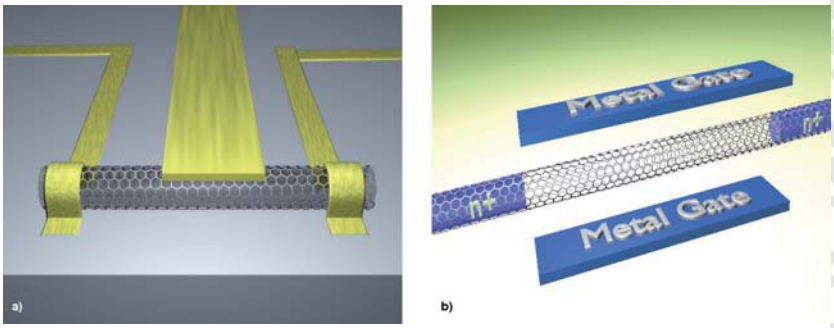

Figure 1: *Artist's representation of the model for the simulation of a single* ***(a)*** *and a double* ***(b)*** *gate carbon nanotube transistors.*

Although a multi-scale approach is more than ever needed at this stage, parameter extraction cannot be performed for a generic material, but must be targeted for the particular device structure being considered, especially for single-molecule transistors. There has to be a closed loop between the atomistic portion of the simulation and the higher-level parts, guaranteeing a seamless integration. This convergence between material and device studies also implies that a much more interdisciplinary approach than in the past is needed, with close integration between chemistry, physics, engineering, and, in a growing number of cases, biology. To make an example, let us consider the simulation of a silicon nanowire transistor: atomistic calculations are needed to determine the specific electronic structure for the cross-section of the device being investigated, then this information can be used in a full-band solver for transport or parameters can be extracted for a simpler and faster transport analysis neglecting interband tunneling; then the obtained device characteristics can be used for the definition of a higher-level model useful for circuit analysis. It is apparent that, for example, the atomistic simulation is directly dependent on the device geometry, and that, therefore, work on the different parts of the simulation hierarchy has to be performed by the same group or by groups that are in close collaboration.

One of the main challenges for modelling in the next few years is thus the creation of well organized collaborations with a critical mass sufficient for the development of integrated simulation platforms and with direct contacts with the industrial world.

Beyond silicon simulation

Amongst the most promising materials for the development of beyond CMOS nanoelectronics, Carbon Nanotubes & Graphene-based materials and devices deserve some particular consideration. Indeed, first, their unusual electronic and structural physical properties promote carbon nanomaterials as promising candidates for a wide range of nanoscience and nanotechnology applications. Carbon is unique in possessing allotropes of each possible dimensionality and, thus, has the potential versatility of materials exhibiting different physical and chemical properties. Diamond (3D), fullerenes (0D), nanotubes (1D-CNTs), 2D graphene and graphene ribbons are selected examples. Because of their remarkable electronic properties, CNTs or graphene-based materials should certainly play a key role in future nanoscale electronics. Not only metallic nanotubes and graphene offer unprecedented ballistic transport ability, but they are also mechanically very stable and strong, suggesting that they would make ideal interconnects in nanosized devices. Further, the intrinsic semiconducting character of either nanotubes or graphene nanoribbons, as controlled by their topology, allows us to build logic devices at the nanometer scale, as already demonstrated in many laboratories (see **Figure 1** for possible implementations of a CNT transistor and **Figure 2** for an artist's view of a graphene nanoribbon device). In particular, the combination of 2D graphene for interconnects (charge mobilities in graphene layers as large as 400.000 $cm^2V^{-1}s^{-1}$ have been reported close to the charge neutrality point) together with graphene nanoribbons for active field effect transistor devices could allow the implementation of completely carbon-made nanoelectronics. To date, the development of nanotubes and graphene science have been strongly driven by theory and quantum simulation **[21,22]**. The great advantage of carbon-based materials and devices is that, in contrast to their silicon-based counterparts, their quantum simulation can be handled up to a very high level of accuracy for realistic device structures. The complete understanding and further versatile monitoring of novel forms of chemically-modified nanotubes and graphene will however lead to an increasing demand for more sophisticated computational approaches, combining first principles results with advanced order N schemes to tackle material complexity and device features, as developed in some recent literature **[23].**

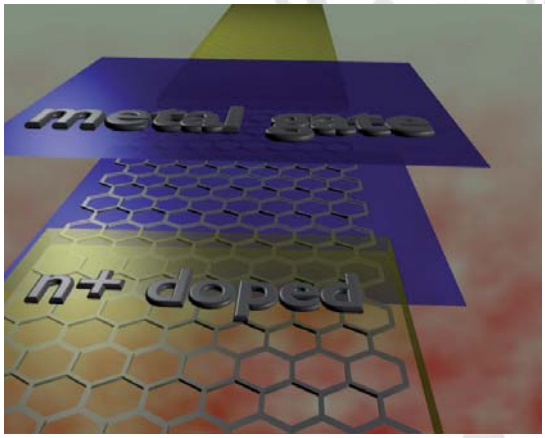

Figure 2: *Double-gate graphene nanoribbon transistor.*

Molecular electronics research continues to explore the use of single molecules as electron devices or for even more complex functions such as logic gates. Experimentally and theoretically the majority of research work concentrates on single molecules between two metallic electrodes or molecular tunnel junctions.
Reproducibility of the measurements and accurate predictions for currents across single molecule tunnel junctions remains a challenging task, although the results of theory and experiment are converging **[24]**. To achieve the goal of using molecular components for computing or storage, or indeed for novel functions, requires refinement of the theoretical techniques to better mimic the conditions under which most experiments are performed. Hence much of the work to date has focused on the underlying physical mechanisms of charge transport across molecules, whereas very little is understood in terms of the use of molecular components in complex, or even simple, circuits. This research area could also be categorized as in its infancy in that very little is known about time-dependent or AC responses of molecules in tunnel junctions or other circuit environments. To exploit molecules in information processing, the use of multi-scale tools as described previously are needed to embed molecular scale components between what are essentially classical objects: leads, dri-vers, and circuits. Further development of the simulations is needed to describe the time-dependent response of the molecules to external voltages and their interaction with light.

Major current deficiencies of TCAD

A clear gap, which has in part been addressed in the previous sections, has formed in the last few years between what is available in the TCAD market and what would actually be needed by those working on the development of advanced nanoscale devices. As already mentioned, classical TCAD tools have not been upgraded with realistic quantum transport models yet, suitable for the current 32 nm node in CMOS technology or for emerging technologies, and, in addition, there are some fields of increasing strategic importance, such as the design of photovoltaic cells, for which no well-established TCAD platforms exist.
Bottom-up approaches, which, if successful, could provide a solution to one of the major bottlenecks on the horizon, i.e. skyrocketing fabrication costs, are not supported by any type of TCAD tools as of now. This may be due to the fact that bottom-up approaches are still in their infancy and have not been demonstrated in any large-scale application, but the existence of suitable process simulation tools could, nevertheless, facilitate their development into actual production techniques. Sophisticated tools that have been developed within research projects are available on the web, mainly on academic sites, but they are usually focused on specific problems and with a complex and non-standardized user interface. An effort would be needed to coordinate the research groups working on the development of the most advanced simulation approaches, the TCAD companies and the final users, in order to

define a common platform and create the basis for multi-scale tools suitable to support the development of nano-electronics in the next decade.

New computational approaches

The development of highly parallel and computationally efficient graphic processors has recently provided a new and extremely powerful tool for numerical simulations. Modern Graphic Processing Units (GPU) approach a peak performance of a Teraflop (10^{12}) floating point operations per second) thanks to a highly parallel structure and to an architecture focusing specifically on data processing rather than on caching or flow control. This is the reason why GPUs excel in applications for which floating point performance is paramount while memory bandwidth in not a primary issue. In particular, GPU hardware is specialized for matrix calculations (fundamental for 3D graphic rendering), which do represent also the main computational burden in many types of device simulations.

As a result, speed ups of the order of 30 - 40 have been observed, for tasks such as the simulation of nanoscale transistors, with respect to state-of-the-art CPUs. Up to now the main disadvantage was represented by the availability, in hardware, only of single-precision operations, but last generation GPUs, such as the FireStream 9170 by AMD, are advertised as capable of handling double precision in hardware, although at a somewhat reduced rate (possibly by a factor of 5). Another impressive feature of GPU computation is the extremely high energy efficiency, of the order of 5 Gigaflops/W in single precision or 1 Gigaflop/W in double precision, an aspect of growing importance considering the costs for supplying power and air conditioning to computing installations.

The latest GPU hardware opens really new perspectives for simulation of nanodevices, also in "production environments," because GPU based systems could be easily standardized and provided to end-users along with the simulation software. Overall, this is a field that deserves investing some time and effort on the part of the device modelling community, because it could result in a real breakthrough in the next few years.

Overview of networking for modelling in Europe and the United States

In the United States, the network for computational nanotechnology (NCN) is a six-university initiative established in 2002 to connect those who develop simulation tools with the potential users, including those in academia, and in industries. The NCN has received a funding of several million dollars for 5 years of activity. One of the main tasks of NCN is the consolidation of the **www.nanoHUB.org** simulation gateway, which is currently providing access to computational codes and resources to the academic community. According to NCN survey **[23]**, the total number of users of nanoHUB.org reached almost 70,000 in March 2008, with more than 6,000 users having taken advantage of the online simulation materials. The growth of the NCN is likely to attract increasing attention to the US computational nanotechnology platform from all over the world, from students, as well as from academic and, more recently, industrials researchers. In Europe an initiative similar to the nanoHUB, but on a much smaller scale, was started within the Phantoms network of excellence **(http://vonbiber.iet.unipi.it)** and has been active for several years; it is currently being revived with some funding within the NanoICT coordinated action.

In a context in which the role of simulation might become strategically relevant for the development of nanotechnologies, molecular nanosciences, nanoelectronics, nanomaterial science and nanobiotechnologies, it seems urgent for Europe to set up a computational platform infrastructure similar to NCN, in order to ensure its positioning within the international competition. The needs are manifold. First, a detailed identification of European initiatives and networks must be performed, and defragmentation of such activities undertaken. A pioneer initiative has been developed in Spain through the M4NANO database (**www.m4nano.com**) gathering all nanotechnology-related research activities in modelling at the national level. This Spanish initiative could serve as a starting point to extend the database to the European level. Second, clear incentives need to be launched within the European Framework programmes to encourage and sustain networking and excellence in the field of computational nanotechnology and nanosciences. To date, no structure such as a Network of Excellence exists within the ICT programme, although the programme NMP supported a NANOQUANTA NoE in FP6, and infrastructural funding has been provided to the newly established ETSF (European Theoretical Spectroscopy Facility, **www.etsf.eu**). This network mainly addresses optical characterization of nanomaterials, and provides an open platform for European users, that can benefit from the gathered excellence and expertise, as well as standardized computational tools. There is also a coordinated initiative focused on the specific topic of electronic structure calculations, the Psi-k network (**www.psi-k.org**).

An initiative similar to the American NCN would be needed in Europe, within the ICT programme that encompasses the broad fields of devices and applications or, better, in conjunction between the ICT and the NMP programme, since the full scope from materials to devices and circuits should be addressed.

Past, present and future European advances in computational approaches

This novel initiative should be able to bridge advanced ab-initio/atomistic computational approaches to ultimate high-level simulation tools such as TCAD models that are of crucial importance in software companies. Many fields such as organic electronics, spintronics, beyond CMOS nanoelectronics, nanoelectromechanical devices, nano-sensors, nanophotonics devices definitely lack standardized and enabling tools that are however mandatory to assess the potential of new concepts, or to adapt processes and architectures to achieve the desire functionalities. The European excellence in these fields is well known and in many aspects overcomes that of the US or of Asian countries. Within the framework of a new initiative, specific targets should be addressed in relation with the modelling needs reported by small and medium sized software companies active in the development of commercial simulation tools, such as SYNOPSYS (**www.synopsys.com**), NANOIDENT (**http://www.nanoident.com**),

NANOTIMES (www.nanotimes-corp.com), SILVACO (www.silvaco.fr), NEXTNANO3 (www.nextnano.de), TIBERCAD (www.tibercad.org).

Similarly, larger companies such as STMicroelectronics, Philips, THALES, IBM, INTEL make extensive usage of commercial simulation tools to design their technological processes, devices and packaging. The sustainable development of the computational simulation software industry, including innovative materials (carbon nanotubes, graphene, semiconducting nanowires, molecular assemblies, organics, magnetic material) and novel applications (spintronics, nanophotonics, beyond CMOS nanoelectronics), could therefore be crucial to foster industrial innovation in the next decade.

Conclusions

Recent advances in nanoscale device technology have made traditional simulation approaches obsolete from several points of view, requiring the urgent development of a new multiscale modelling hierarchy, to support the design of nanodevices and nanocircuits. This lack of adequate modeling tools is apparent not only for emerging devices, but also for aggressively scaled traditional CMOS technology, in which novel geometries and novel materials are being introduced. New approaches to simulation have been developed at the academic level, but they are usually focused on specific aspects and have a user interface that is not suitable for usage in an industrial environment. There is therefore a need for integration of advanced modelling tools into simulators that can be proficiently used by device and circuit engineers: they will need to include advanced physical models and at the same time be able to cope with variability and fluctuations, which are expected to be among the greatest challenges to further device downscaling.

In addition, as dimensions are scaled down, the distinction between material and device properties becomes increasingly blurred, since bulk behavior is not observed any more, and atomistic treatments are needed. There is therefore a convergence between material and device research, which should be reflected also in the formulation of research projects. Furthermore, new materials, such as carbon, are emerging, with an impressive potential for device fabrication and with completely new requirements for simulation.

A unique opportunity is now surfacing, with powerful new modeling approaches being developed and new low-cost computational platforms (such as GPUs) with an unprecedented floating point performance. The combination of these two factors makes it clear that the time is ripe for a new generation of software tools, whose development is of essential importance for the competitiveness and sustainability of European ICT industry, and which requires a coordinated effort of all the main players.

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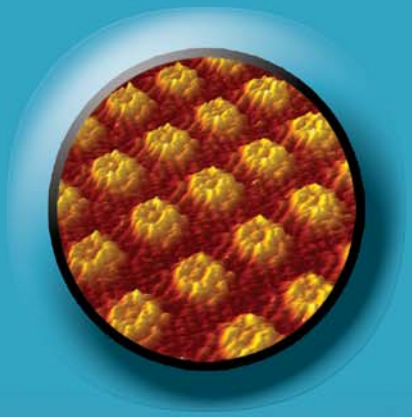
SURFACE ANALYSIS

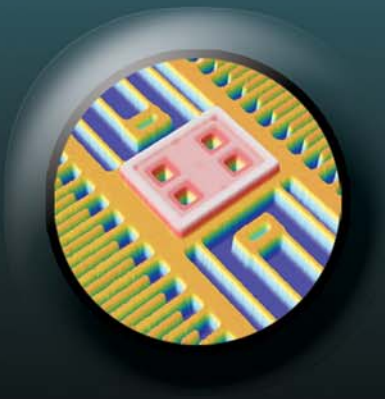


AFM / STM

Materials, polymers, biology, electrochemistry...

SNOM Microscopy

Reflection, transmission, Apertureless...
SECM, Deep Trench, nanopipette probes...



3D Optical Profilometry

New confocal technology...
Interferometry (PSI/VSI)...

And also...

Mechanical profilometry, nano-indentation...

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