Carbon Nanotube Working Group NanoICT

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NanoICT – Carbon Nanotubes: September 2008

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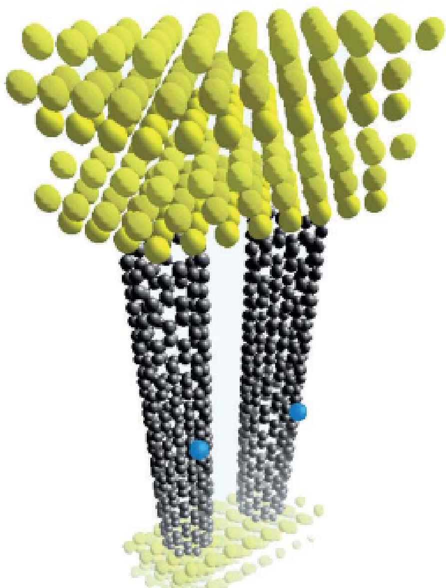
http://www.phantomsnet.net



nanoICT coordination action

NanoICT Position Papers

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

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]

[1] Cambridge University, UK; [2] CEA, Grenoble, France; [3] Philips Research Laboratories, Aachen, Germany; [4] University of Ulster, UK; [5] AIXTRON, Germany; [6] Sheffield University, UK; [7] TU Denmark; [8] Oxford University, UK; [9] CEA-LETI, Grenoble, France (Formely Nanomix Inc. USA); [10] CEA-INAC, Grenoble, France; [11] CEA-LETI, France

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

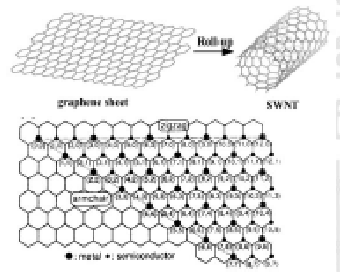


Figure 1: (top) A graphene sheet rolled up to obtain a single-walled CNT. (bottom) The map shows the different single-walled CNT configurations possible. Were the graphene sheet to roll up in such a way that the atom at (0,0) would also be the atom at (6,6), then the CNT would be metallic. Likewise, 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].

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].

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

Talk Summary

What are carbon nanotubes?

What determines their properties?

How are carbon nanotubes made?

- -Summary of growth methods.
- -Controlling the growth by CVD

Applications (and challenges)

- -Thermal management
- -Transparent conductors
- -Supercapacitors and batteries
- -Summary of other applications

Research Agenda

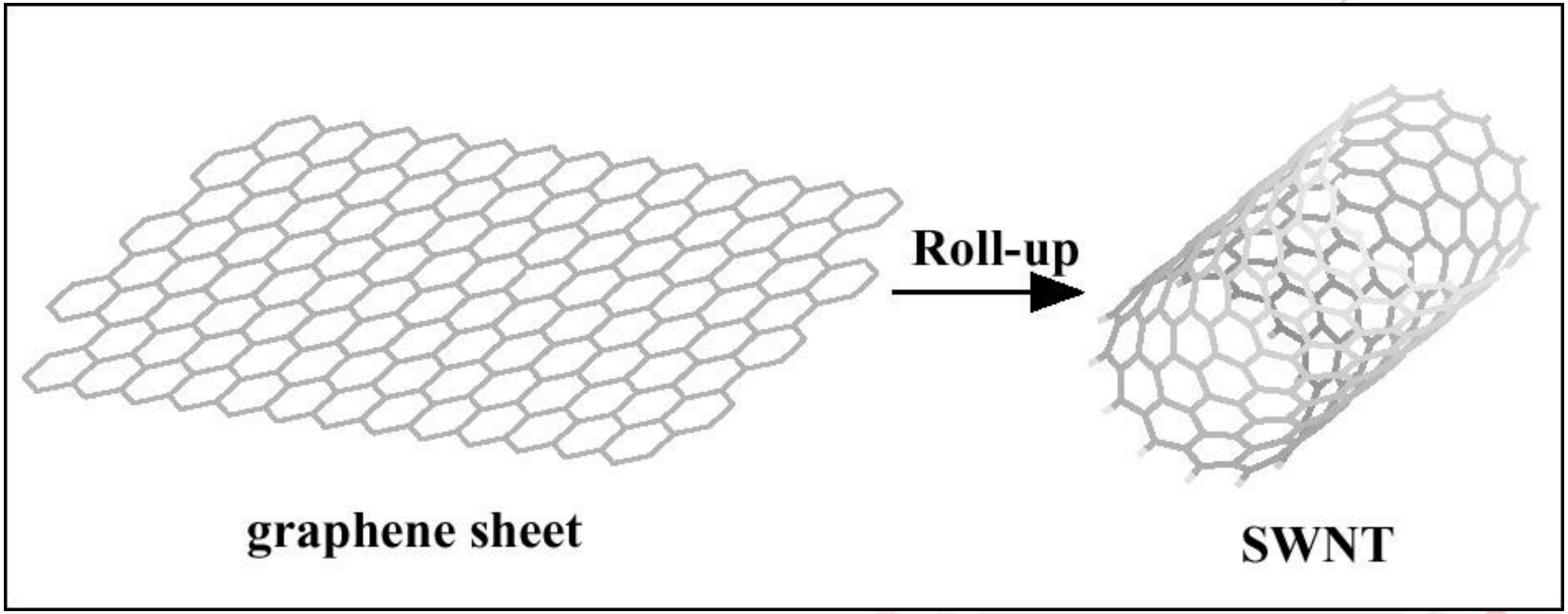
Working Group activities

Future NanoICT sponsored symposia

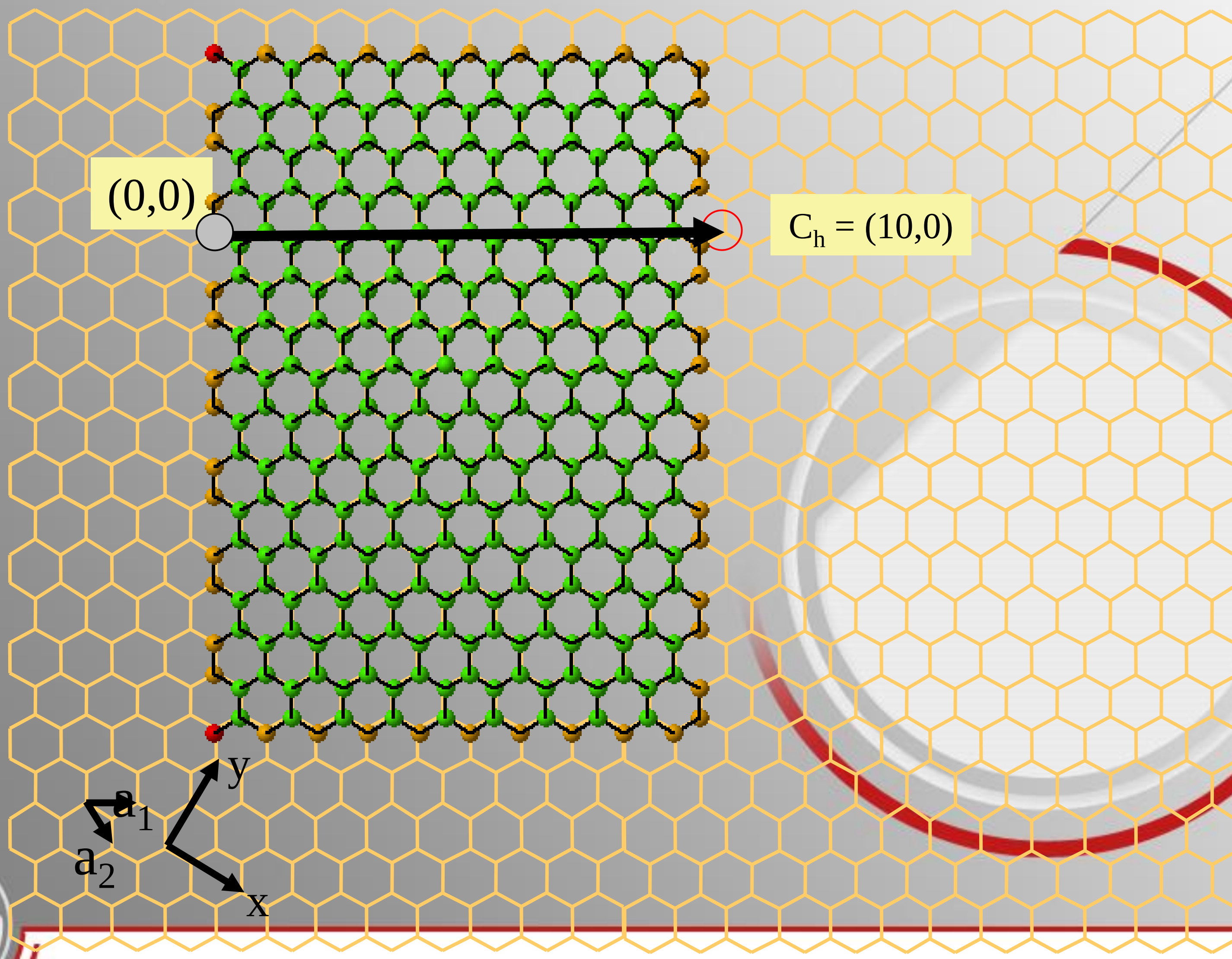
(For more refer to:

“Carbon Nanotubes” W.I. Milne, **M. Mann**, J. Dijon, P. Bachmann, J. McLaughlin, J.Robertson, K.B.K. Teo, A. Lewalter, M. de Souza, P. Boggild, A Briggs, K. Bo Mogensen, J.-C. P. Gabriel, S. Roche and R.Baptist. E-Nano Newsletter nº 13 (2008).)

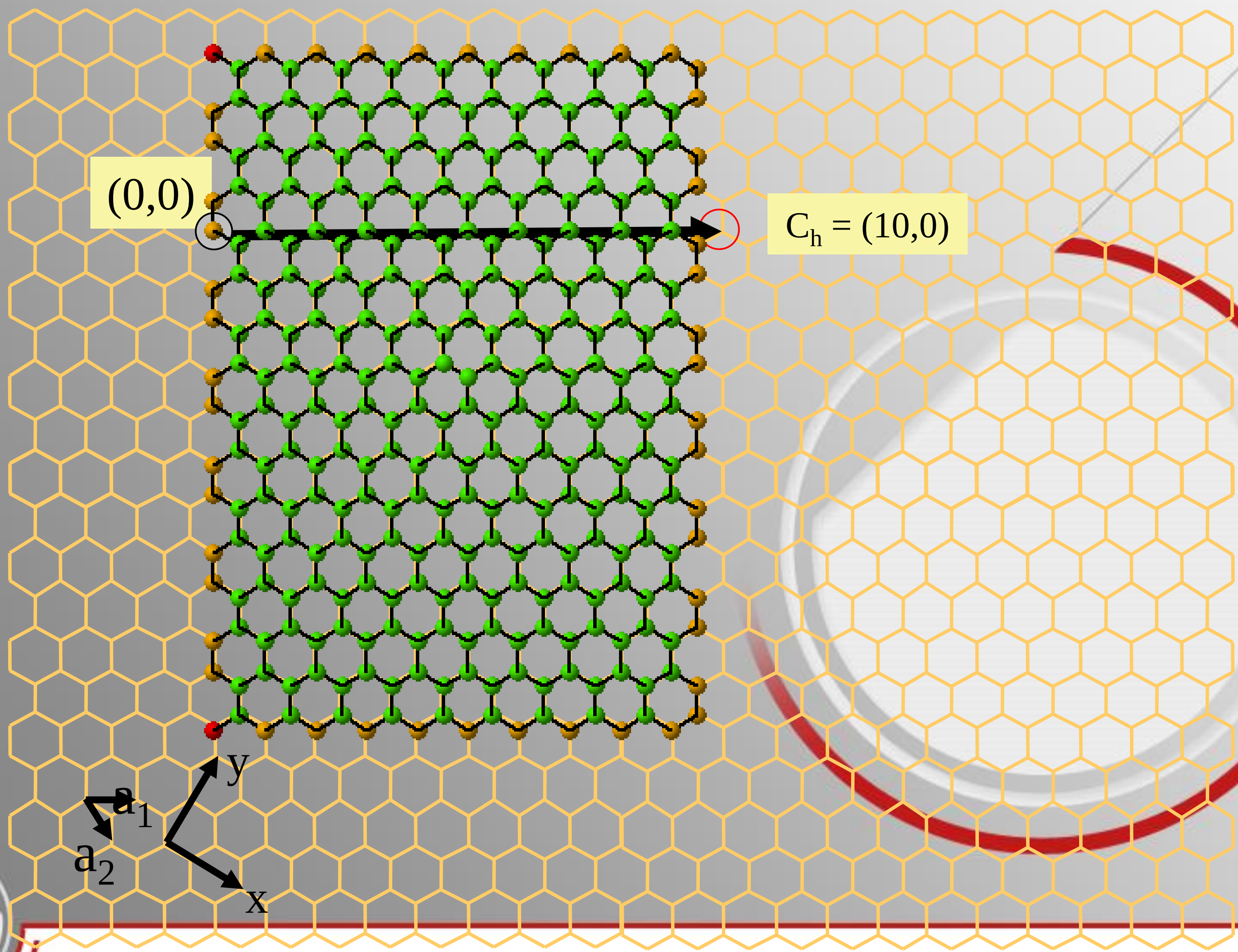
What are Carbon Nanotubes?



Wrapping (10,0) SWNT (zigzag)

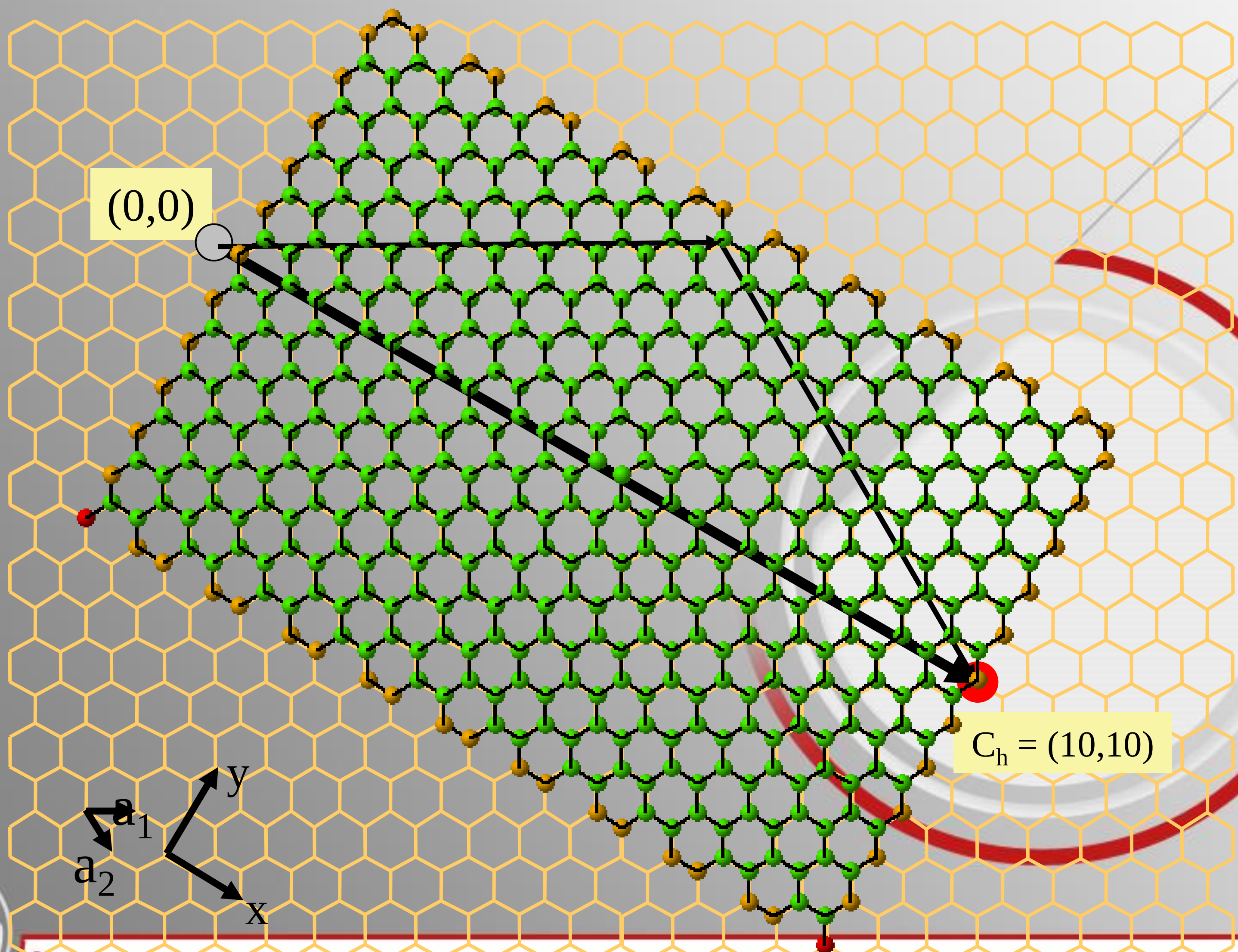


Wrapping (10,0) SWNT



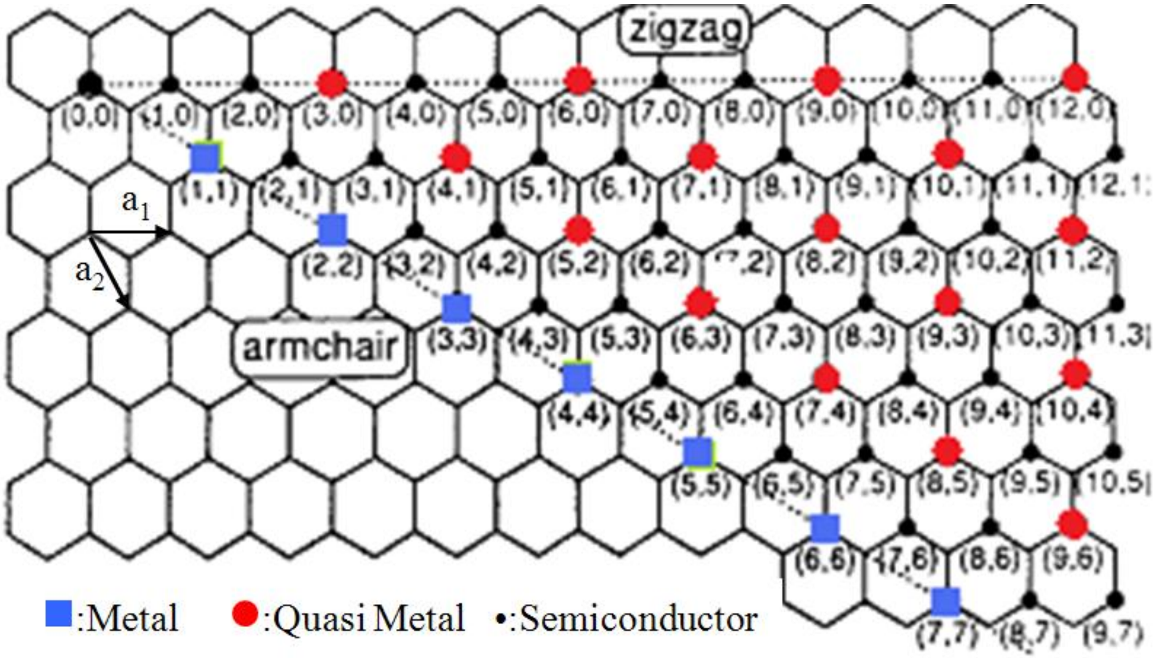
Animation: Shigeo Maruyama, Tokyo University

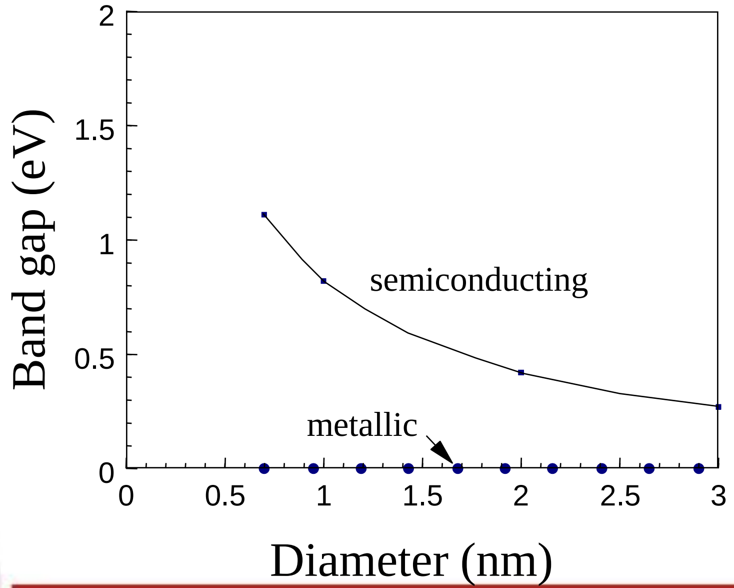
Wrapping (10,10) SWNT (armchair)



Animation: Shigeo Maruyama, Tokyo University

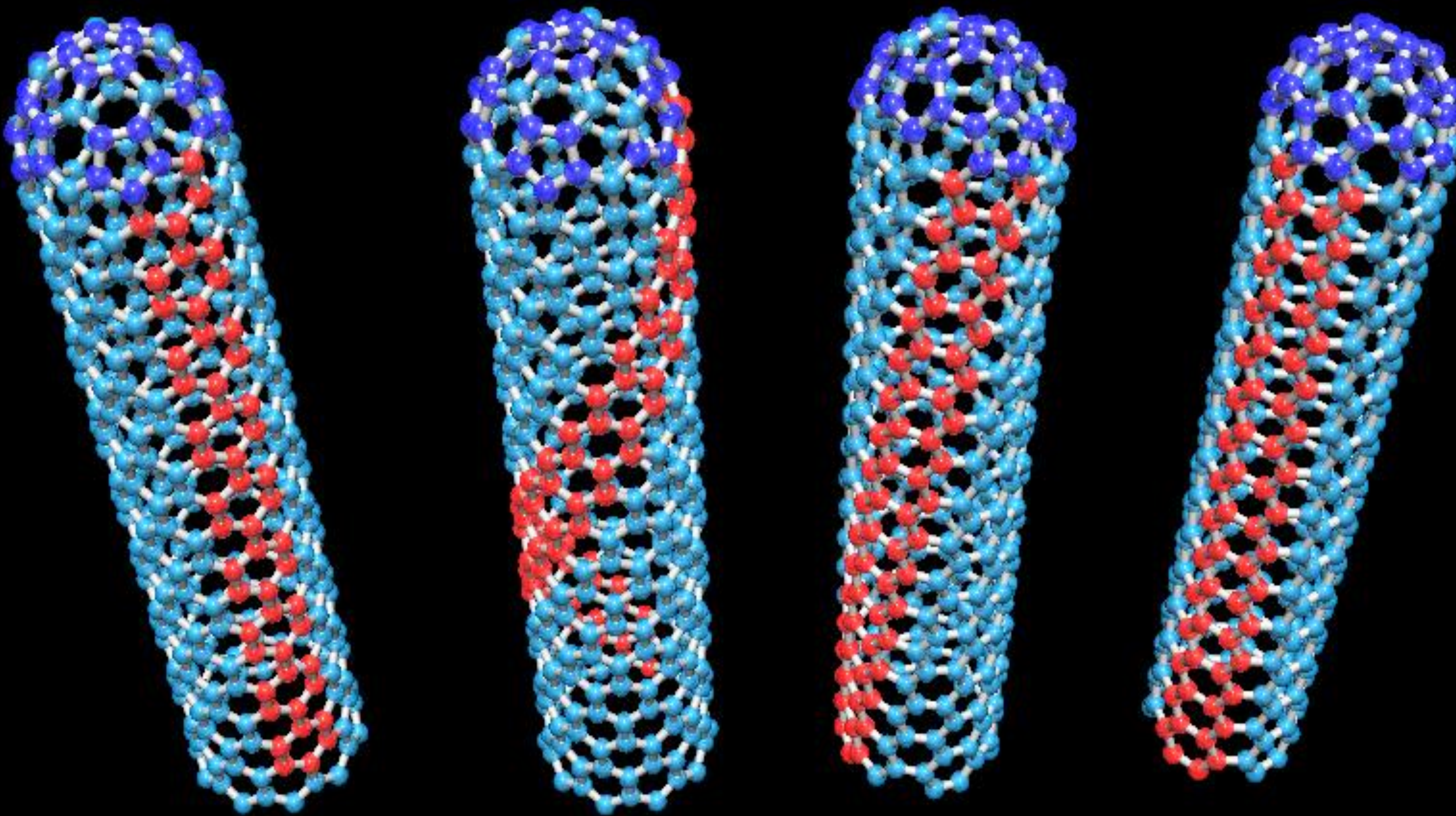
2/3 semiconducting
1/3 metallic





Saito

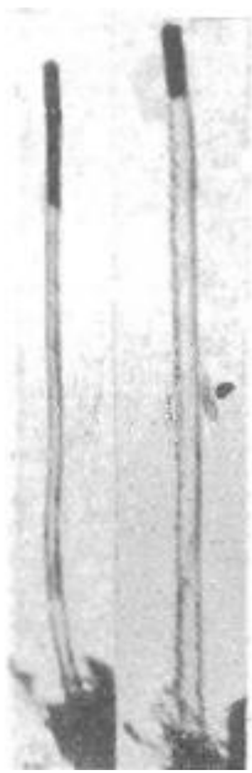
Picture: M. Endo

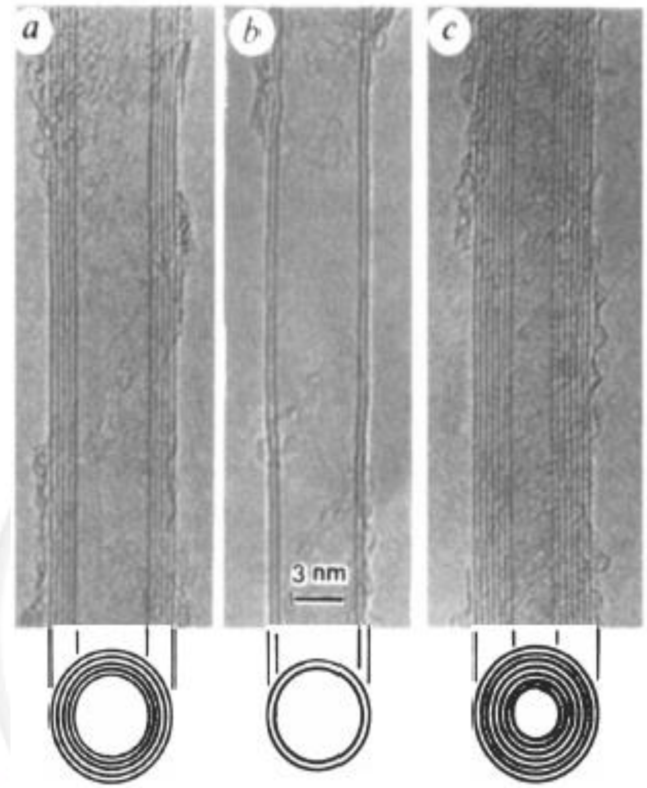


Zigzag-tube Chiral-tube Armchair-tube

Multi-walled Carbon Nanotubes

- Rolled up graphite sheets
- Multi-walled are "semi-metallic"



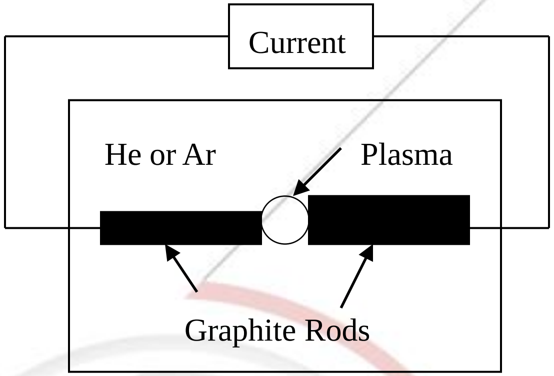


L. V. Radushkevich and V. M. Lukyanovich. (1952). *Soviet Journal of Physical Chemistry* **26**: 88–95.

Synthesis Techniques

1. Arc-discharge Method

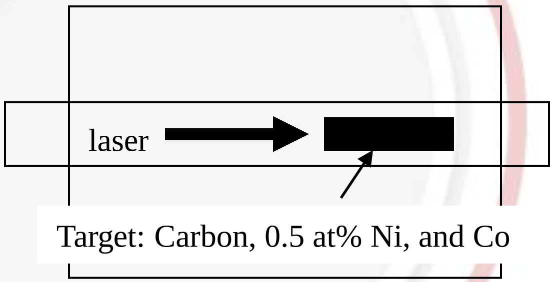
- Producing MWNT & SWNT
- Two graphite rods are used as electrodes and He or Ar gas used for inert atmosphere condition during arc-discharge



(a) arc-discharge

2. Laser Ablation Method

- Producing SWNT
- Intense laser pulses are utilized to ablate a carbon target containing 0.5at % of nickel and cobalt.



(b) laser ablation

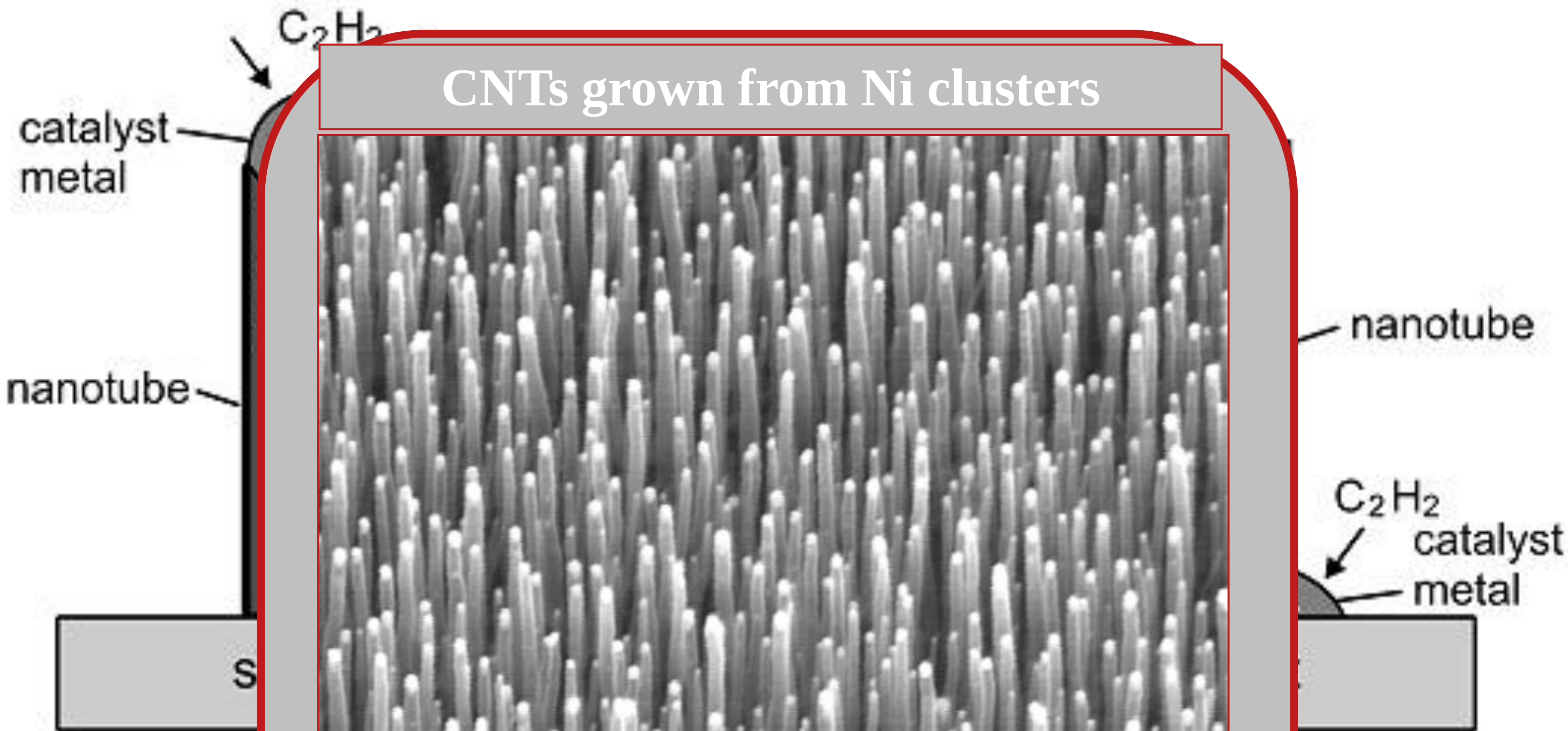
*** Advantage** -Production of high quality carbon nanotubes

*** Disadvantages** -High temperature process

-Grow carbon nanotubes in highly tangled forms with unwanted carbon and metal impurities.- need to purify

-Hard to control

Catalytic Chemical Vapour Deposition



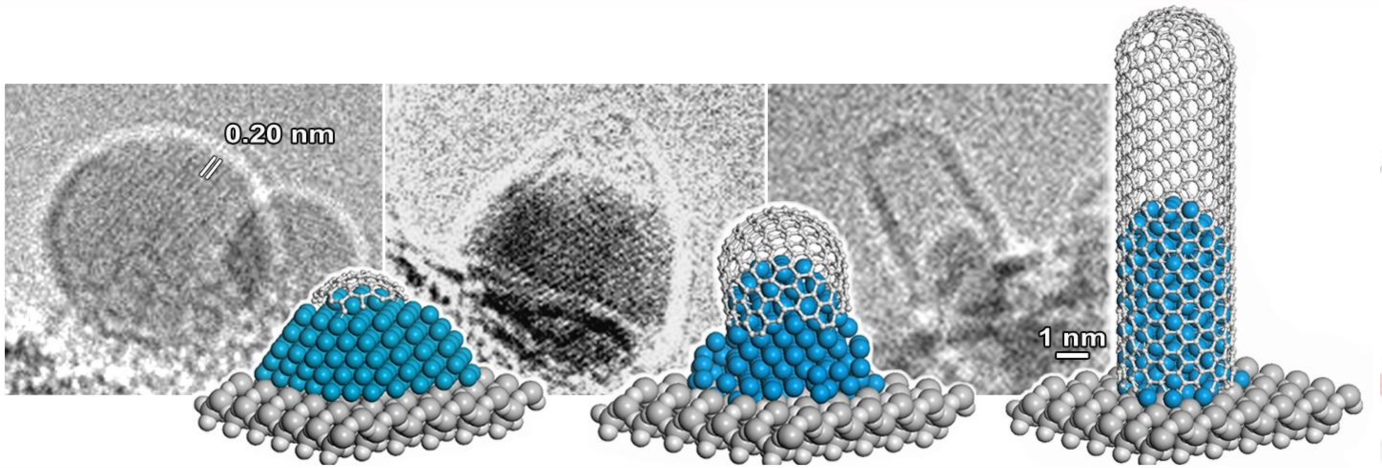
CNTs grown from Ni clusters

1µm

Bright dot at CNT top = catalyst cluster

Advantag … trate growth
vertical fl …
Disadvanta …

Carbon Nanotube growth by CVD

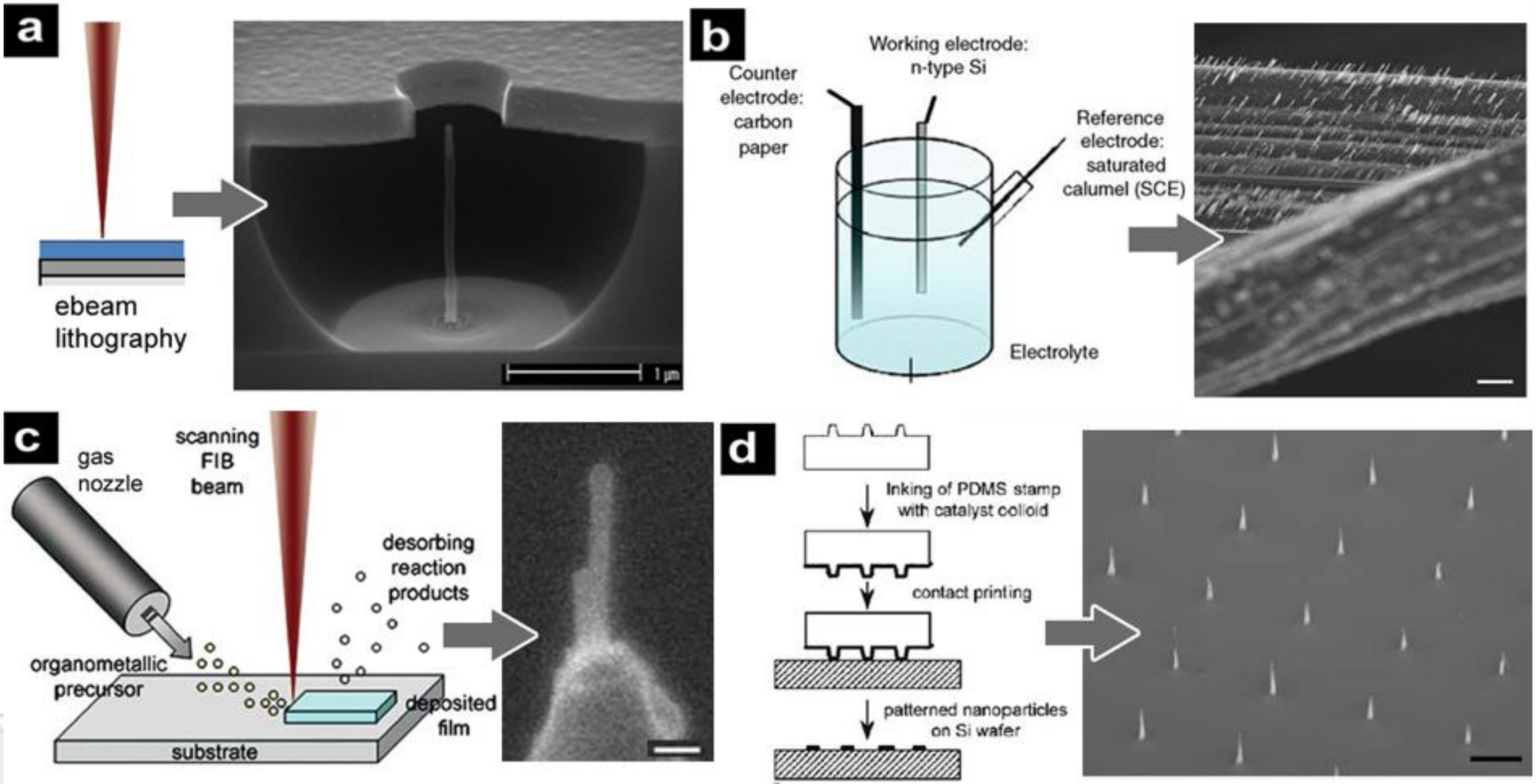


Environmental-TEM image sequence of Ni-catalyzed SWNT root growth recorded in 8×10^{-3} mbar C_2H_2 at 615 °C and schematic ball-and-stick model.

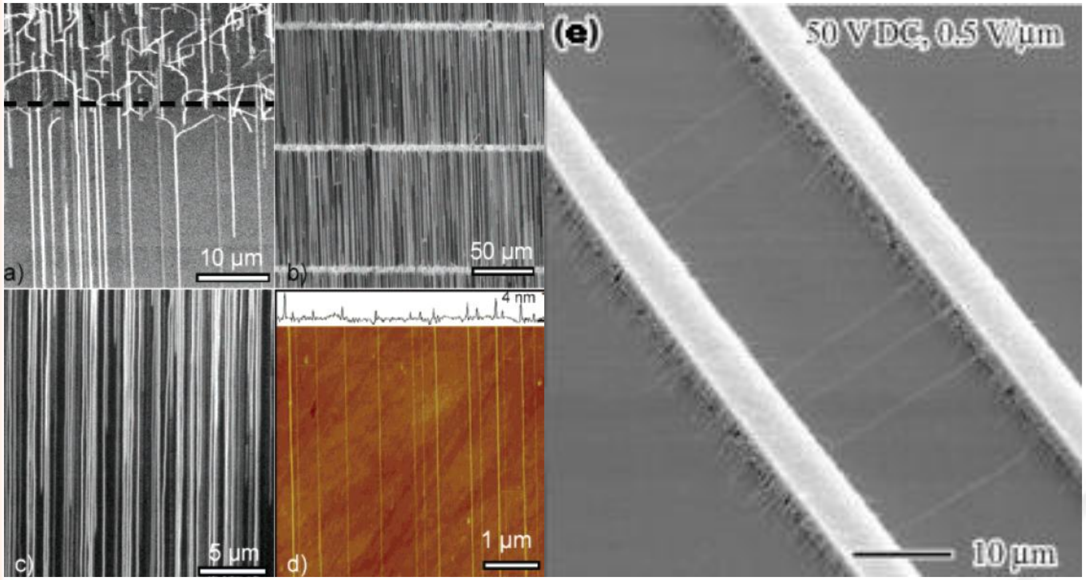
S. Hofmann *et al.*, *Nano Lett.* **7**, 602 (Mar, 2007).

Catalyst preparation

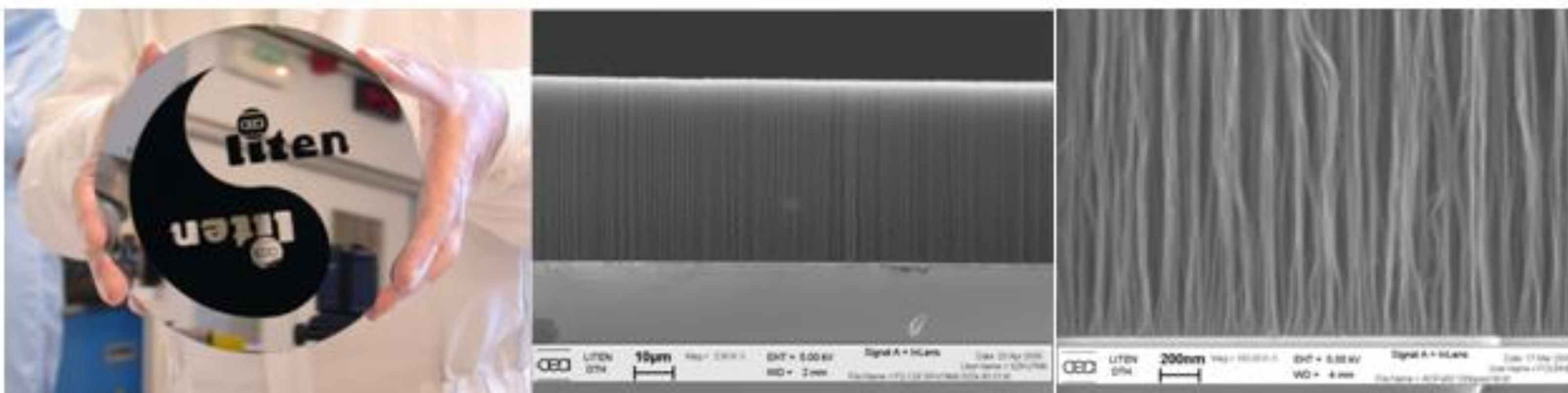
For bulk growth, thin films are deposited by PVD or by wet chemistry



Growth possible by CVD and PECVD



Left: (a-d) CNTs grown along quartz crystal planes by the Rogers group
Seong Jun Kang *Nature Nanotechnology* **2**, 230 - 236 (2007)
(e) Horizontally aligned CNTs grown by Dai's group using field to align the CNTs.
Y. Zhang, Y. Li, W. Kim, D. Wang, H. Dai, *Appl. Phys. A* **74**, 325 (Mar, 2002).



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)

Uniqueness of CNTs

MECHANICAL PROPERTIES	
Young's modulus of multi-walled CNTs	~0.8-1.3 Tpa [28, 29]
Young's modulus of single-walled CNTs	~1-1.3 TPa[30, 31]
Tensile strength of single-walled nanotube ropes	> 45 GPa[32]
Tensile strength of multi-walled nanotube ropes	1.72GPa[33]
Stiction	~10^{-7} N on 5 µm latex beads[34]
Hydrophobicity of MWNT forest	126^{o}[35]-161^{o}[36] contact angle
THERMAL PROPERTIES AT ROOM TEMPERATURE	
Thermal conductivity of single-walled CNTs	1750-5800 WmK[37]
Thermal conductivity of multi-walled CNTs	>3000 WmK[38]
ELECTRICAL PROPERTIES	
Typical resistivity of single- and multi-walled CNTs	10^{-8} - 10^{-6} Ωm[39]
Typical maximum current density	>10^{8} A cm^{2}[40]
Quantized conductance, theoretical/measured	$(6.5\ k\Omega)^{-1}/(12.9\ k\Omega)^{-1}$ per channel
ELECTRONIC PROPERTIES	
Single-walled CNT band gap	
Whose n=m, armchair	0 eV (metallic)
Whose n-m is divisible by 3	<0.1eV (quasi metallic)[41]
Whose n-m is non-divisible by 3	0.4-2eV(semiconducting)[42, 43]
Multi-walled CNT band gap	~0 eV (non-semiconducting)

Applications: in order of distance to market combined with size of market

Thermal management

Transparent conductors/contacts.

Batteries/supercapacitors

Interconnects/vias

Sensors (bio-medical sentence)

Field emission (SEM/TEM, backlighting, FED Microwave, x-ray, electronic propulsion)

NEMS/MEMS

Fuel Cells

Solar panels

Nanofluidics

Liquid crystal microlenses

Transistors (flexible, large area, high frequency)

Quantum computing etc

Thermal management

As a thermal interface material for high brightness LED's, CNT has been shown to outperform silver epoxy and other metal systems

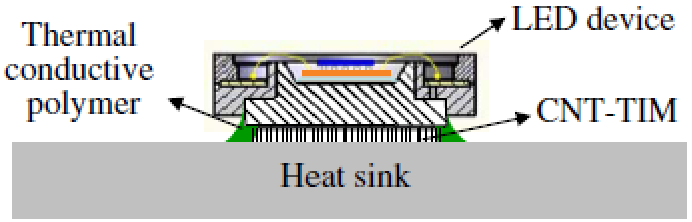


Figure 3. Schematic side view of an HB-LED package with CNT-TIM.

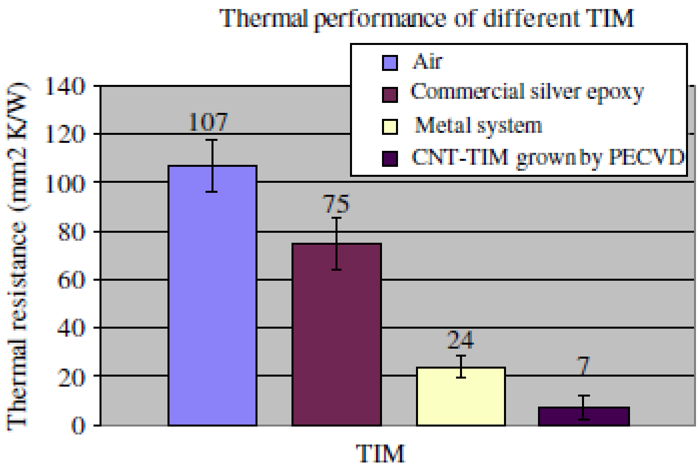
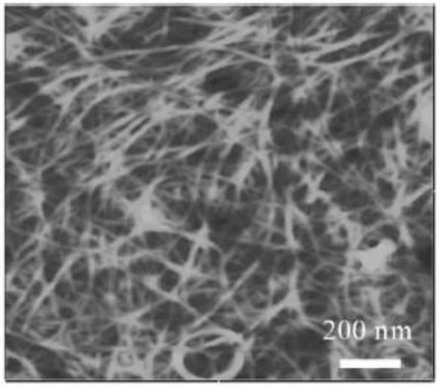
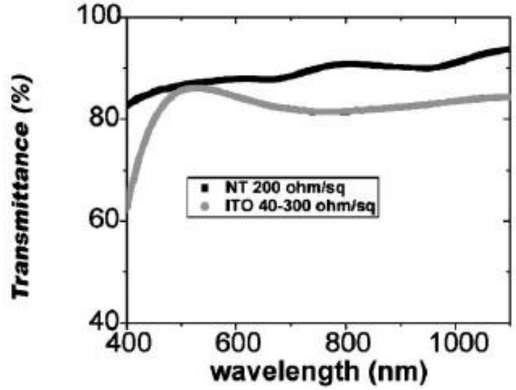


Figure 5. Measured total thermal resistance R^{TIM} of different TIMs.

Transparent conductors



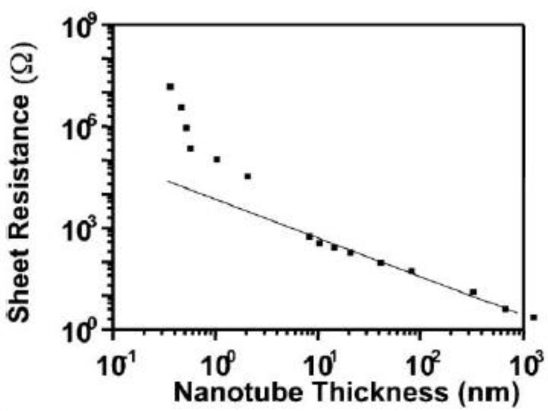
(a)

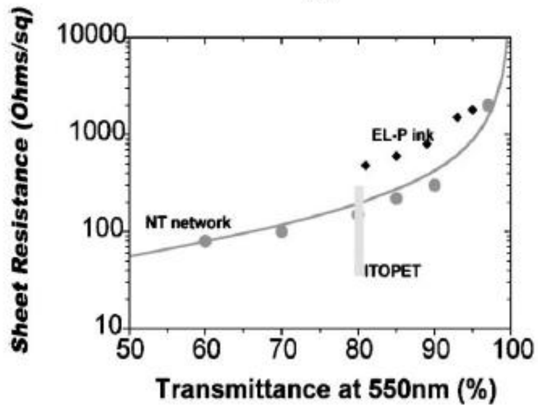


(a)

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.

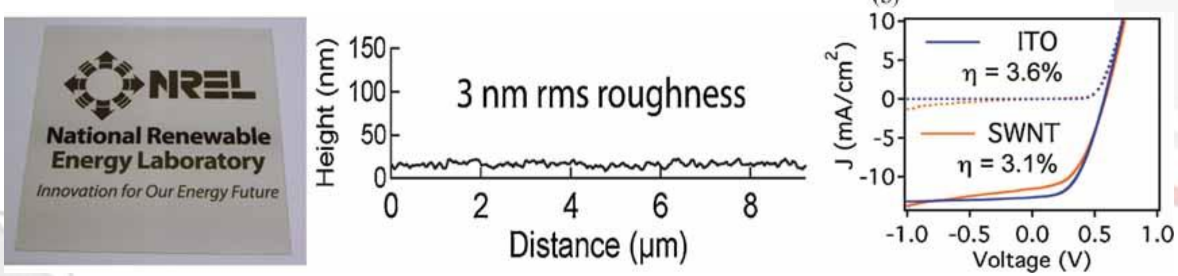
George Gruner J. Mater. Chem., 2006, 16, 3533–3539





(b)

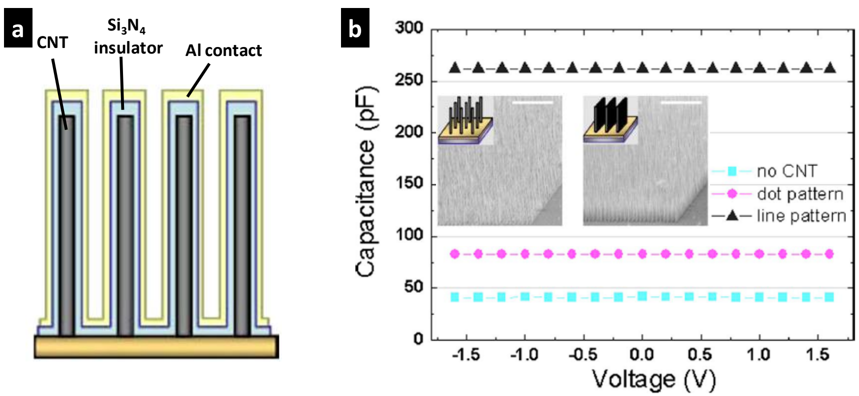
Despite this progress, the sheet resistance of SWNT networks has remained at ~ 100 Ω/sq (abount an order of magnitude higher than ITO) at transparency of 85%



Tenent et al. Adv Mat Volume 21, Issue 31, Date: August 21, 2009, Pages: 3210-3216

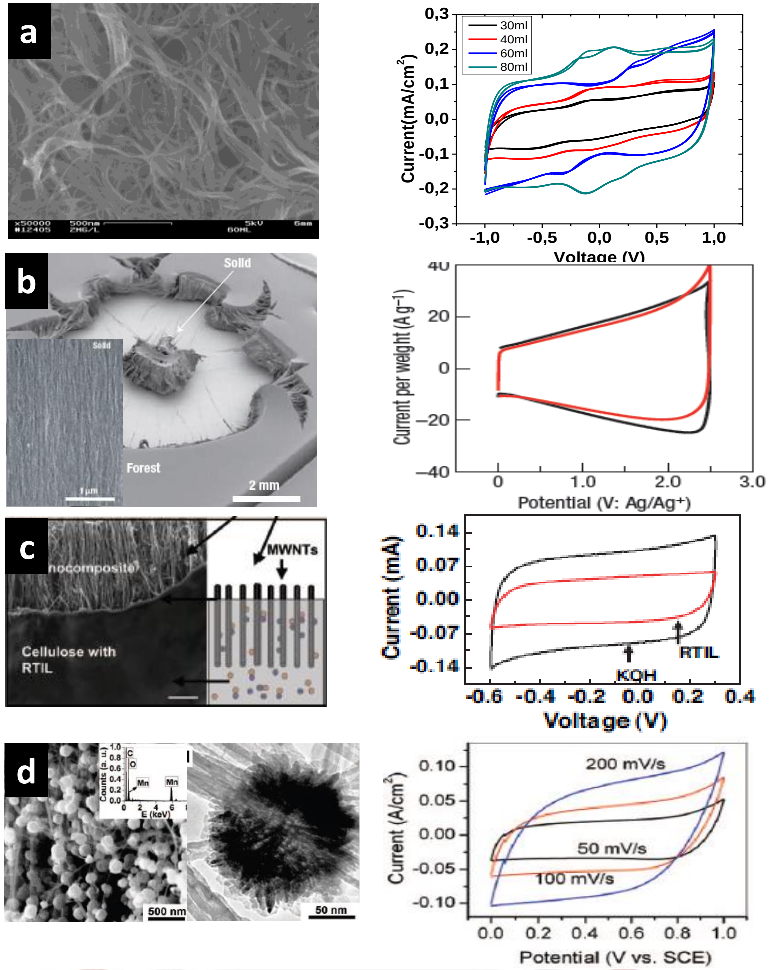
Batteries and supercapacitors

Research efforts in the field are directed towards combinations of materials with high dielectric constant (for higher capacitance values) and high breakdown strengths (for the ability to sustain higher voltages). Alternatively, the effective surface area can be enhanced by using nanomaterials.



Enhancement of a capacitor performance by enhancing its surface area by using a ordered CNT backplane (a) Device structure (b) Comparison of capacitance of flat and CNT enhanced structures. Inset shows SEM images of the respective CNT arrays.

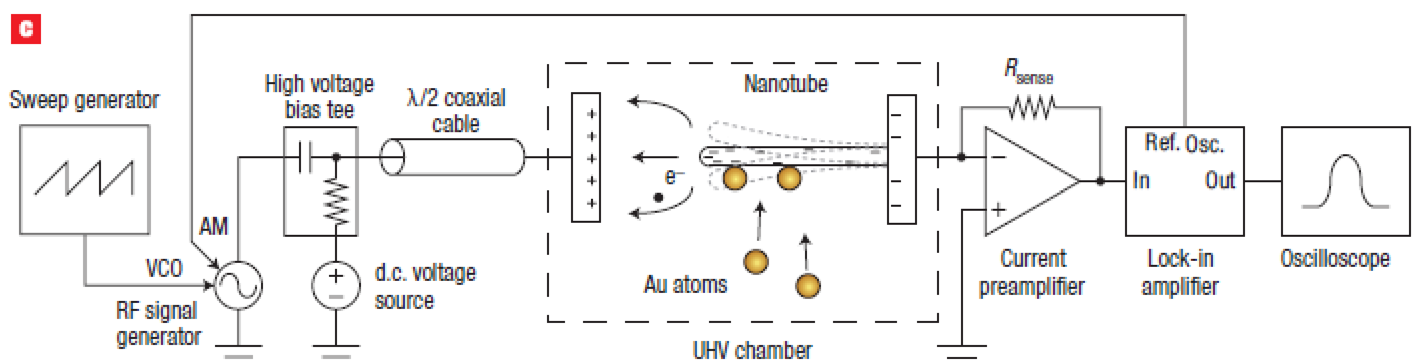
J.E. Jang et al. Applied Physics Letters, vol. 87, 2005, p. 263103



(a) SWCNT random thin film (b) Ordered aligned array of SWCNTs, which have been compressed with liquid. (c) An array of freestanding pre-grown MWCNTs embedded in a cellulose matrix, resulting in a paper-like electrode. (d) An array of MWCNTs used as a scaffold to hold low conductivity but high capacitance MnO_2.

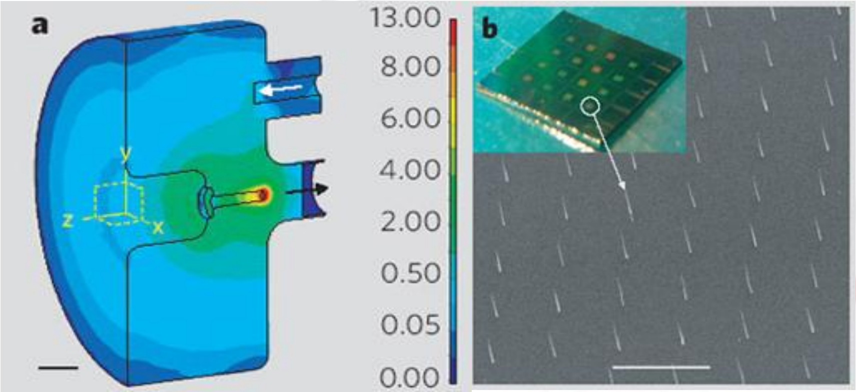
Other applications

- Interconnects and vias
  - Used to increase the current densities beyond that which can be achieved by copper without electromigration. $5x10^{-12}$ A/cm^2
  - Strong interest shown by Intel (Ireland)
- Sensors and resonators
  - Very good for their high aspect ratio and surface area to volume ratio
  - High aspect ratio and supersharp tips for Atomic Force Microscopes
  - Functionalized/non-functionalized networks of CNTs
  - Not necessarily limited to CNTs. Metal oxide nanowires are also candidates. Selectivity can be a problem
  - K. Jensen, K .Kim, A. Zettl, "An Atomic Resolution nanomechanical mass sensor" Nature Nanotechnology, 3, 533 (2008)



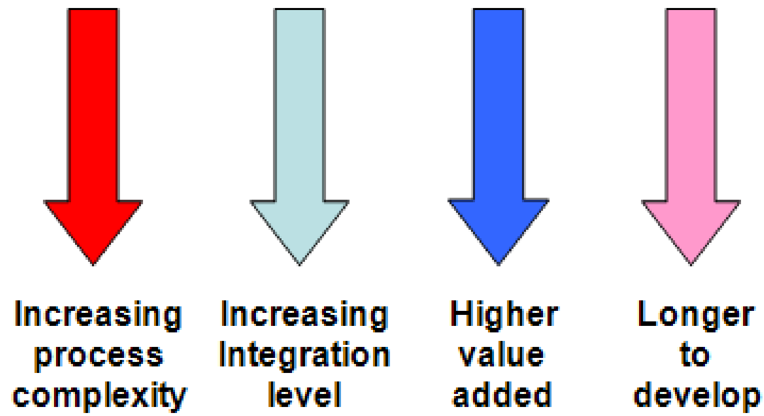
Other applications

- Field emission
  - SEM/TEM sources explored because of high brightness and stable structure.
  - Arrays employed for microwave amplifiers and x-ray sources to provide high current density
  - Relatively small market size
- Transistors
  - Due to high carrier mobility, CNTs are potentially very promising candidates for high frequency operation.
  - IEMN and CEA are French groups working on this
  - Largely abandoned for standard electronics due to poor yield and device density
- Hydrogen Storage
  - Largely abandoned



Roadmapping

- Bulk applications
- Coating applications
- Device applications

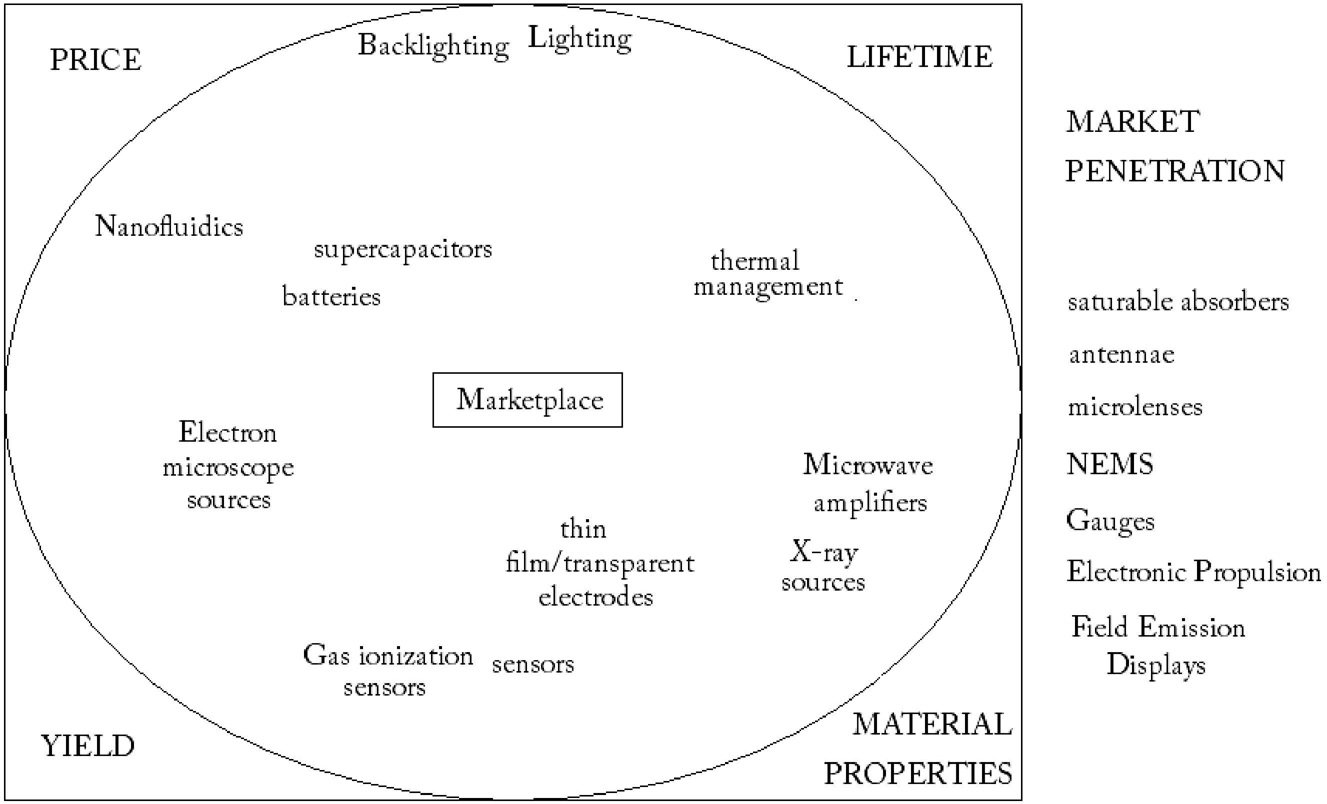


Balanced risk vs reward

Applications	Process risk	Integration risk	Impact/value added
VLSI interconnects	High	High	Very high
Spintronics for data storage	High	High	Very high
Smart gas sensors	Medium	Medium	Very high
X-ray medical tubes	Low	High	Very high
Microwave tubes	Low	High	High
Lab-on-chip chemical analyser	Low	Medium	High
Cell analyser	Low	Medium	High
Supercapacitors	Low	Low	Low
Thermal management	Low	Low	Low

Balance between various risks with regard to processing, integration and market impact.

Potential near-term applications



Overview of the possible near-term applications of CNTs. Distance from the centre indicates relative time to market; position dictates the key issues that need to be addressed. Outside the circle, market penetration is the issue, where the proposed devices have yet to justify their application or replacement of an established competing technology.

Working Group – last meeting Feb 17th 2010

Attendees:

Mark Mann

Bill Milne

John Robertson

Stephan Hofmann

Ken Teo

Jim McLaughlin

Peter Boggild

Contributors to new reports:

Meeting attendees plus

Pritesh Hiralal

Merlyne De Souza

Manish Chhowalla

Daping Chu

Yan Zhang

Tim Wilkinson

Zahid Durrani

JC Gabriel

Vincent Derycke

Andrew Briggs.

CALL FOR PAPERS

NanoCarbon 2010 Symposium

Organized by:

Electrical Engineering Division, Engineering Department, University of Cambridge, *U.K*

School of Electronic Science and Engineering, Southeast University, *P.R. China*

Nokia, ***Finland***

NanoICT, Spain

UNIVERSITY OF CAMBRIDGE
Department of Engineering

SOUTHEAST UNIVERSITY 東南大學 1902 南京 止於至善

NOKIA
Connecting People

nanoICT
coordination action

14th – 16th October 2010

Nanjing, P.R. China

NanoCarbon invited speakers

Sumio Iijima Director of the Research Center for Advanced Carbon Materials, National Institute of Advanced Industrial Science and Technology, Japan

Bill Milne Head of the Electronics, Power and Energy Conversion Group, Engineering Department, University of Cambridge, U.K.

Gehan A. J. Amaratunga Head of the Electronics, Power and Energy Conversion Group, Engineering Department, University of Cambridge, U.K

Shoushan Fan Director of Department of Physics and Tsinghua-Foxconn Nanotechnology Research Centre, Tsinghua University, Beijing, P.R. China

Alan Windle Department of materials and metallurgy, University of Cambridge, U.K

Shuit Tong Lee Professor (Chair) of Materials Science, Department of Physics and Materials Science, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong

Li-Chyong Chen Center for Condensed Matter Sciences, National Taiwan University, Taipei 106, Taiwan

Xiaowei Sun School of Electrical & Electronic Engineering, Nanyang Technological University Nanyang Avenue Singapore 639798

Sishen Xie Institute of Physics, Academician of Chinese Academy of Sciences, P.R. China

Ravi Silva Director of the Advanced Technology Institute, University of Surry, U.K.

Didier Pribat Laboratoire de Physique des Interfaces et des Couches Minces, CNRS UMR 7647, Ecole Polytechnique, F-91128 Palaiseau Cedex, France

Arokia Nathan London Center for Nanotechnology, University College of London, London, UK.

Lian-Mao Peng Key Laboratory for the Physics and Chemistry of Nanodevices and Department of Electronics, Peking University, Beijing, China

Manish Chhowalla Head of the Nanomaterials and Devices Group, Department of Materials Science and Engineering, Rutgers University, USA

Zhongfan Liu Center for Nanoscale Science & Technology and College of Chemistry and Molecular Engineering, Peking University, Beijing, China

ITC 2011 Cambridge

Sponsored nanoICT session on carbon nanotubes in Cambridge, March 2011