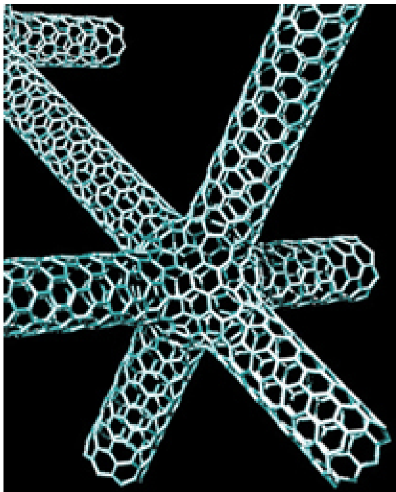
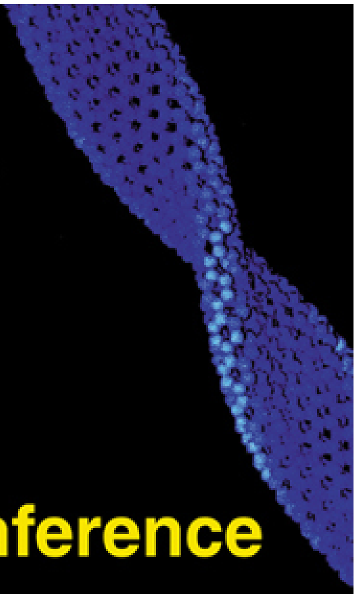
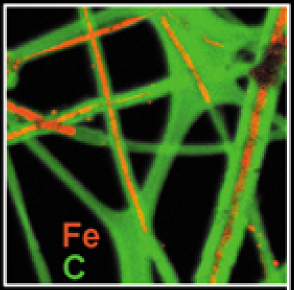




Fifth
International Conference on the Science and Application of Nanotubes

NANOTUBE 2004

ABSTRACTS



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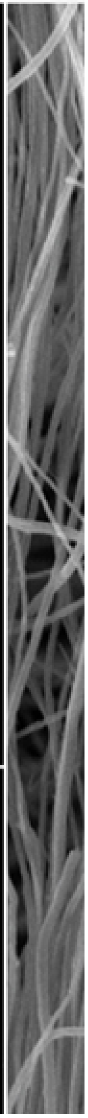
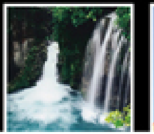
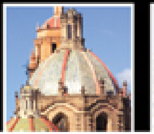


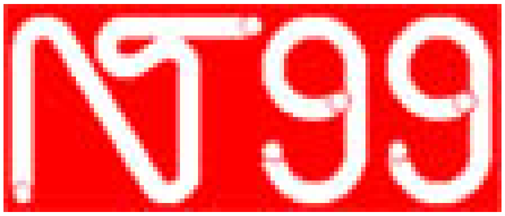


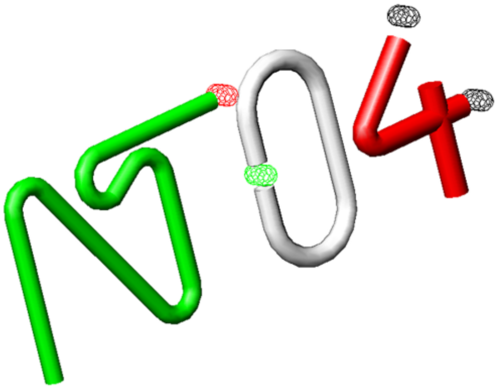


ABOUT THE CONFERENCE

On July 19-24, 2004, the International Conference on the Science and Application of Nanotubes (NT'04) will be held in San Luis Potosí, México. This will be the 5th conference of this kind.

Previous conferences were held in East Lansing, Michigan, U.S.A. in 1999. Potsdam, Germany in 2001, Boston Masachussetts, U.S.A. In 2002, and in Seoul, Korea in 2003.





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Following the spirit of the Nanotube'99, Nanotube'01, and Nanotube'02 conferences, sessions with invited talks will be accompanied by extended afternoon Poster-PLUS sessions. Priority in registration will be offered to those participants who present a contribution. The Poster-PLUS sessions are organized as follows:

- A Chairperson will introduce the topic and situate it in the context. He/she will present a link between the individual contributions
- Next, participants will be invited to present a two-viewgraph/two-minute motivation introducing their work.
- Ample time will be provided to discuss individual contributions at the posters.

SCIENTIFIC PROGRAM

TIME	SUNDAY 18	MONDAY 19	TUESDAY 20	WEDNESDAY 21	THURSDAY 22	FRIDAY 23	SATURDAY 24
08:50-09:00		OPENING CEREMONY		TOUR SAN MIGUEL ALLENDE GTO INCLUDED IN REGISTRATION			
09:00-09:40		**A1** MORINOBU ENDO			**I1** MILDRED S. DRESSELHAUS	**L1** MING ZHENG	**P1** MICHAEL S. STRANO
09:40-10:10		**A2** DAVID B. GEOHEGAN	**E1** DANIEL E. RESASCO		**I2** ADO JORIO	**L2** JONATHAN N. COLEMAN	**P2** JISOON IHM
10:10-10:40		**A3** STIG HELVEG	**E2** SHIGEO MARUYAMA		**I3** YOSHIYUKI MIYAMOTO	**L3** CHARLES MOSKOWSKI	**P3** RICHARD MARTEL
10:40-11:00		COFFEE BREAK	COFFEE BREAK		COFFEE BREAK	COFFEE BREAK	COFFEE BREAK
11:00-11:30		**B1** KIM BOLTON	**F1** SIVARAM AREPALLI		**J1** TOBIAS HERTEL	**M1** AJAY K. SOOD	**Q1** ORAL SESSION
11:30-12:00		**B2** JIE LIU	**F2** DMITRI GOLBERG		**J2** MARCUS FREIGTAG	**M2** JEAN-CHRISTOPHE CHARLIER	CONCLUDING REMARKS
12:00-14:00	REGISTRATION	CONFERENCE LUNCH	CONFERENCE LUNCH		CONFERENCE LUNCH	CONFERENCE LUNCH	CITY LUNCH AND TOUR OF DOWNTOWN SLP CALLEJONEADA Mezcal Shots!!
14:00- 14:15		**C** Poster++ Talk	**G** Poster++ Talk		Challenge and Future of NT Research and Technology Funding Panel with NSF, CONACyT, Research Institutions and Companies 4 Talks and panel discussion are scheduled	**N** Poster++ Talk	
14:15-14:30		**C** Poster+ Oral Session	**G** Poster+ Oral Session			**N** Poster+ Oral Session	
14:30-16:00		**C** Poster Session	**G** Poster Session			**N** Poster Session	
16:00-16:30		COFFEE BREAK	COFFEE BREAK			COFFEE BREAK	
16:30-16:45		**D** Poster++ Talk	**H** Poster++ Talk			**O** Poster++ Talk	
16:45-17:30		**D** Poster+ Oral Session	**H** Poster+ Oral Session			**O** Poster+ Oral Session	
17:30-19:00		**D** Poster Session	**H** Poster Session			**O** Poster Session	
19:00-22:00	WELCOME PARTY		DINNER				

REGISTRATION (SUNDAY 18): Begins at 12:00, in the main entrance of Hotel Real de Minas (venue), and ends at 19:00

WELCOME PARTY (SUNDAY 18): Begins at 19:00, in the garden of the Hotel Real de Minas (venue).

CONFERENCE DINNER (TUESDAY 20): Begins at 20:30, in Hotel Real de Minas (venue).

TOUR SAN MIGUEL DE ALLENDE (WEDNESDAY 21): Departure time(SLP): 08:30, travel time (approximately): 2.5 - 3 hours. Departure time (San Miguel): 17:00, travel time (approximately): 2.5 - 3 hours. Arrival time (SLP): 20:00.

CITY LUCH AND TOUR OF DOWNTOWN SLP (SATURDAY 24): The lunch will be in a beautiful and historical building of downtown of SLP. After the conference lunch, we will walk in the most important streets of downtown.

SUGGESTIONS FOR YOUR "POSTER+" PRESENTATION:

Keep it compact - do not pack a whole talk into 2 minutes!

Get the audience intrigued - tell the problem, not the solution!

Consider this an "advertisement" for your poster - make it interesting and fun!

ABOUT POSTER SESSION

You will find poster sessions at NT'04 different from other conferences. We want your contribution to 'play the first violin'. To make this possible, we kept only the mornings for invited talks, and reserved the afternoons for contributed presentations. We believe that structured, interactive poster sessions are the best forum for contributed presentations.

We intend to sort contributions into poster sessions with a unifying theme. At the beginning of each poster session, the chairperson will briefly introduce the significance of the new results. In the "Poster+" session, each poster will be allocated a 2 viewgraph/ 2 minute (sharp!!) plenary oral presentation. This presentation should summarize the problem addressed and motivate the participants to discuss more at the poster site. Contributed submissions may further be elected for a 15 minute oral "Poster++" presentation.

Following the Poster+ and Poster++ presentations, ample time will be provided for further asynchronous discussions at the posters. Presenting authors will know, when they are expected to "man their poster", and when they are free to move around. At the chairperson's choice, the poster session may be concluded by a focussed panel discussion, or in a different way.

Multiplying the expected number of posters (400) with the oral presentation time (2 minutes) amounts to more than 10 hours total for Poster+ presentations only. We believe that this time, which will be spread over the conference afternoons, will be time very well spent!

Contents

A Invited Session (Monday Morning)

Growth and Properties of Carbon Nanotubes

Keynote Lecture

Large scale production of carbon nanotubes and their current application

Morinobu Endo

Shinshu University
Contact e-mail:endo@endomoribu.shinshu-u.ac.jp

Extra-ordinary chemical and physical properties of carbon nanotubes and also the success of large-scale production by a catalytic chemical vapour deposition method, particularly with the use of a floating reactant technique [1, 2], make them applicable in the fabrication of adsorbent, electrochemical electrode, field emitter and functional filler in composite at a possible low cost. Through judicious selection of transient metal, support materials and synthetic conditions (temperature, duration), it is possible to produce different types of carbon nanotubes such as multi-walled carbon nanotubes (MWNTs), double-walled carbon nanotubes (DWNTs) and single-walled carbon nanotubes (SWNTs), selectively. In this study, we will describe the catalytic synthesis of various carbon nanotubes from the point of synthetic conditions, and structural changes by heat treatment will be discussed in terms of structural stability, and finally their practical applications of these carbon nanotubes will be described from the industrial point of view.

References:
[1]A.Oberlin, M.Endo, T.Koyama, J.Cryst.Growth, 32,335(1976).
[2]M.Endo,Chem.Tech. (Leipzig) 18,568(1988).

IN SITU KINETICS MEASUREMENTS OF CARBON NANOTUBE ARRAY GROWTH DURING CHEMICAL VAPOR DEPOSITION

D. B. Geohegan, A. A. Puretzky, G. Eres, I. N. Ivanov*, H. Cui, Z. Pan*, H. M. Christen, K. Belay**, S. Jesse, A. A. Kinkhabwala and J. Y. Howe*

Oak Ridge National Laboratory, Oak Ridge, TN 37831,
* University of Tennessee, Knoxville, TN 37996,
** Florida A&M University, Tallahassee, FL 32307
Contact e-mail:odg@ornl.gov96

In situ measurements of carbon nanotube growth kinetics have been performed during chemical vapor deposition (CVD) in order to understand the processes limiting rapid growth of nanotubes to long lengths. With optical reflectivity and remote microscopy, the height of vertically-aligned arrays of carbon nanotubes (VAA-NT) can be measured directly *throughout a growth run*, providing growth rates, comparisons of catalyst efficiencies, observation of growth termination and a basis for modeling the relevant processes during CVD nanotube synthesis. In addition, these optical diagnostic techniques permit *in situ* methods to control nanotube lengths or restart growth. Attenuation of a reflected HeNe laser beam and Fabry-Perot fringes are used to measure and control the length of VAA-NT arrays throughout the first 10 microns of growth. For growth of arrays to millimeters in height, remote microscopy and time-lapse photography are used. Based upon these measurements, adjustment of the growth parameters (including combinatorial catalysis) is described in order to grow VAA-NT millimeters long at high rates for composite applications. A simple rate equation model is considered to explain the observed growth kinetics and to discuss the main processes responsible for the growth of VAA-NTs. Absolute growth rates determined in these measurements will be compared with those estimated from time-resolved diagnostics of single-wall carbon nanotube growth by laser vaporization. Research supported by the U. S. Department of Energy, Division of Materials Science, Basic Energy Sciences.

Atomic-scale imaging of carbon nanofiber growth

Stig Helveg[1], *Carlos López-Cartes*[1], *Jens Sehested*[1], *Poul L. Hansen*[1], *Bjerne S. Clausen*[1], *Jens R. Rostrup-Nielsen*[1], *Frank Abild-Pedersen*[2], *Jens K. Nørskov*[2]

[1] Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Kgs. Lyngby, Denmark. [2] Center for Atomic-scale Materials Physics, Department of Physics, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark
Contact e-mail:sth@topsoe.dk

Recent advances in in situ techniques for research in heterogeneous catalysis have opened up the possibility of studying gas-solid interactions at the atomic level (1). Here we present in situ transmission electron microscopy observations of carbon nanofibers growing by catalytic decomposition of methane over oxide-supported nickel nanocrystals (2). By means of time-resolved, high-resolution imaging, the carbon nanofibers are seen to develop through a reaction-induced reshaping of the nickel nanocrystals which assists the alignment of graphene layers into graphitic nanofibers. Specifically, the nucleation and the growth of graphene layers are found to couple to a dynamic formation and restructuring of mono-atomic step edges at the nickel surface. The finding that metallic step sites act as growth centers is attributed to the stronger bonding of carbon atoms to step sites than to facet sites (3). From an interplay with density functional theory calculations, the dynamic observations are consistently explained by a growth mechanism involving surface diffusion of nickel and carbon atoms.

References:
(1) H. Topsoe, J. Catal. **216**, 155 (2003).
(2) S. Helveg, C. López-Cartes, J. Sehested P. L. Hansen, B. S. Clausen, J. R. Rostrup-Nielsen, F. Abild-Pedersen, J. K. Nørskov, Nature **427**, 426 (2004).
(3) H. S. Bengaard, J. K. Nørskov, B. S. Clausen, L. P. Nielsen, A. M. Molenbroek, J. R. Rostrup-Nielsen, J. Catal. **209**, 365 (2002).

B Invited Session (Monday Morning)

Growth of Carbon Nanotubes

Molecular Dynamics Simulations of Single-Walled Carbon Nanotube Nucleation

Kim Bolton, Feng Ding and Arne Rosen

School of Physics and Engineering Physics, Göteborg/Chalmers University
Contact e-mail:kim@fy.chalmers.se

Molecular dynamics simulations based on an empirical potential energy surface were used to study iron catalyzed nucleation and growth of single-walled carbon nanotubes (SWNTs). The simulations show that SWNTs grow from the iron-carbide (FeC) particle at temperatures between 800 and 1400 K, whereas graphene sheets encapsulate the particle at temperatures below 600 K and a three-dimensional (3D) soot-like structure is formed above 1600 K. Nucleation of these carbon (C) structures can be divided into three stages: i) at short times all C atoms dissolve in the FeC particle, ii) at intermediate times the FeC cluster is highly supersaturated in C and carbon strings, polygons and small graphitic islands nucleate on the cluster surface, iii) at longer times the FeC cluster is supersaturated in C and a graphene sheet, SWNT or soot-like structure is grown. At low temperatures the kinetic energy is not sufficient to overcome the attractive forces between the graphitic islands (that ar e formed in stage ii) and the particle, and the island grows into a graphene sheet encapsulates the cluster. At temperatures above 800 K the kinetic energy is sufficiently high to overcome these attractive forces, and the graphitic island lifts off the particle to form a cap. Between 800 and 1400 K these caps grow into SWNTs, and at temperatures higher than 1600 K the large number of defects in the growing carbon structure produces a 3D soot-like structure. The calculations also reveal that the growing SWNT maintains an open end on the FeC cluster due to the strong bonding between the nanotube end atoms and the cluster. The number of defects in the SWNT structure can be reduced by lowering the rate of carbon addition to the FeC cluster.

CVD Grown Carbon Nanotubes: From Synthesis to Applications

Qiang Fu, Chenguang Lu, Cheng Qian, Hang Qi, Jie Liu

Duke University
Contact e-mail:j.liu@duke.edu

An overview of our research efforts on chemical vapor deposition (CVD) grown carbon nanotubes will be presented. The discussion includes the controlled synthesis of single walled carbon nanotubes and small diameter few walled carbon nanotubes (FWNTs) as well as application development using the materials. More specifically, it includes the growth of long and well aligned single walled nanotubes; the fabrication of electronic devices and sensors using the aligned nanotubes; the effect of surface charges on the device characteristics of nanotube field effect transistors; the synthesis of small diameter FWNTs and the development of field emission devices using these materials.

C Contributed Session (Monday Afternoon)

Oral Poster++ *Presentation*

Selective synthesis of double-walled carbon nanotubes by catalytic chemical vapor deposition of alcohol on mesoporous silica

P. Ramesh[1], *T. Okazaki*[2], *R. Taniguchi*[2], *J. Kimura*[2], *T. Sugai*[2]
and H. Shinohara[1,2]

[1] CREST, Japan Science and Technology Agency, c/o Department of Chemistry,
Nagoya University, Nagoya 464-8602, Japan.
[2] Department of Chemistry and Institute for Advanced Research, Nagoya University,
Nagoya 464-8602, Japan.
Contact e-mail:ramesh@nano.chem.nagoya-u.ac.jp

Double walled carbon nanotubes (DWNTs) exhibit electronic properties as single-walled nanotubes (SWNTs) and structural stability as multi-walled nanotubes (MWNTs). They are promising materials for the long-term stable field emitters with low threshold voltages. Selective synthesis of DWNTs has been achieved by catalytic chemical vapor deposition of alcohol over Fe/Co loaded mesoporous silica. Several mesoporous silica materials with desired pore diameter, pore wall thickness and morphology have been investigated for the DWNT growth. The diameter distribution and yield of the DWNT are found to depend on the reaction temperature, pore size and thermal stability of the support material. When high temperature stable mesoporous silica is used as a catalyst support, about 80% of nanotubes synthesized at 900 °C are found to be DWNTs. These DWNTs have been characterized using HRTEM and Raman spectroscopy. The outer diameter of DWNTs is found to be in the range of 1.5-5.4 nm with a 'd' spacing of 0.38(+/-)0.02 nm between inner and outer layers which is much larger than those of MWNTs.

C.1 *CVD Synthesis of Carbon Nanotubes I*

A NOVEL AEROSOL METHOD FOR SINGLE WALLED CARBON NANOTUBE SYNTHESIS

ALBERT G. NASIBULIN[a], *ANNA MOISALA*[a], *HUA JIANG*[b], *DAVID P. BROWN*[a], *ESKO I. KAUPPINEN*[a,b]

[a] Centre for New Materials, Helsinki University of Technology, P.O.Box 1602,
FIN-02044, Finland;
[b] VTT Processes, Aerosol Technology Group, P.O.Box 1602, FIN-02044, Finland
Contact e-mail:Esko.Kauppinen@vtt.fi

We have developed a novel aerosol method to produce SWCNT's. The catalyst particles were formed by physical evaporation, subsequent nucleation-condensation of the supersaturated vapour and further introduction of the catalyst particles inside the reactor, where the favourable conditions for the CNT formation were maintained. The experimental investigations of CNT growth were carried out in a laminar flow reactor using Fe as catalyst particle material and both CO and ethanol as carbon sources. The growth of SWCNTs occurred in the temperature interval of 870 to 1500°C with the corresponding average residence time in the reactor hot zone of 3.7 to 2.4 seconds. The size of catalyst particles varied from 1 to 3 nm, while the corresponding diameter of CNTs varied from 0.6 to 2 nm. The important role of hydrogen in the processes of single walled CNT growth is shown. The distributions of CNT properties, including size, length and their chirality, were determined from HR-TEM images. The results of Computational Fluid Dynamics calculations for CNT growth conditions inside the reactor are presented. The mechanisms of CNT formation in the gas phase are proposed.

Aerosol-Based Synthesis of Carbon Nanotubes

Kirsten Edgar, and John L. Spencer

MacDiarmid Institute for Advanced Materials and Nanotechnology, Victoria
University of Wellington
Contact e-mail:kirstenedgar@fastmail.fm

MWNTs can be synthesized by reacting aerosols of metal catalysts such as ferrocene with a carbon source at moderate temperatures, with speculation that there is potential to control the diameter of the resultant nanotube by controlling the size of the aerosol droplet [1]. We report here an alternate approach to the aerosol based method in which differently sized molecular cluster materials are used as the catalysts and entrained in an aerosol in which each droplet is intended to contain only one preformed cluster. This aerosol is introduced into a furnace at 900-1000 °C in the presence of a carbon source such as methane and the resulting material characterized using techniques such as TEM and Raman spectroscopy. Correlations between the size of the catalytic particle and the nanotube diameter will be discussed.

[1] M. Mayne et al, Chem. Phys. Lett., 338, 101 (2001).

Enhance of Methane Conversion for SWCNT Syntheses by BET Measurements

G.N. Ning, F. Wei, G.H. Luo, Y. Jin

Department of Chemical Engineering, Tsinghua University, Beijing, China
Contact e-mail:ninggq@flotu.org

SWCNT syntheses were conducted by methane crack over Fe/MgO catalysts. BET measurement was conducted between twice methane crack, and the methane conversion was markedly enhanced, such as from 0.06 to 0.24, after BET measurement. The circle of conversion rate decrease during carbon deposition and increase after BET measurement was kept before the methane conversion dropped to zero. The as-prepared materials contain abundance of SWCNTs without CNFs, MWCNTs and other impurities. The nitrogen adsorption was considered as an important factor for the enhance of methane conversion.

CVD SYNTHESIS OF SINGLE-WALL CARBON NANOTUBES FROM ETHANOL

G. Ortega-Cervantez, G. Rueda-Morales and J. Ortiz-López

Departamento de Física, Escuela Superior de Física y Matemáticas Instituto
Politécnico Nacional, 07738 México D.F.
Contact e-mail:jortiz@esfm.ipn.mx

We have implemented a chemical vapor deposition (CVD) system for the synthesis of single-wall carbon nanotubes using ethanol as the carbon source. Our system is based on the one described by Maruyama et al. [1]. In our case, we use and test several substrates such as quartz, conductive glass (tin oxide film deposited on soda-lima glass), porous alumina and TEM copper grids. Acting as catalysts, ethanol solutions of hydrated cobalt acetate (CH3CO2)2Co-4H2O and iron acetate (CH3CO2)2Fe are deposited on the substrates and allowed to dry. The substrates are placed inside a quartz tube inserted into a cylindrical oven. Ethanol vapor is injected when the temperature of the substrates is raised to 600 ^{o}C. Our samples are analyzed with atomic force microscopy as well as with scanning electron microscopy.

References:

1. S. Maruyama et al., Chem. Phys. Lett., 362, 229 (2002).

Synthesis of cabon nanotubes using an oxy-acetylene combustion flame methode

H. Okuno, J.-F. Despres, A. Palnichenko, J.-P. Issi and J.-C. Charlier

Unité PCPM Université catholique de Louvain
Contact e-mail:charlier@pcpm.ucl.ac.be

An oxy-acetylene combustion flame method has been widely studied for diamond synthesis since the technological development by Hirose et al. in 1988[1]. In this work, we demonstrate the catalytic synthesis of carbon nanotubes (CNTs) using this simple technique. A Ni-Co thin film is deposited as a catalyst on the substrate surface. The O2/C2H2 gas ratio and the substrate temperature are the key parameters to obtain the CNTs. The straight CNTs obtained at high substrate temperature range in large amount have a perfect hollow structure with well-graphitized graphene layers, similar to the ones grown by arc-discharge. Under certain experimental condition, we observed a formation of polyhedral crystals around these straight CNTs. Although the polyhedral crystals can be grown directly from substrate surface toward the flame source without catalyst [2], these are formed selectively around the CNTs in the presence of the catalyst because of a resemblance of these two structures consisting of the cylindrical graphitic layers. This fact is useful to control the formation of polyhedral crystals by a pre-deposition of CNTs. In addition to the industrial large yield synthesis, this technique can be applied also for local deposition, such as on the tip of STM probe.

[1] Y. Hirose and K. Komaki, Eur. Pat. EP 0 324 538 A1 (1988)
[2] H. Okuno, J.-F. Deprés, A. Palnichenko, J.-P. Issi and J.-C. Charlier, submitted to Carbon (2004)

Synthesis and characterization of high-quality double-walled carbon nanotubes using catalytic chemical vapor deposition method

S. H. Lee[1], *S. I. Jung*[1], *C. B. Kong*[1], *T. J. Lee*[1], *S. K. Choi*[1], *M. H. Park*[2], *C. W. Yang*[2], *C. Y. Park*[3,4], *C. J. Lee*[1]

[1] Department of Nanotechnology, Hanyang University, Seoul 133-791, Korea.
[2] Department of Advanced Materials Engineering, Sungkyunkwan University, Suwon 440-746, Korea.
[3] Department of Physics, Sungkyunkwan University, Suwon 440-746, Korea.
[4] Center for Nanotubes and Nanostructured Composites, Sungkyunkwan University, Suwon 440-746, Korea
Contact e-mail: cjlee@hanyang.ac.kr

High-quality double-walled carbon nanotubes (DWNTs) have been produced by catalytic chemical vapor deposition of carbon containing molecules such as propanol, THF, hexane, benzene, alcohol over Fe-Mo embedded MgO or Al2O3 support material. The produced carbon materials indicate high-purity DWNT bundles free of amorphous carbon covering on the surface. Our results show that the amount of DWNTs is over 90 % of tatal carbon product. The diameters of DWNTd were dependent on process conditions and carbon sources. DWNTs have the inner tube diameters in the range of 0.6 - 3.4 nm and the outer tube diameter in the range of 1.4 - 4.5 nm. The interlayer spacing between graphene layers ranges from 0.35 - 0.38 nm. Transmission electron microscopy and Raman analysis show that produced carbon materials have low defect level in the atomic carbon structure, indicating the synthesis of high-quality DWNTs. We will discuss field emission properties from DWNTs in detail.

Large bundles of triple-walled carbon nanotubes

Yu Hao, Zhang Qunfeng, Ning Guoqing, Wang Qixiang, Luo Guohua, Wei Fei

Chemical Engineering Department, Tsinghua University, Beijing, China
Contact e-mail:yuhao@flotu.org

It has been widely reported that the single-walled nanotubes(SWNTs) tend to grow in bundles. Similar bundle-like growth of double-walled nanotubes (DWNTs) were also observed and characterized. However, the growth of bundles of the nanotubes with the thicker and well-identified layers is often regarded difficult due to their defects. In this work, we will show the experimental evidence of the existence of triple-walled nanotubes(TWNTs). Acetylene was decomposed on Fe/MgO catalysts at 950°C with argon and hydrogen existence. The carbon deposition was characterized by HRTEM, SEM and Raman spectroscopy. Thickset TWNT bundles, with hundreds of nanometer in length and an aspect ratio of about three, were observed in the sample. The nanotubes in bundles have the almost same structural parameters, e.g. the inner and outer diameter of 0.4nm and 2.1nm respectively, the number of layers. The bundles have the plane base or tips, suggesting that the nanotubes grow from a certain facet as substrate. Basing on our experimental evidences, a mechanism of growth of nanotube bundles on Fe/MgO catalysts is proposed.

Molecular dynamics study of catalytic ability of transition metals in nucleation process of SWNTs

Yasushi Shibuta and Shigeo Maruyama

Dept. of Mech. Eng. The University of Tokyo
Contact e-mail:shibuta@photon.t.u-tokyo.ac.jp

Interaction between catalytic metals and carbon atoms on formation process of SWNTs are studied by the home-made multi-body potentials base on density functional theory calculations of small metal-carbon binary clusters. The Co cluster has a partially crystal structure where metal atoms are regularly allocated and embedded in the hexagonal carbon network. On the other hand, carbon atoms cover the entire surface of the Fe cluster. The number of hexagonal rings in the Co cluster increase about two times faster than in the Fe cluster. This implies stronger interaction between the graphitic lattice and Co atoms than Fe atoms. The difference of graphitization ability may reflect the ability as a catalyst on the formation process of SWNTs.

Atomic scale modelization of the nucleation of C-SWNT

H. Amara[1], *C. Bichara*[2], *J.P Gaspard*[3], *F. Ducastelle*[1]

[1] LEM, ONERA-CNRS,92322 Chatillon, France,
[2] CRMCN, CNRS, 13288 Marseille, France
[3] Physique de la Matiere condensee, ULG, 4000, Belgium
Contact e-mail:amara@onera.fr

The nucleation of SWNTs is enhanced by early transition metals or rare earth catalysts. The similarities between the samples synthesized from different techniques, observed in transmission electron microscopy, suggest a common growth mechanism. The proposed scenario is the following : first a condensation step ; carbon atoms condense at high temperature in a low density amorphous state followed by the formation of metallic catalyst particles which dissolve significant amounts of carbon. Then a nucleation and growth process at 1500-2000K : the solubility of carbon decreases; carbon segregates to the surface and the growth proceeds via a root mechanism.

To go beyond this phenomenological approach, Tight - Binding (TB) Monte Carlo simulations are performed in order to simulate the nucleation of C-SWNTS on a metallic (Ni) substrate. A minimal set of parameters is used to obtain a transferable TB parametrization of the C-C, Ni-Ni and Ni-C interactions applicable to binary systems. We have investigated in detail the carbon segregation process and the adhesive properties of C on the Ni surface.

Spatial distributions of metal atoms during carbon SWNTS formation:measurements and modelling

M. Cau(1), N. Dorval(1), B. Attal-Trétout(1), J.L. Cochon(1), A. Loiseau(2), S. Farhat(3), I. Hinkov(3), C.D. Scott(4)

(1) Onera, 91761 Palaiseau, France;
(2) LEM, Cnrs-Onera, 92322 Chatillon France;
(3) LIMHP, Université Paris 13, 93430 Villetaneuse, France;
(4) NASA, Houston, Texas 77058, USA.
Contact e-mail:loiseau@onera.fr

Experiments and modelling have been undertaken to clarify the role of metal catalysts during single-wall carbon nanotube formation [1]. A reactor has been developed for synthesis by continuous CO2-laser vaporisation of a carbon-nickel-cobalt target in laminar helium flow. The laser induced fluorescence technique [2] is applied for local probing of gaseous Ni, Co and C2 species throughout the hot carbon flow of the target heated up to 3500 K. A rapid depletion of C2 in contrast to the spatial extent of metal atoms is observed in the plume, asserting that C2 condenses earlier than Ni and Co atoms. The depletion is even faster when catalysts are present, suggesting that an interaction between metal atoms and carbon dimers takes place in the gas. Two methods of modelling are used: a spatially 1-D calculation developed originally for the arc process [3], and a zero-D time dependent calculation, solving the chemical kinetics along the streamlines [4]. The latter includes Ni cluster formation. The peak of C2 density is calculated close to the target surface where the temperature is the highest. In the hot region, C3 is dominant. As the carbon products move away from the target and mix with the ambient helium, they recombine into larger clusters as demonstrated by the peak of C5 density around 1 mm. The profile of Ni-atom density compares fairly well with the measured one. The early increase is due to the drop of temperature, and the final decrease beyond 6 mm results from Ni particle formation at the eutectic temperature (∼1600 K).

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Localized Lateral Growth of Single-Walled Carbon Nanotube from Catalyst Mixed SOG

H-H Wang, P-Y Lo*, J-H Wei*, M-J Lai*, M-J Kao*, M-J Tsai**

[1]* Div. Of Semiconductor Device Technology, ERSO/ITRI
[2]+ Heterogeneous Catalysis Dep., UCL/ITRI
Contact e-mail: pylo@itri.org.tw

We report one method of localized and lateral growing of single-walled carbon nanotube (SWNT) on two layers catalyst mixed spin-on glass (SOG) substrate. The growing process was based on chemical vapor deposition (CVD) with ethanol as the carbon source and we choose cobalt ion as the synthesize catalyst. SWNT grew only from the side wall of patterned SOG layer and we can use it to fabricate field-effect transistors (FET).

Synthesis of CNTs from coal gas by CVD method

Yuliang An, Jieshan Qiu

Carbon Research Laboratory, Center for Nano Materials & Science, Department of
Materials Science and Chemical Engineering, Dalian University of Technology, 158
Zhongshan Road, P. O. Box 49, Dalian 116012, China
Contact e-mail:anyuliang_mail@yahoo.com

It is well known that research on carbon nanotubes was increased since the discover in 1991[1]. Due to their particular structures and extraordinary properties, carbon nanotubes are promising for multiple applications including nanoelectronic devices, catalyst, strong composite materials and adsorbents for gas separation or storage, etc. Here we present a route of preparation of carbon nanotubes (CNTs) by chemical vapor deposition (CVD) of coal gas over patterned catalyst. Ferritin with homogeneous nanometer iron cores was found to be an ideal catalyst that can be located on specific sites on substrate surfaces. Civil coal gas was adopted as convenient carbon feedback for growth of CNTs. The asymmetrical Y-branches in CNTs found in our experiments may be related to presence of sulfur in the coal gas. The structure and morphology of CNTs can be controlled by catalyst and process parameters. The growth mechanism of the CNTs derived from coal gas was discussed in terms of the catalyst property and the coal gas composition. The products were characterized by SEM, TEM, and Raman spectroscopy.

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CCVD Synthesis of Carbon Nanotubes from (Mg, Co, Mo)O Catalysts

E. Flahaut, A. Peigney, and Ch. Laurent*

CIRIMAT/LCMIE, University Paul Sabatier, 31062 TOULOUSE Cedex 4, FRANCE
Contact e-mail:flahaut@chimie.ups-tlse.fr

The influence of the proportions of Cobalt and Molybdenum within (Mg, Co, Mo)O catalysts has been studied in details for the CCVD synthesis of carbon nanotubes (CNTs) in a H_2-CH_4 atmosphere. The MgO matrix and most of the residual (Co, Mo) catalyst are easily dissolved by a HCl soaking, leading to CNTs samples with a high elemental purity (up to 98.6 at. % of carbon). The variation of the ratio between cobalt and molybdenum was found to modify both the yield in CNTs and their basic characteristics (number of walls, diameter distribution, quality and purity). Increasing the molybdenum proportion until $x < 0.67$ leads to an increase in the yield in CNTs. However, this also leads to an increase in the number of walls of the CNTs, together with a growing proportion of CNTs with a large amount of structural defects (bamboo-like structures), as well as the presence of some deposits of poorly-organised carbon. Fine tuning the key synthesis parameters such as the ratio between cobalt and molybdenum and the total amount of these elements in the starting oxide, the reduction temperature and the atmosphere composition, should allow a better control on the number of walls.

Thermal CVD of CNTs from Fe/Mo Catalysts: Morphology Transitions Mediated by Gas Temperature and Substrate Topography

Anastasios John Hart, Alexander H. Slocum

Department of Mechanical Engineering, Massachusetts Institute of Technology,
Cambridge, MA, USA
Contact e-mail:ajhart@mit.edu

We studied carbon nanotube growth by atmospheric pressure thermal CVD of methane, from Al_2O_3/Fe/Mo and Fe/Mo catalysts deposited by e-beam evaporation. In prior work, the Al_2O_3 underlayer is often deposited using a different process than the catalysts [1], or formed by oxidizing an aluminum layer [2,3]. We sequentially evaporated 20/1.5/3.0 nm of Al_2O_3/Fe/Mo onto polished silicon wafers and onto silicon microstructures (1-20 mm width and depth), and did not clean or oxidize the substrates before growth.
Experiments with long samples (100 mm long, 15 mm wide) centered in a tube furnace show sharp transitions from 200 nm diameter carbon clusters, to "spider"-like MWNT agglomerates growing from the clusters, to a dense web of SWNTs and thin MWNTs. This occurs as the gas (300/100 sccm CH_4/Ar) temperature changes along the sample, from approximately 800°C to 925°C. HRTEM with in-situ EDX analysis indicates that the clusters have layered graphitic walls with sharp corners, and are impregnated with Fe. Tangled films grow from vertical sidewalls of RIE-etched features, and isolated NTs stretch across gaps of several microns between structures. When Fe/Mo is deposited without Al_2O_3, only sparse kinked MWNTs grow from horizontal surfaces, yet isolated straight NTs as long as 200 mm grow across fields of silicon "grass" structures.

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Ultra-Long Carbon Nanotubes by Chemical Vapour Deposition

Lianxi Zheng, Michael J. O'Connell, Stephen K. Doorn, XiaoZhou Liao, Mark A. Hoffbauer, obbi J. Roop, Quanxi Jia, Jie Liu, and Yuntian T. Zhu

Chemistry and Materials Science Divisions, Los Alamos National Laboratory
Contact e-mail:l: skdoorn@lanl.gov

Carbon nanotubes have attracted much attention due to their unique structure and electronic properties, but many of their advantages cannot be realized in applications because of their short length and other handling issues. Intensive research on their synthesis has been done via arc-discharge, laser ablation, and catalytic chemical vapour deposition, and it is found that early encapsulation of catalyst by graphite is the main reason for growth termination. In this study we report a simple chemical-vapour-deposition method to grow long carbon nanotubes. Long carbon nanotubes were successfully grown on a substrate. Atomic force microscopy and Raman spectroscopy were performed, indicating that resulted carbon nanotubes are single walled with a diameter range of 1nm$\sim$ 2.25nm. The evolution of surface morphology according to growth conditions was also studied using scanning electronic microscopy, and possible growth mechanism will be discussed. Success of long carbon nanotubes will revolutionize many advanced technologies. For example, they can be used to make fibers more than an order of magnitude stronger than any current engineering fibers, scaffolding for neuronal growth, neuronal and other medical implants, conducting coils in micro electric motors, and nano optical and electronic cables.

Large-scale synthesis of single-walled carbon nanotubes by catalytic decomposition of ethylene

S. H. Lee, S. I. Jung, C. B. Kong, J. H. Cho, H. J. Kang, S. H. Seo, H. J. Seo, and C. J. Lee

Department of Nanotechnology, Hanyang University, Seoul 133-791, Korea
Contact e-mail:cjlee@hanyang.ac.kr¿

We have synthesized a large-scale synthesis of single-walled carbon nanotubes (SWNTs) by catalytic decomposition of ethylene over Fe-Mo / MgO catalyst at 700°C. The produced carbon materials indicate the SWNT bundles with the diameter ranging from 11 -29 nm. The produced SWNTs which have the diameter of 0.7-2.8 nm, reveal no amorphous carbon deposit on the surface according to HRTEM observation and Raman analysis. The yield of nanotubes is over 550 wt%, which is obtained relative to the weight of Fe-Mo metal in Fe-Mo / MgO catalyst. Besides ethylene, we will discuss the large-scale synthesis of SWNTs according to different carbon containing sources such as acetylene and xylene.

CNT-Ropes synthesized in CVD on TEOS substrate

G. Pinzon, M. Baquero, Y. Hernández, G. Holguin, F. Gomez-Baquero

Universidad Nacional de Colombia
Contact e-mail:yrhernandezp@unal.edu.co

CNT-Ropes were synthesized using a CVD system on TEOS substrate with FeO2 and NiO2 as catalyst particles. Preparation of the substrate was made using sol-gel method. The precursor was Ar/CH4 (5%) at atmospheric pressure and at 750 °C of temperature. Characterization of the sample showed formation of CNT-ropes and carbon micro-trees.

Continuous Fabrication of Amorphous Carbon Nanotubes by Fluidized-bed Reactor

T. Setoguchi, Y. Yokomichi, H. Nakaoka*, and Y. Fujioka*

Mitsubishi Heavy Industries, Ltd., *Osaka Gas Co., Ltd
Contact e-mail:toshihiko_setoguchi@mhi.co.jp

Amorphous carbon nanotubes (a-CNTs) are expected as a gaseous adsorbent because of its particular amorphous structures. Since continuous mass production technology is necessary for the future applications, authors have developed the continuous fabrication of a-CNT by using fluidized-bed technologies. In this presentation, the fabrication method, the process concept, reaction mechanism, and the properties of a-CNTs, including hydrogen adsorption, are discussed.

Fluidized-bed CVD synthesis of carbon nanotube on Co-Mo/MgO

M.M.Akbarnejad[1], *N.Manteghian*[2], *E.Ahmadvand*[2] *and*
A.M.Rashidi[1]

[1]Research Institute OF Petroleum Industry(RIPI),Theran,Iran
[2]Tarbiat Modaress University,Theran,Iran
Contact e-mail:akbarnejadm@ripi.ir

Carbon nanotubes were synthesized by the fluidized-bed CVD synthesis of methane on a nanoporous magnesium oxide (MgO) impregnated with a cobalt nitrate (Co (NO3) 3·6H2O) and ((NH4) 6Mo7O24.4H2O) solution. Large quantities of nanotubes can be produced by this technique due to the high specific surface area ($210\text{m}^2 \cdot g^{-1}$) of the nanoporous MgO and the good convection in the fluidized bed. Different synthesis parameters such as the Co-Mo content in the MgO (2-10%), the synthesis temperature (800-1000° C) and the synthesis time (5-40 min.) were investigated. TEM, SEM, TGA, X-ray diffraction, Raman spectroscopy and BET characterized the synthesized material. The purified samples consist of high carbon nanotube yield (100%) and quality. The results shown that the fluidized-bed CVD synthesis of carbon nanotubes on Co-Mo/MgO is very well suited to produce large quantities.

Study on the carbon nanotubes growth by using bimetallic film as the catalyst

C.Y. Chen, C.C. Chiu and N.H. Tai

Department of Materials Science and Engineering, National Tsing-Hwa University,
Hsin-Chu, Taiwan, R. O. C.
Contact e-mail:g923594@oz.nthu.edu.tw

Effects of catalysts on the synthesis of carbon nanotubes via the thermal chemical vapor deposition process were investigated. Bimetallic catalysts were co-deposited by a DC sputtering system on the thermal oxidized silicon substrates. After heating the as-deposited films at temperature between 700 and 900○C catalytic islands formed, and carbon nanotubes were synthesized when acetylene was adopted as the precursor . It is found that Fe was the most active catalyst to grow carbon nanotubes compared to Co and Ni. By adding second metal such as Al, Mo and Cr as co-catalyst, thin-walled carbon nanotubes with different diameters, densities and morophology were synthesized. We have optimized the thickness and the composition ratio of bimetallic layers to control the density of carbon nanotubes. In this study, the crystalline structure of the bimetallic catalysts is studied, and the influences of crystalline structure on CNTs growth are also investigated.

Study of carbon nanotubes growth on different metal underlayers

R.E.Morjan, M.S.Kabir, O.Nerushev, E.E.B.Campbell

Department of Experimental Physics, Gothenburg University and Chalmers
University of Technology
Contact e-mail:ralumax@fy.chalmers.se

For electronic applications of carbon nanotubes it is necessary to have a good electrical contact between the tube and the electrodes. It is also advantageous for applications to directly grow the nanotubes on electrodes prepared on patterned silicon chips. Most of the investigations of CNT growth were made on non-conducting substrates. These types of substrates are obviously not suitable as electrodes for devices. Therefore, the deposition of a conducting metallic underlayer on the substrate beneath the catalyst is required [1]. In this study we report the growth of carbon nanotubes using plasma-enhanced CVD on substrates with the following configuration: 10nmNi/10nm X/50nm M/ 400nmSi02, where X= insulator (Si, Al2O3) and M = metal (Pt, Pd, Ti, Mo, W, Cr). The experimental growth conditions were reported in [2]. After growth, the samples were characterised by SEM. The contact resistance between the nanotubes and the metal underlayer was measured.

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CVD synthesis of carbon nanotube on Co-Mo/MgO using nanoporous MgO

A.M. Rashidi[1], *A.A. Khodadadi*[2],*Y.Mortazavi* [2], *M.M. Akbarnejad*[1]

[1]Gas and Catalyst Research Division, Research Institute of Petroleum Industry (RIPI), Tehran, Iran
[2]Department of Chemical Engineering, University of Tehran, Tehran, Iran
Contact e-mail:rashidiam@ripi.ir

Carbon nanotubes were synthesis by chemical vapor deposition synthesis of methane on Co-Mo/MgO nanoporous MgO, that synthesis by sol-gel method. Large quantities of nanotubes can be produced by this technique due to the high specific surface area (210 m2/g) of nanoporous MgO. The main advantage of MgO is its high solubility in hydrochloric acid. Different synthesis parameters such as the Co-Mo content in the catalyst (2-10%), the synthesis temperature (800-1000 °C) and the synthesis time (5-40 min.) were investigated. TEM, SEM, TGA, X-ray diffraction, Raman spectroscopy and BET characterized the synthesized material. The best experimental condition could result in carbon nanotube yield and high quality. Purified samples consist of high yield of carbon nanotube (100%) and more than 60% SWNTs.

Monodispersity of double-walled carbon nanotubes in some bundles produced by CVD: An electron diffraction study

J.F. Colomer, L. Henrard, Ph. Lambin, G. Van Tendeloo, and P. Launois

Facultes Universitaires N.D.P, B 5000 Namur, Belgium;
University of Antwerp, B 2020 Antwerp, Belgium;
Universite de Paris-Sud, F 91405 Orsay Cedex, France
Contact e-mail:philippe.lambin@fundp.ac.be

Carbon nanotubes were synthesized by decomposition of methane on Co/MgO catalyst in a temperature range from 900 to 1000 C. The samples were purified by a hydrochloric acid treatment. The structure of small bundles of these nanotubes was investigated by selected area electron diffraction and analyzed with the kinematical theory of diffraction. Most of the bundles studied were made of nanotubes presenting unique or double helicities [1]. The diffraction pattern of some bundles with unique or double helicities is undoubtedly produced by double-walled carbon nanotubes [2], which are known to be syntesized under the experimental conditions used here [3]. It is then concluded that the majority, if not all, of the double-wall nanotubes in a given such bundle have the same helicities. The synthesis of a bundle composed of identical double-wall nanotubes most likely results from a co-operative mechanism taking place on a catalyst particle.

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The Continued Growth of Single Wall Carbon Nanotubes from Seed Crystals

Yuhuang Wang, Myung Jong Kim, Hongwei Shan, Carter Kittrell, Sivaram Arepalli, David B. Geohegan, Robert H. Hauge, Richard E. Smalley

[1] Department of Chemistry and Center for Nanoscale Science and Technology, Rice University, Houston, TX 77005.
[2] G.B. Tech/NASA-Johnson Space Center.
[3] Oak Ridge National Laboratory.
Contact e-mail:yhw@rice.edu

We have demonstrated the continued growth of single walled carbon nanotubes (SWNTs) from seed SWNTs in a way analogy to molecular epitaxy. The SWNTs grew preferably along the same direction of aligned SWNT substrates and, as Raman spectra suggested, have the same diameter and chirality as those of the SWNT seeds. In this new approach, the seed SWNTs are assembled into “bed-of-nails” substrate or an “in-plane” membrane such that each tube is in side-by-side van der Waals contact with six others and the “live” end of the tube is exposed. The tube end is etched open, allowing a nanometer sized metal catalyst “dock” to the open end. We are currently optimizing the conditions in order to grow a continuous fiber. If successful this may present a first step toward the synthesis of continuous fibers of crystalline nanotube materials comprising long, parallel nanotubes in an ordered array that have all the same extraordinary mechanical, chemical, thermal, and electrical properties that SWNTs exhibit on the nanometer scale.

Low Temperature Growth of Multi Walled Carbon Nanotubes by Chemical Vapor Deposition method

Akio Kawabata[1,3], *Masahiro Horibe*[2,3], *Daiyu Kondo*[1], *Mizuhisa Nihei*[1,3], *and Yuji Awano*[1,3]

[1] Fujitsu Laboratories LTD., Nanotechnology Research Center,
[2] Fujitsu Laboratories LTD., Yokoyama Fellow group,
[3] Fujitsu LTD. Atsugi, Japan
Contact e-mail:kawabata.akio@jp.fujitsu.com

We aim to utilize the excellent characteristics of Multi-walled carbon nanotubes (MWNTs) for electronics applications. The growing ideal MWNTs by a thermal chemical vapor deposition (CVD) method typically requires a temperature higher than 800°C, which is too high for LSI applications. We demonstrate that by controlling the thickness of catalyst metal and base metal, MWNTs were grown at 450°C by CVD method. We used titanium metal as the base metal, and nickel, cobalt and iron as the catalyst metal. The thickness of catalyst metals was 1nm. The growth condition is as follows: the substrate was heated to 450°C, and was cleaned for ten minutes in a hydrogen gas at 1kPa. Subsequently, a mixture of acetylene and argon gases was introduced for MWNTs growth. The pressure of the mixture gases was 1kPa. The result was that MWNTs were successfully grown at 450°C by using cobalt as a catalyst. There are no MWNTs in the case of nickel or iron catalyst at the same growth conditions. We conformed by TEM image that these MWNTs had well-graphitized graphen sheets. The growth of the MWNTs also depends on whether the catalyst is on the base metal or not.
This work was supported by the Advanced Nanocarbon Application Project, which was consigned to Japan Fine Ceramics Center (JFCC) by New Energy and Industrial Technology Development Organization (NEDO) of Japan.

Growth of Millimeter-Long and Vertically-Aligned Multi-Walled Carbon Nanotubes by Grid-Inserted Plasma-Enhanced CVD

Y. Kojima[1], *S. Kishimoto*[1], *Y. Ohno*[1,2], *and T. Mizutani*[1]

[1]Dept. of Quantum Eng., Nagoya Univ., Nagoya, Japan
[2]PRESTO-JST, Japan
Contact e-mail:yosihi_k@echo.nuee.nagoya-u.ac.jp

Millimeter-long and vertically-aligned MWNTs have been successfully grown by grid-inserted plasma-enhanced CVD. The key growth technologies are (1) a grid insertion between anode and cathode to suppress the ion bombardment damage and (2) thin Fe (1 nm)/Ti (1 nm) double layer catalyst. The ion bombardment damage was suppressed when grid-cathode voltage was 2 - 10 V. The thicknesses of both Fe and Ti were very important to grow the long MWNTs. When the thicknesses of metals became larger than 5 nm, the growth rate drastically decreased. 0.6 mm long MWNTs were grown at 600 C for 60 minutes using CH_4. Ni and Cr were not effective as buffer layer to grow long MWNTs.

Production and Growth Mechanism of Individually - and Vertically - Aligned Single-Walled Carbon Nanotubes under the Plasma-Enhanced Chemical Vapor Deposition Method

T. Kato[1], *G.-H. Jeong*[1], *T. Hirata*[1], *R. Hatakeyama*[1], *K. Tohji*[2]

[1] Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan
[2] Graduate School of Environmental Studies, Tohoku University, Sendai 980-8579, Japan
Contact e-mail:kato@plasma.ecei.tohoku.ac.jp

The detailed structure-control of single-walled carbon nanotubes (SWNTs) is one of the critical problems for SWNT applications to industrial fields. Especially, though the individual SWNT is an ideal shape for full use of SWNT potential abilities, its production is difficult due to van der Waals attraction effect. In order to overcome this critical problem, we have attempted to realize vertical-alignment control of SWNT using plasma-enhanced chemical vapor deposition (PECVD). Actually, we have recently succeeded for the first time in the SWNT production by PECVD [1]. Owing to intensive high ion-bombardment effects, however, we are confronted by a difficulty in controlling the vertical alignment of SWNTs. Thus, a method of decreasing the ion impact is pursued, where the operation time of PECVD is precisely adjusted. Based on this modified PECVD, it has been found that SWNTs are grown from zeolite with vertical alignment. Furthermore, the detailed transmission electron microscopy observation reveals that only the SWNT with short length forms an individual shape. This result indicates that our method might serve as a promising guide in high-density freestanding SWNT production. We also investigate the plasma effects on the SWNT growth. According to this study, the radical densities of hydrogen and CH appear to have a close relation to the SWNT growth.

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Low-temperature growth of vertically aligned carbon nanotubes using chemical vapor deposition method

Lujun Pan, Goichi Takeda, Takuo Nishiyama, Seiji Akita and Yoshikazu Nakayama

Department of Physics and Electronics, Osaka Prefecture University
Contact e-mail:pan@dd.pe.osakafu-u.ac.jp

In order to fabricate vertically-aligned-high-quality carbon nanotubes (CNT) at a low-temperature below glass transition point by CVD process, preheating of the reaction gas, carbonization of the catalysts and selection of the binary catalysts, have been investigated. It is found that (1) The preheating at 700 °C enhances the reactivity of a carbon source gas of acetylene and contributed to the decomposition of the gas in high efficiency on the surfaces of the catalysts heated at 550 °C; (2) The catalyst of iron is activated by the carbonization using a mixture of a carbon source gas and an inert gas at a temperature below 500 °C; (3) For the selection of binary catalysts, Al/Fe and Co/Ti were used. It has been confirmed that using Al, which has a low melting point, as a grounding film facilitates Fe-particle formation at low temperature and also prevents the Fe particles from aggregation. Co/Ti animates Co catalyst to grow aligned CNTs at a low temperature even without the carbonization process. This is because Co is difficult to intermingle with Ti and hold high reactivity. It is evidenced that the three kinds of techniques are very effective in the CNT growth at a low temperature of 550 °C.

Studies on the production of aligned carbon nanotube mats

I.A. Kinloch, J. Boratynski, C. Buchel, I.Y. Antypas, J. Fields, J. Summer, K.K.K. Koziol, C. Singh, A. H. Windle, C. Leung (2), Y. Chen (2) and R.E. Palmer (2), M. Nolte (3), W. Bauhofer (3) and K. Schulte (3)

(1) Dept. of Materials Science and Metallurgy, University of Cambridge, UK
Contact e-mail:iak21@cam.ac.uk

The pyrolysis of ferrocene and toluene is a useful route to the production of aligned carbon nanotubes "mats". These mats can be produced on the gramme scale and have been successfully used in a range of applications studies due to their good dispersability. Here, we present a detailed study on this mode of nanotube growth in order to understand their growth mechanism and control their morphology. Various substrates are used and the reaction conditions varied. A wide range of techniques has been used to study the resultant mats, including Raman spectroscopy, electron microscopy, AFM and image analysis. The repeatability of the product and the effect of the experimental parameters on the alignment and size of the nanotubes will be discussed. In particular, it is found that millimetre thick mats can be produced under suitable, stable growth conditions.

Vertically Aligned Peapod Formation with Position-controlled Multi-walled Carbon Nanotubes and Their Electrical Properties

Daiyu Kondo[1], *Masahiro Horibe*[2], *Akio Kawabata*[1], *Mizuhisa Nihei*[3], *and Yuji Awano*[3]

[1] Nanotechnology Research Center, Fujitsu Laboratories Ltd.,
[2] Yokoyama Fellow Group, Fujitsu Laboratories Ltd.,
[3] Fujitsu Limited
Contact e-mail:kondo.daiyu@jp.fujitsu.com

Characteristics of carbon nanotubes, such as electrical and thermal properties, can be possible to modulate by filling their internal spaces with fullerenes and other elements. These structures are called "Peapod"[1]. We succeeded in making peapod structures with position controlled vertically aligned multi-walled carbon nanotubes (MWNTs), grown on a substrate using hot filament chemical vapor deposition. Opening the tips of the MWNTs was performed at 870 K using oxygen and C60 molecules were then deposited on them to fill their inner spaces. We confirmed that the MWNTs were open at the tips and filled with C60 molecules using transmission electron microscopy. To investigate the modulation in electrical properties caused by C60 molecules, we performed two-terminal current-voltage DC measurements of the peapod structures and the original MWNTs. We found that the electric resistance of the peapod structures was about 30% lower than the original MWNTs. In our presentation, we will discuss a possible mechanism of the modulation in electrical properties.

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[1] Smith, B. W. et al. (1998), Nature 396: 323-4.

Growth of Aligned Carbon Nanotubes by Microwave Heating.

Oxana Vasilievna Kharissova, Humberto Terrones**.*

*FCFM, UANL, Mexico, **IPICYT, S.L.P., México
Contact e-mail:okhariss@ccr.dsi.uanl.mx

Shape and dimensionality are two important parameters that affect the properties of materiales at nanometer scale. Carbon can be grown into different forms of nanostructures. Periodicaly aligned carbon nanotubes have many potential applications in electronics, optics.etc.The development of a hightly efficient one-step technique long and aligned carbon nanotubes with or without Fe filling. The aligned CNTs were synthesized by microwave (MW) irradiation heating from a ferrocene FeC10H10. In this research, atomic force microscopy (AFM), scanning electron micriscopy(SEM) and Transmission electron microscopy (TEM) is used for study the growth of aligned carbon nanotubes by microwave heating. As a contribution of this method, the aligned multi-layer carbon nanotubes were obtained. CNTs have a metal particle at the tip of each tube. This carbon nanostructure, promises to become important in fuel cells, and in nanoscale engineering of other systems in which electrical, mechanical, and chemical interactions are integrated to produce macroscale effects.

Control of carbon nanotube density by using the catalyst precipitation on the metal substrate

C.C. Chiu[1] *and N.H. Tai*[1]

[1] Department of Materials Science and Engineering, National Tsing-Hua University,
Hsin-Chu,Taiwan, R.O.C.
Contact e-mail:d897512@oz.nthu.edu.tw

In the applications of carbon nanotubes (CNTs) for lighting and display, field emission properties are affected significantly by the density of CNT emitter. In order to avoid the screen effect, low density of carbon nanotubes (CNTs) for field emission display is required. In this work, low density CNTs can be synthesized by controlling the precipitation of catalyst on metal substrate. Catalyst and metal film with the thickness of several and several tens nm, respectively, were coated on SiO2 substrate by DC sputter. Different grain sizes can be obtained by controlling the annealing and cooling processes. Catalyst with the size of several nanometers can be formed at the triple junction between three grains. The synthesized nano-sized catalysts were then adopted as the growth site of CNTs in a rapid-annealing-cooling system. Microstructure of the synthesized CNTs was examined by SEM and HRTEM, and the images revealed that thin walled CNTs can be derived in this process. Moreover, field emission properties were measured to investigate the influence of CNT density on the electron emission properties.

Nano-fabrication of hexagonally ordered carbon nanotube multi-layer

Young Koan Ko, Ki Young Kwon, Do Hwan Choi, Hee-Tae Jung

Organic Optp-Electronic Materials Laboratory, Dept. of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science & Technology
Contact e-mail: zat0223@kaist.ac.kr

We selected block copolymer with BCC structure to fabricate patterned CNT array, and have developed CNT multi-layered template underneath block copolymer thin film with hexagonally ordered hole-arrays. CNT multi-layer was constructed via consecutive amidation reactions with the aid of a linker molecule (ODA) and a condensation agent (HATU) on an amine-terminated glass substrate. Thin film of PS-b-PMMA was prepared by spin casting from 1wt% toluene solution at 3000∼4000rpm and 30∼60s onto CNT multi-layered glass substrate. The specimen was annealed at 160 °C for PS-b-PMMA over 24hrs. PMMA segments were selectively removed by UV(254nm) irradiation for 30min. Porous polymer film was obtained through this process, but the pattern still remained in the polymer films, not on the substrate. The pattern was transferred onto the substrate using RIE. Those CNT multi-layered templates can be used as replicas for the nano-electronic applications as well as biological sensors.

Patterned growth of carbon nanotubes synthesized by Fe -catalyzed chemical vapour processes on different substrates

Vincenzo Vinciguerra, Francesco Buonocore*, Maria Fortuna Bevilacqua# and Salvo Coffa*, Renato Angelucci+, Rita Rizzoli+, Franco Corticelli+*

*STMicroelectronics, Stradale Primosole 50, 95121 Catania (Italy),
#STMicroelectronics, Via Remo De Feo 1- 80022 Arzano, Naples (Italy),
+CNR-IMM Sez Bo, via Gobetti 101, 40129 Bologna, (Italy)
Contact e-mail: vincenzo.vinciguerra@st.com

Carbon nanotubes (CNTs) have been synthesized by using a properly designed CVD (chemical vapor deposition) equipment. A few nanometer thick patterned layer of iron was evaporated on Si, porous silicon, Si oxide and porous silicon oxide. With such substrates we investigated different CVD synthesis processes and their influence on the control of the patterned growth. In fact, the CNTs have been grown on the Fe-patterned substrates by thermal decomposition of methane at 900°C and 750 torr conditions, by mixing the hydrocarbon with Ar and these results have been compared with those obtained by using acetylene in the same pressure conditions, at a lower substrate temperature of 700°C. All the reported findings show that the CVD patterned growth is more controllable in the latter case, although the acetylene induced growth is a rapid process. Structural and spectroscopic investigations demonstrate the control over the position, the crystalline degree and nature (multi or single-walled) of the so-grown CNTs. Moreover, according to the wetting of the Fe-patterned substrates and the temperature conditions, the nucleation of the CNTs can even be hampered, giving new hints on the control of the CNTs growth.

Role of Metal-Support Interaction in the CVD Growth of Carbon Nanotubes Studied with Size-Controlled Nanoparticles

H. Ago, K. Nakamura, S. Imamura, M. Tsuji

Inst. Mater. Chem. & Eng., Kyushu Univ., Japan
Contact e-mail:ago@cm.kyushu-u.ac.jp

We report on roles of metal-support interaction in the growth of carbon nanotubes. The size-controlled iron oxide nanoparticles with two different diameters, 4 and 10 nm, supported on MgO powder were subjected to chemical vapor deposition (CVD). Both nanoparticles catalyzed the growth of double-wall carbon nanotubes (DWNTs) together with a small amount of single-wall carbon nanotubes (SWNTs). MWNTs with more than three layers were seldom observed. We found that the inner- and outer-diameters of the DWNTs were modified by the initial nanoparticle size; smaller nanoparticles catalyzed the growth of the DWNTs with smaller diameters. These results suggest that the MgO support strongly influence the catalytic activity of nanoparticles by reducing the catalytically-active size.

INVESTIGATION ON CARBON NANOTUBE GROWTH BY SITE SELECTIVE CVD WITH NICKEL CATALYST

R. ANGELUCCI [1] , *R. RIZZOLI* [1], *S. GUERRI* [1], *A. PARISINI* [1],
F. ODORICI [2] , *L. MALFERRARI* [2], *M. CUFFIANI* [3]

[1] CNR - IMM Sez. Bologna , via P. Gobetti 101, 40129, Bologna, Italy
[2] INFN Sez. Bologna, viale Berti Pichat 6/2, 40127, Bologna, Italy
[3] Dipartimento di Fisica dell'Universita di Bologna, V.le Berti Pichat 6/2, 40127 Bologna, Italy
Contact e-mail::angelucci@bo.imm.cnr.it

A highly needed major breakthrough in the carbon nanotubes technology for electronic applications is the development of a fabrication method capable of producing well organized nanotube structures, with reproducible electronic properties. In our Institute we have been developing site-selective CVD synthesis both on flat substrates with patterned catalyst layers and in nanotemplates, in order to get ordered arrays of vertically aligned nanotubes. Several types of substrates such as silicon, silicon oxide and silicon nitride have been prepared. Transition metal catalysts, such as nickel, have been considered as seeds to nucleate the growth of nanotubes. Various CVD process parameters, such as carbon gas precursor type (methane and acetylene) and percentage in the gas mixture, use of etching or carrier gases (ammonia and argon) in the gas mixture and deposition temperature, have been investigated to obtain organized and reproducible structures of carbon nanotubes. In this work we present some results on the CNTs synthesis obtained on flat substrates, with evaporated Ni layers, 2 - 4 nm thick, as catalyst, by varying the CVD process parameters. The CNTs structural characterization by SEM and TEM observations is reported. Further insights into the mechanism of carbon nanotube growth can be inferred.

Carbon nanotube growth from size-classified catalyst particles injected into holes for ULSI interconnects

Shintaro Sato [1,2], *Akio Kawabata* [1,2], *Masahiro Horibe* [1,2], *Daiyu Kondo* [1,2], *Mizuhisa Nihei* [1,2], *and Yuji Awano* [1,2]

[1] Fujitsu Limited, Atsugi, Kanagawa, Japan
[2] Fujitsu Laboratories Ltd.
Contact e-mail:sato.shintaro@jp.fujitsu.com

For future applications of carbon nanotubes (CNTs) to LSI interconnects, size-classified catalyst particles have been injected into holes for LSI interconnects and aligned carbon nanotubes have been grown in the holes. Size-classified cobalt particles were obtained using a method reported previously [1]. Briefly, particles were produced by laser ablation, annealed with a furnace, and size-classified with a differential mobility analyzer at a pressure of 1.1 kPa. 5nm cobalt particles thus produced were injected into a high vacuum chamber (pressure: 1 x 10^{-3} Pa) utilizing differential pumping to make a directed particle beam. The particles were directed to a substrate with holes for LSI interconnects. They were deposited at the bottom of the holes with a diameter as small as 150 nm and an aspect ratio (depth/diameter) of 2.8. CNTs were then grown by hot filament chemical vapor deposition using acetylene. The growth temperature and pressure were 540 degrees Celsius and 1 kPa, respectively. Aligned multi-walled carbon nanotubes were successfully grown in the holes. This work was supported by the Advanced Nanocarbon Application Project, which was consigned to Japan Fine Ceramics Center (JFCC) by New Energy and Industrial Technology Development Organization (NEDO) of Japan.

MOCVD-synthesis with organogermanium precursors of Ge-filled carbon nanotubes covered with “diamond-like carbon” films and their electron field emission properties.

G.A.Domrachev[1]*, *K.B.Zhogova*[2], *A. M.Obédkov*[1], *B. S.Kaverin*[1], *S. N.Titova*[1], *A.A. Zaitsev*[1], *A.S.Strakhov*[1], *E.G. Domracheva*[3], *M.V.Kruglova*[4]

[1] G.A.Razuvaev Institute of Organometallic Chemistry, RAS, Nizhny Novgorod, Russia;
Contact e-mail:domrachev@imoc.sinn.ru

Ge-filled carbon nanotubes covered with “diamond-like carbon” films (Ge-filled CNTs with “DLC” films) from organogermanium precursors [(C2H5)4Ge and (n-C4H9)4Ge] with an average diameter of around 15-150 nm have been prepared by MOCVD growth technique at 4500 - 6000C and characterized by X-ray diffraction, transmission electron microscopy, atomic force microscopy, scanning Auger microscopy, Raman spectroscopy and electron field emission measurements. XRD and TEM methods showed that inside this nanostructure there is pure, highly ordered cubic crystalline Ge nanowire. The Raman data also indicate that the nanowires consist of cubic single-crystalline Ge and are encapsulated into thin carbon films of the DLC type. An array of emitters of the Ge-filled CNTs as cathode was formed from (C2H5)4Ge on Si (100) substrate with PdO layer to investigate field emission of these nanostructures. Diameter of CNTs was 100-140 nm. A glass wafer with aluminium layer was used as an anode (an anode-cathode distance 250 mm). The tips with these Ge-filled CNTs exhibit good electron field emission properties. Emitted current density was Je= 1mA/cm2 at the applied field 8 V/mm. Thus the promising electron field emission property observed for Ge-filled CNTs with “DLC” films indicates to a new perspective hybrid nanomaterial. The reaction mechanism, structure and morphology of this nanomaterial and its electron field emission properties are discussed. This work was supported by the ISTC project No.2511 and President grant of RF 1652.2003.3.

CVD nucleation and growth mechanisms of aligned films of carbon nanotubes.

CS Cojocaru, O. Ersen, B. Vigolo, J. Mane-Mane, P. Parent**, K. Lafon**, F. Le Normand**

* IPCMS, UMR 7504 CNRS, Po Box 43, Bat 69, 23, rue du Loess, 67 034
STRASBOURG Cedex, FRANCE;
** LURE, B. 209D, Centre Universitaire Paris Sud, 91 405 ORSAY Cedex, FRANCE
Contact e-mail:francois.le-normand@ipcms.u-strasbg.fr

We have compared many CVD processes, involving classical thermal and activated CVD processes, to grow films of aligned carbon nanotubes and other carbon nanostructures (nanofibers, nanocones, ...) with a high selectivity. Activation of the gas phase was carried out by hot filaments (HF CVD), by a gas discharge (DC CVD) or by the use of both activation pathways (DC HF CCVD). Prior to the CVD growth, a dispersion of either Co or Fe catalytic particles on SiO2 (8nm)/Si(100) was in situ performed through an effusive cell in ultra high vacuum directly connected to the CVD reactor (limiting pressure 10-9 mbar). This ensures a high reproducibility and a narrow size distribution down to 2 nm of the catalytic particles. Samples before and after CVD were characterized by SEM, TEM, HRTEM, X ray absorption (XAS)and Raman spectroscopies and in situ XPS, AES, ELS.
It is found that the DC HF CVD process is by far the most efficient process to get aligned nanotubes as it combines the activation of the gas mixture (C2H2:H2) both by a plasma created between two electrodes and by hot filaments. Thus both ions and highly reactive neutral radicals are formed with a high density and they are focussed onto the substrate which is slightly negatively biased relative to the cathode. Therefore we propose a mechanism of nanotubes nucleation and growth that account for the occurrence of ions and highly reactive radicals. The nucleation occurs through a nest of carbon that cannot further develop due to etching and sputtering. We also found that the occurrence of carbon nanotubes, relative to other carbon nanostructures, is highly sensitive to the ratio of the power input into the hot filaments and into the DC discharge, respectively. This ratio governs the density of highly reactive neutral and ions, respectively. Finally with highly dispersed Fe nanoparticles, individual and aligned single or double wall nanotubes were grown with density higher than 1012 cm-2. The alignment of the

films of carbon nanotubes has been quantitatively studied by angular X-ray absorption spectroscopy (XAS) on the C K edge. It is found that the p —–> p* transition at 285.2 eV is highly sensitive to the mutual orientation of the carbon nanotubes. However the XAS spectra are strongly surface sensitive and the molecules adsorbed on the tube must be preliminary removed by a thermal treatment.

D Contributed Session (Monday Afternoon)

Oral Poster++ *Presentation*

Direct Spinning of Carbon Nanotube Fibres from Chemical Vapour Deposition

Ya-li Li, Ian A. Kinloch, Marcelo Motta and Alan H. Windle

Dept. of Materials Science and Metallurgy, University of Cambridge, UK
Contact e-mail:ahw1@cam.ac.uk

Many routes have been developed for the synthesis of carbon nanotubes, but their assembly into continuous fibres has only so far been achieved through post-processing methods. Here, we will show that it is also possible to spin fibres and ribbons of carbon nanotubes directly from the CVD synthesis zone of a furnace using a liquid hydrocarbon as the carbon feedstock, ferrocene as the catalyst and thiophene as a promoter (1). The nanotubes form rapidly upon the precursors entering the furnace, with the nanotubes produced interacting to form an aerogel sock. This aerogel is then mechanically drawn out of the furnace to produce the fibres. Alternatively, the aerogel may be spin-coated onto preformers to produce non-woven pre-pregs for composites with a high loading of nanotubes.

The effect of the variation of the precursors will be discussed, including the importance of oxygen containing hydrocarbons on achieving a spinnable product. The relative ratios of the precursors are also found to control whether single or multi-walled nanotubes are produced. Finally, preliminary mechanical property data for the fibres will be discussed.

1. Li et al. Science, in press

D.1 *CVD Synthesis of Carbon Nanotubes II*

Low Temperature Peapod Synthesis in Single-Walled Carbon Nanotubes Using Supercritcal Fluids

David A. Britz, Andrei N. Khlobystov, Jiawei Wang, S. Adam O'Neil, Gavin W. Morley, Kyriakos Porfyrakis, T. John S. Dennis, Martyn Poliakoff, Arzhang Ardavan and G. Andrew D. Briggs

University of Oxford, Department of Materials and Clarendon Laboratory,
Department of Physics
Contact e-mail: david.britz@materials.ox.ac.uk

One-dimensional molecular arrays assembled inside nanotubes exhibit functional properties different to the bulk crystal and promise to find many applications ranging from catalysis to quantum computing. We discovered that single-walled carbon nanotubes can be efficiently filled with fullerenes in supercritical fluids at temperatures as low as 30-50 deg. C. Despite the low solubility of fullerenes in supercritical fluids the nanotube filling was particularly effective in supercritical carbon dioxide producing Cn@SWNT structures in 70% yield at 50 deg. C. This method was applied for functionalized and endohedral fullerenes C61(COOEt)2, Er3N@C80, and N@C60. We demonstrate that this method allows insertion of thermally unstable molecules which would be impossible to insert in nanotubes using standard techniques. We discuss the advantages of using supercritical fluids as compared to conventional solvents and propose the mechanism for fullerene encapsulation at low temperatures.

Questions of dynamics, statistics and criteria of successful formation of the single-walled carbon nanotubes(SWNT) in the fullerines'gas(plasma) (C-60).

G.A.Skorobagat'ko[1], *V.I.Maslov*[2]

[1]Kharkov National (Karazin's) University(KhNU),Kharkov,Ukraine
[2]NSC KIPT, Kharkov,Ukraine
Contact e-mail:skorobagatko_ph@ukr.net

In this paper are presented the new original results of the according work , in which were received: Criteria of a break (stability) of such the nanotubes that impact about them the fullerines of the gas; The critical value of an external electric field at which excess, in the given system, electrical charged nanotubes become “unsensitive” to impacts about them the fullerines of the gas i.e. occurs “straightening” of the nanotubes in external electric field. Also the process of the formation of the single-walled carbon nanotubes from the fullerines' (C-60)gas above the substrate was statistically considered .In result were received: The distribution of the nanotubes by their lengths, as the function of the parameters of the system was described above; Average waiting times of the occurrence in system of the nanotubes with the given lengths and - average waiting times of the filling of the given area of the substrate by a one-fullerine's layer, and it is also received here the radial distribution of such stratifications around of the given nanotube. Also, expressions for the average speeds are received: for the average speed of the growth of the nanotube with the given length and for the average speed of the “redial” growth of the one-fullerine's stratifications- accordingly;the comparison of these sizes is carried out. Besides that , the expression for the average growth rates of all structure of the nanotubes in system, as a whole ,is received too. On the basis of the received results the analysis of optimum conditions of the formation of the single-walled carbon nanotubes from the fullerine's gas with the given lengths is carried out.

Naturally short carbon MWNTs as an upcoming commercial product

Vladislav A. Ryzhkov

Rosseter Holdings Ltd, Limassol, Cyprus
Contact e-mail:slava@e-nanoscience.com

All developed carbon nanotubes can be roughly divided in two groups by production methods, CVD and carbon arc discharge. CVD nanotubes are proposed as likely meeting the price of $80/kg that is the "green" light for nanotubes' commercialization. However, CVD nanotubes have lower quality than arc-produced. Conventional Gas-phase Carbon Arcs (GCA) methods are not capable to meet the required price. Self-regulated Liquid-phase Arc discharge (SLA) being provided in proper hydrocarbon liquids produce raw deposits of naturally short Multi Wall Nanotubes (with 50-70% of the sh-MWNTs) in bulk (so far, up to 150g/h per anode), enabling their commercialization in 1-2 years. variation of the SLA regimes allows controlling sh-MWNTs' structure, median lengths (within the range of 150-350nm), outer (7-10nm) and inner (1.5-3.5nm) diameters, facilitating their further applications as superior field electron emitters, enhancing additives to composites (polymer, metal, ceramic, glass), ideal supports for catalysts, true catalysts, etc.

Synthesis of carbon nanocoils using Fe-In-Sn-O powder catalysts

Nobuharu Okazaki 1), Toshiki Goto 1),2), Shoji Hosogawa 2),
and Yoshikazu Nakayama 1), 3)

1) Innovation Plaza Osaka, Japan Science and Technology agency.
2) Otsuka Chemical Co. Ltd.
3) Department of Phisics and Electronics, Osaka Prefecture University
Contact e-mail: n.okazaki@osaka.jst-plaza.jp

Carbon nanocoils are expected to applications such as nano-springs, electromagnetic wave absorbers, and field emission displays due to their unique shape. By using iron coated indium-tin-oxide substrates as catalysts, carbon nanocoils can be grown in high yield with catalytic chemical vapor deposition. For mass-production of carbon nanocoils, we have developed powder catalysts consisting of oxides of Fe, In, and Sn. In this study, Fe-In-Sn-O powder catalysts were prepared by coprecipitating Fe, In, and Sn ions with alkaline solution. To find the optimum composition ratios of Fe, In, and Sn, we prepared Fe-In-Sn-O powder catalysts with various composition ratios and performed chemical vapor deposition of carbon nanocoils using these powder catalysts. In this study, it is found that the optimum composition ratio of Fe-In-Sn-O powder catalysts lies between Fe:In:Sn=3:0.3:0.1 and Fe:In:Sn=3:1:0.1. From X-ray diffraction measurements of the catalysts prepared in this study, it is also found that the particle size of Fe_2O_3 in the catalyst is controlled by In_2O_3 and SnO_2 and this is crucial for the growth of carbon nanocoils.

Mechanistical studies of SWCNT formation from CO and ethanol in laminar flow aerosol reactor

A. Moisala[1], *A.G. Nasibulin*[1], *D.P. Brown*[1], *H. Jiang*[2], *E.I. Kauppinen*[1], 2

[1] Helsinki University of Technology, Center for New Materials, PO Box 1602, 02044 VTT, Finland
[2] VTT Processes, Aerosol Technology Group, PO Box 1602, 02044 VTT, Finland
Contact e-mail:Anna.Moisala@vtt.fi

Results from mechanistical investigations of SWCNT synthesis via aerosol method in vertical ambient pressure laminar flow reactor are presented. Catalyst nanoparticles were obtained via ferrocene (vapour pressure p=0.7 Pa) and iron pentacarbonyl (p=0.3-4 Pa) decomposition and utilised in combination with CO (p=1 atm) and ethanol (p=200 Pa in N_2) to produce SWCNTs. Experiments were carried out at 800-1300°C with the average residence time of 3-6 seconds in the reactor. The product properties were studied by TEM imaging and on-line aerosol number size distribution measurements. The metal catalyst particle size was controlled by the metal precursor vapour concentration, the rate of particle formation via temperature of metal precursor feed, and the residence time. Iron pentacarbonyl decomposition in CO led to excessive catalyst particle growth and yield of SWCNTs was low. The morphology of the product from ferrocene was varied depending on the carbon precursor and reaction temperature, i.e. abundant SWCNT formation was observed from CO disproportionation between 900-1150°C, while ethanol decomposition resulted in the formation of SWCNTs at 950°C and carbon fibers at 1150°C. Mechanisms of SWCNT formation and growth are proposed based on detailed characterisation of the reactor conditions via computational fluid dynamics calculations and analysis of the experimental data.

Effect of forced convective heat transfer on formation of carbon nanoparticles in submerged arc discharge

Tawatchai Charinpanitkul(1), Noriaki Sano(2), Tatsuo Kanki(2), Wiwut Tanthapanichakoon(1)

[1] Center of Excellence in Particle Technology, Faculty of Engineering, Chulalongkorn University THAILAND;
[2] Department of Mechanical System Engineering,Himeji Institute of Technology, University of Hyogo JAPAN
Contact e-mail: ctawat@pioneer.chula.ac.th

Effect of forced convective heat transfer on the formation of carbon nanoparticles (CNPs) synthesized by a simple method of submerged arc discharge was investigated experimentally and theoretically. Introduction of the water flow rate of 0 - 3.2 dm3/min (0 - 7.1 m/s) could remarkably affect the arc discharging, which in turn gave rise to the change of CNPs properties and production rate. With TEM, Raman and DLS analyses, it was proven that the mixtures of CNPs consisting of polyhedral particles and multi-walled carbon nanotubes. With the water flow rate of 1.36 dm3/min, the highest yield and production rate of CNP-rich product could be obtained at 48.5 % and 9.32 g/h, respectively. An increase in water flow rate gave rise to faster heat transfer rate resulting in the decreasing average hydrodynamic diameter of CNPs produced. It could be implied that a further increase in water flow and heat removal leads to accelerated rate of formation of nano-onions or nano-polyhedr

Mass-production and purification of high-crystallinity single-wall carbon nanotubes by electric-arc technique

X. Zhao, S. Inoue, T. Suzuki, T. Kadoya, Y. Ando

21st COE Program "Nano Factory", Department of Materials Science and
Engineering, Meijo University, Nagoya 468-8502, Japan
Contact e-mail:zhao@ccmfs.meijo-u.ac.jp

A new method was developed for mass-production of high crystallinity SWNTs at high-yield and low cost, and the produced SWNTs can be easily purified. This will accelerate the studies of physical properties and practical applications of bulky SWNTs. High-yield SWNTs have been prepared by arc discharge evaporation of carbon electrode containing 1.0 at.% Fe catalyst in hydrogen mixed gas (i.e., H2-inert gas, or H2-N2). When a whole C-Fe electrode (6 mm diameter, 100 mm long and 4 g mass) was evaporated (dc arc current, 50 A) for 20 min in 40%H2-60%N2 mixture gas under a pressure of 200 Torr, a huge SWNT web with the mass of more than 200 mg could be obtained. SEM, HRTEM and Raman spectroscopy studies indicate that SWNTs have high crystallinity, "clean" surface, and yield higher than 70 at.%.

MOCVD grown carbon nanotubes on porous alumina - optimization towards field emission applications

G. Müller [1], J. Engstler [2], D. Lysenkov [1], J.J. Schneider [2]

[1] FB C Physics Department, Bergische Universität Wuppertal, D-42097 Wuppertal, Germany,
[2] FB Chemie, Eduard-Zintl-Institut, TU Darmstadt, D-64287 Darmstadt, Germany
Contact e-mail:mueller@venus.physik.uni-wuppertal.de

Carbon nanotubes (CNTs) are well-suited as electron field emitters (FE) because of their high aspect ratio, sufficient conductivity and high mechanical stability. Key properties for FE applications are high emitter number densities N, stable emission currents I at low electric fields E and long cathode lifetimes. We have synthesized CNTs on porous alumina membranes (PAM) using ferrocene and related structures which provide the advantage of catalytically active metals and carbon sources in a stoichiometrically well-defined ratio. Two growth processes occur during MOCVD: (i) tubular structures within PAM and (ii) CNTs on the surface. AFM, SEM, EDX and HRTEM investigations showed that (i) are composed of pyrolytic carbon with embedded metallic nanoscale particles and (ii) leads to irregular CNTs of small diameter. Integral FE-measurements of these CNTs in a spacer-free diode configuration with luminescent screen (IMLS), CCD-camera and video-recorder suggest surface-CNTs as emiss ion sites with tubular structures as electrical base-contact. High N$\sim$10000/cm2 and I$<$32mA/cm2 were obtained at E$<$10V/m. Long-term processing effects at pressures up to 5x10-4mbar resulted partially in degradation and activation of emitters as revealed by IMLS-images. High-resolution measurements with the field emission scanning microscope (FESM) showed Fowler-Nordheim-behavior of single emitters for I$<1\mu$A and saturation for dc I$<12\mu$A. The FE of these phenomena and their impact for applications will be discussed.

Optimization of carbon nanotubes grown by thermal chemical vapor deposition for field emitters

B.Y. Kong [1], *J.Y. Seon* [1], *S.J. Jung* [1], *S.H. Lee* [1], *N.S. Lee* [1]
H.J. Kim [2], *I.T. Han* [2], *and J.M. Kim* [2]

[1] Dept. of Nano Science and Technology, Sejong University, Seoul 143-747, Korea,
[2] FED Project Team, Samsung Advanced Institute of Technology, P.O. Box 111,
Suwon, Korea
Contact e-mail: nslee@sejong.ac.kr

Since demonstrating the carbon nanotubes (CNTs) as excellent field emitters, much effort has been made to control their growth for optimal field emission characteristics. We have controlled the growth of multiwalled CNTs in terms of the populations and diameters by thermal chemical vapor deposition. The intermediate density of CNTs synthesized on Si substrates showed better field emission characteristics than high or low density. The diameters of CNTs were controlled as small as 10-30 nm by introducing a buffer layer underneath the metal catalyst, being also related to the field emission properties. Repeated electrical conditioning of CNTs demonstrated an improvement of the field emission uniformity as well as the long-term stability, but decreased their field enhancement factors with some physical damages to CNTs observed. This study will also discuss our recent results on the field emission of CNTs.

Synthesis of Amorphous Carbon Nanotubes and Their Properties

Y. Yokomichi, H. Nishino, H. Nakaoka, R. Nishida, M. Yamada, M. Sakai, T. Matsui[1]

Osaka Gas Co., Ltd.
[1] KRI Inc.
Contact e-mail:y-yokomichi@osakagas.co.jp

Amorphous carbon nanotubes (a-CNTs) were synthesized using one step chemical reaction, in which the mixtures of poly(tetrafluoroethylene) (PTFE) and transition metal halides were heated up to 1073-1473K. A-CNTs showed various interesting properties such as hydrogen adsorption, and easy dispersion into some kind of polymers and solvents. In this presentation, the synthetic method, the reaction mechanism, the structure of the sidewall, and the properties of a-CNTs are discussed.

Single-Walled Carbon Nanotubes by Microwave Plasma-Chemical Vapor Deposition

M. Maschmann, Amit. Goyal, Zafar. Iqbal, Tim Fisher, Roy Gat

Purdue Univ. New Jersey Inst of Tech. Sekitechnotron USA
Contact e-mail: rgat@sekitech.com

For the first time Single-walled carbon nanotubes (SWCNTs) were grown by microwave plasma-enhanced chemical vapor deposition (PECVD). The substrate temperature was 800°C. The gas mixture was methane and hydrogen. The catalysts was bimetallic Mo/Co supported on MgO and dispersed on a silicon wafer.

The nanotubes grew in bundles, each comprising of 5 to 10 individual single walled tubes with diameter distribution sharply peaked at 0.9 and 1.3nm. Raman analysis indicated the presence of both metallic and semiconducting tubes. Field-effect scanning electron microscopy and atomic force microscopy show that the bundles are approximately 5 to 10 nm in diameter and up to a few micrometers in length.

Methane cracking on CoMo/SiO_2 catalysts for carbon nanotubes formation

Irma Calette, Tomás Viveros

UAM-I
Contact e-mail:ircamimx@yahoo.com.mx

Carbon nanotubes are produced by several methods: electric arc, laser ablation and heterogeneous catalysis. For carbon formation and hydrogen production via catalytic methods, the most used are: partial oxidation, reforming and methane cracking; and in comparison to those that produce a mixture of hydrogen, carbon oxides and water, methane cracking yields only carbon and hydrogen. In this work we have employed bimetallic Co and Mo supported on SiO2 to perform the cracking of methane to produce carbon nanotubes. The effects of Co:Mo ratio (1:2 and 2:1) and the reaction temperature (°C and 800°C) on the conversion of methane, formation of nanotubes and hydrogen production, were observed. The methane conversion increases from 2.5% at 650°C and a 5% methane feed concentration to 4.5% at 800°C and 20% methane concentration. Using TEM carbon nanotubes were observed on both catalysts, being more defined for the Co:Mo 2:1 catalyst at both temperatures. This variable seems to affe ct the nanotube dimensions.

D.2 *Non-CVD Synthesis of Nanotubes*

Synthesis of Single-Wall Carbon Nanohorns and Nanotubes by Arc Discharge in Water

N. Sano, J. Nakano, and T. Kanki

Graduate School of Mechanical System Engineering, Himeji Institute of Technology,
University of Hyogo
Contact e-mail:sano@mech.eng.himeji-tech.ac.jp

Single-wall carbon nanohorns and nanotubes can be synthesized by submerged arc in water with support of N2 gas injection into the plasma zone to keep rapid quenching of carbon vapor in relatively inert environment. These single walled structures can be collected as floating powders separately from multi-wall carbon nanotubes which are contained in heavy deposits. This technique does not require costly facilities used in well-known methods for nanohorns production, such as pulsed-laser source. When pure graphite was used for anode, nanohorns was selectively produced. Single-wall carbon nanotubes were produced when a metallic catalyst such as Ni, Fe or Gd was doped in the graphite anode. There are the optimized concentrations of the doped catalysts and the current densities in this method.

Study on the properties of CNTs and the influence of carbon cathode electrode in a dc arc discharge process

H.H.Kim, H.J.Kim

School of Materials Science & Engineering, Seoul National University, Seoul, Korea
Contact e-mail:ssdra99@snu.ac.kr

We have grown carbon nanotubes (CNTs) by a dc arc discharge process and have investigated the influence of the shape changing of carbon cathode electrode. Without catalytic metal powder in carbon anode electrode, we used small, medium, large and Ni deposited square flat carbon cathode electrodes for preparing CNTs. The prepared CNTs were observed by the scanning electron microscope, thermogravity analysis, X-ray diffraction, Raman spectroscopy and tunneling electron microscope. The experimental results showed that yield and structural types of CNTs were varied by the shape changing of carbon cathode electrode. From this result, growth mechanism of CNTs is discussed thermodynamically and the probable methods of large-scale CNTs fabrication process will be suggested.

Mechanism of Carbon Transfer in the Arc Synthesis of DWNTs

A.P. Moravsky, R.O. Loutfy

MER Corporation, Tucson, Arizona
Contact e-mail:moravsky@mercorp.com

Selective synthesis of DWNTs in the arc discharge process [1] has been kinetically studied. Formation of hydrocarbons in the carbon arc in a H2/Ar atmosphere has been established by MS analysis that identified acetylene, ethylene, methane and traces of ethane in the gas sampled from the reactor. Most of the carbon is transferred from the anode through the gas phase to the metal catalyst particles as acetylene and polyynes C2nH2, the products of carbon hydrogenation in the arc gap area. The DWNT catalyst particle consumes amorphous carbon for the feedstock as well. It is shown that kinetics of DWNT formation is governed by the same hydrodynamic factor as for SWNTs: the rate of cooling the reaction mixture by the buffer gas. Arc synthesis of DWNTs in hydrogen atmosphere is a CVD process that grows one DWNT from an equal diameter catalytic metal particle. Diffusion of carbon through the bulk metal catalyst particle is the rate-limiting step of DWNT growth.

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Surface carbon transport on metal catalysts: a low activation energy pathway for low temperature growth of carbon nanotubes

S. Hofmann1, G. Csanyi2, A. C. Ferrari1, C. Ducati3, B. Kleinsorge1, J. Robertson1

1Department of Engineering, University of Cambridge, Cambridge, UK
Contact e-mail:sh315@cam.ac.uk

Lowering the growth temperature of carbon nanotubes and nanofibres is an essential step for their direct integration in devices. Plasma enhanced synthesis has mainly been pursued to achieve vertical alignment and little is known to date about possible growth activation and low temperature growth. We present a systematic study of the temperature dependence of the growth rate and the structure of as-grown nanofibers using a plasma enhanced chemical vapor deposition system with a C2H2/NH3 gas mixture and sputtered or evaporated, patterned thin transition metal films as catalysts [1]. An onset of growth is observed at temperatures as low as 120 C. We derive growth activation energies of 0.23-0.4 eV. This is much lower than what is reported for thermal deposition (1.2-1.5 eV) [2] and similar to the activation energies of carbon surface diffusion on the corresponding transition metal [3]. The carbon diffusion on the catalyst surface and the stability of the precursor gas (C2H2) are investigated by first principles plane wave density functional calculations using the CASTEP code. We find a low activation energy ($\sim$0.5 eV) for surface diffusion of carbon atoms on the Ni and Co (111) planes. A high barrier exits for the (100) planes, which, however, do not feature dominantly in the Wulff construction for equilibrium shapes of fcc catalyst clusters [4]. Even in this case a relatively low barrier subsurface C diffusion pathway is found. The barrier for catalytic C2H2 dissociation appears to be higher than 0.5 eV on Ni(111). Thus we suggest that the limiting step for plasma-enhanced growth is carbon diffusion on the catalyst surface, whilst an extra barrier can be present in pure thermal growth for the gas decomposition on the catalyst surface. Bulk diffusion can efficiently contribute only at high temperatures, but surface diffusion is always active. This could also be a possible low temperature growth path for single walled carbon nanotubes.

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Y/Ni AND Ru/Fe CATALYTIC ROUTE TO CARBON NANOTUBE SYNTHESIS BY HYDROGEN ARC DISCHARGE

Z. Martinez [1], *F. Hidalgo* [2], *J. Ortiz-López* [1], *J.S. Arellano-Peraza* [3], *C. Mejía-García* [1], *J. Chávez-Carvayar* [4]

[1] Departamento de Física, Escuela Superior de Física y Matemáticas, Instituto Politécnico Nacional, 07738 México D.F.,2.
[2] CETIS No. 8, Rafael Donde, DGETI-SEP, 11320 México D.F.
[3] Area de Física Atómica Molecular Aplicada, U.A.M.-Azcapotzalco, México D.F.
[4] Instituto de Investigaciones en Materiales, U.N.A.M., 04510 México D. F.
Contact e-mail:jortiz@esfm.ipn.mx

Single wall carbon nanotube (SWNT) synthesis with arc discharge methods are usually performed under an inert gas atmosphere like He or Ar. The use of a non-inert gas like H2 may also result in efficient SWNT synthesis if sulphur or a sulphur containing compound is added as catalyst [1]. Arc discharge under hydrogen gas using Ni/Fe/Co/FeS as catalysts has been shown to be a high-yield method for the synthesis of SWNT [1, 2]. In order to evaluate the efficiency of SWNT hydrogen arc discharge synthesis under various conditions, we assayed novel catalytic routes using Y/Ni/FeS and Ru/Fe/FeS mixtures. We find that Ru/Fe/FeS is better but still less efficient than a Ni/Fe/Co/FeS mixture. Our samples are analyzed with Raman scattering, photoluminescence and transmission electron microscopy. We compare our data with reported production of SWNT by other methods involving similar catalytic mixtures.

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Catalytic nanotube formation from amorphous carbon rod prototyped using beam-induced deposition

Masahiko Ishida [1], *Toshinari Ichihashi* [1], *Jun-ichi Fujita* [2], *and Yukinori Ochiai* [1]

[1] NEC Fundamental and Environmental Research Labs, Tsukuba, Japan
[2] Institute of Applied Physics, University of Tsukuba, Japan
Contact e-mail:ishida@ah.jp.nec.com

We will present solid state nanotube formation from a thin amorphous carbon (a-C) rod and in-situ transmission electron microscopy (TEM) [1]. A 10-nm thick a-C rod was fabricated using electron-beam induced deposition on an Fe-doped a-C block that had been previously grown on a Molybdenum grid [2]. Uniformly dispersed Fe atoms in the a-C block were segregated into nano-sized particles by increasing the specimen temperature to over 600°C, and some of the particles showed spontaneous and irreversible movement. The origin of the movement can be explained by simultaneous a-C dissolution and tubular graphite precipitation through the eutectic Fe-C molten particles. Consequently, some of the particles also permeated the rod and transformed the rod into a multi-walled carbon nanotube, finally stopping at the end. The nanotubes are presently defective due to the discontinuous movement of the particles. However, the position-selective nature of this method will be helpful for understanding the growth mechanisms and device applications.

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Synthesis of Carbon Nanotubes with Colloidal Solution of Co/Mo and Fe in Organic Solvents

N.J. Jeong, S.J. Lee, K.S. Song, I.S. Ryu, S.P. Yu and Y.S. Seo

Korea Institute of Energy Research
Contact e-mail:njjeong@kier.re.kr

Carbon nanotubes have been synthesized with catalytic metal particles and organic solvents in a pyrolysis furnace installed horizontally. The colloidal solution of the metal particles in organic solvents was atomized to fine droplets less than 10 micrometer using an ultrasonic sprayer. The colloidal solution of homogeneous catalytic metal particles was prepared by a reverse micelle method using a surfactant [1]. In order to investigate effects of synthesis parameters on shape and size of carbon nanotubes, transition metals such as Co/Mo and Fe were used and organic solutions of toluene and octane were used as source materials of carbon. Carrier gases like He and H2 were employed to entrain the fine droplets from the sprayer to the reaction zone of the furnace. The pyrolosis furnace was controlled in a range of 1100 to 1300°C.

For the characterization of synthesized carbon nanoparticles, XRD, TEM, BET and Raman spectra were used. The XRD pattern and Raman spectra showed a well graphitized structure of MWCNTs. TEM photographs revealed that carbon nanoparticles are composed of nanotubes and onion-typed nanocapsules. The details of preparation method and results will be presented in the post session.

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Synthesis of Peapods Directly on Substrates

Y. Ohno [1,2], *Y. Kurokawa* [1], *T. Shimada* [3], *Y. Murakami* [4], *A. Sakai* [1], *K. Hiraga* [5], *M. Ishida* [3], *T. Okazaki* [3], *S. Kishimoto* [1], *S. Maruyama* [4], *H. Shinohara* [3,6], *and T. Mizutani* [1]

[1]Dept. of Quantum Eng., Nagoya Univ., Japan,
[2]PRESTO/JST, Japan,
[3]Dept. of Chemistry, Nagoya Univ., Japan,
[4]Dept. of Mechanical Eng., The Univ. of Tokyo, Japan,
[5]Inst. of Material Res., Tohoku Univ., Japan,
[6]CREST/JST, Japan
Contact e-mail:yohno@nuee.nagoya-u.ac.jp

C_{60} and Gd@C_{82} peapods have been synthesized directly on substrates. First, high-quality and high-density SWNTs were synthesized on a quartz substrate by dip-coating of catalysts and alcohol CCVD. The cap of SWNTs was opened by annealing in dry air at 430∼500 degree C for 30 min. Here, Raman scattering spectroscopy was performed to investigate damages introduced by the cap-opening process. Finally, fullerenes were doped into the SWNTs by annealing the substrate in fullerene vapor at 450∼500 degree C for 2 days. By TEM observation, we have confirmed the encapsulation of fullerenes in the samples cap-opened above 450 degree C. We have also successfully fabricated FETs with Gd@C_{82}-peapod channel synthesized directly on a SiO_2/Si substrate by using the present method.

Synthesis of aligned carbon nanotube on anodic aluminum oxide via channel guiding effect

*Ju-Hye Ko, Soo-Hwan Jeong, Donghun Kang, Eunju Bae, and Wanjun Park**

MD Lab., Samsung Advanced Institute of Technology (SAIT) P.O. Box 111, Suwon 440-600, Korea
Contact e-mail:juhyeko77@samsung.com

Anodic aluminum oxide (AAO) has been widely used as a nanotemplate for the fabrication of one-dimensional nano-materials in recent years. Using AAO template-based technique, we fabricated carbon nanotubes (CNTs) aligned perpendicular to the surface with a narrow distribution of diameter. However, these CNTs have low crystallinity due to the amorphous carbon deposition at the AAO wall. In our studies, CNTs were grown via catalytic reaction of Co particles at the bottom of AAO pores. To separate the catalytic actions of the pore wall and Co catalysts, Co catalysts having a smaller diameter than that of the AAO pore were prepared. In this structure, the pore only played a role in guiding CNT growth. The electrodeposition of Co catalyst with short pulsed method was employed to prepare the small size catalyst. The electrodeposition time in each pulse cycle was so short that only a small number of catalyst metal ions were reduced resulting in the formation of small catalyst at the bottom of AAO pore. Through this approach, CNTs with high crystallinity and good alignment were obtained. It is expected that the proposed method in this study gives an efficient and simple way to grow crystalline and aligned CNTs with prescribed dimensions.

Thermal and Plasma Systems for SWCNT and MWCNT Deposition

R. Gat

Sekitechnotron USA, Sunnyvale CA
Contact e-mail: rgat@sekitech.com

Recently (Dai et al) have combined thermal CVD approach with plasma discharge to generate SWCNT at low temperature (600°C). This encouraging result may ultimately enable CMOS compatible manufacturing of CNT for electronic applications.

Presented here are the details of a robust deposition system which combines microwave plasma discharge, RF induction heater and DC bias to provide a wide parameter space for deposition of aligned MWCNT, SWCNT, diamond films and several types of nano-rods.

We analyse the opportunity of novel material develpment using the combined plasma/thermal approach and report deposition parameters and material properties, morphologies and characterizaiton results.

Carbon Nanotubes Formed in a Composite Material

M. Teresa Martínez-Martínez, Mauricio Terrrones and Humberto Terrones

Instituto Potosino de Investigación Científica y Tecnológica
Contact e-mail: teresa@ipicyt.edu.mx

Multi-walled carbon nanotubes are produced in a metal matrix composite made of Zn-21%Al-2%Cu reinforced with (Cu-31.5%Sn) particles, after mechanical milling at ambient temperature and hot extrusion at 300°C and subsequent thermal annealing at 900°C for 30 minutes in Ar gas. The hot extrusion produces cracks in the surface of the samples with microtubes inside, and the thermal annnealing activates the nanotube growth. Carbon nanotubes containing a metal particle (Fe) at their tips are observed, the carbon comes from the lubricant (graphite in ethanol) used in the hot extrusion and the iron particles come from the milling vesels (stainless steel), hardened steel balls and impurities in Al. Iron as contaminant had a positive catalytic role in nanotube formation. The straight parallel fringes observed in the nanotubes suggest a well-crystallized tubular structure. The heating temperature and the time of the thermal treatment are the parameters that control the queantity and th e thickness of the nanotubes. HRTEM, EDS and SEM have been performed to characterize the samples.

D.3 *Formation and Characterization of Unusual Nanostructures*

Influence of catalyst chemical state in carbon nanotube growth investigated by in situ x-ray photoemmission spectroscopy

T. de los Arcos [1], *M. G. Garnier* [2], *J. W. Seo* [3], *L. Forró* [3], *V. Thommen* [1], *D. Mathys* [4], *and P. Oelhafen* [1]

[1] Institute of Physics, University of Basel, Switzerland
[2] Institute of Physics, University of Neuchatel, Switzerland
[3] Institute of Physics of Complex Matter, EPFL, Switzerland
[4] Zentrum für Mikroskopie, University of Basel, Switzerland
Contact e-mail:t.arcos@unibas.ch

Using in situ x-ray photoemission spectroscopy (XPS) we have determined that particles of both pure Fe and iron oxide (FeO) are efficient catalysts for carbon nanotube growth, although the growth mechanism could be radically different, judging from the growth rates and characteristics of the resulting nanotubes. The changing chemical composition of the Fe catalyst has been followed during the different steps of the CVD growth. The interaction of Fe with the substrate is modified by the deposition of different intermediate layers (Al_2O_3, TiN or TiO_2) between the catalyst and the Si substrate. After annealing and hydrocarbon exposure, the originally pure Fe layer suffers a series of structural and chemical modifications that depend on the nature of the buffer layer employed: Strongly oxidized particles form onto Al_2O_3 layers, while bigger metallic islands form onto TiN and TiO_2. The formation of FeO particles ont o Al_2O_3 is correlated with fast and dense growth of straight and thin (1 to 5 walls) CNTs. On the other hand, nanotubes grown from the metallic particles have a bigger number of walls (more than 20), and show many metallic inclusions and structural defects. With this work we want to emphasize the importance of a precise characterization of the catalyst as a previous step to understanding the growth mechanism involved in carbon nanotube growth.

Vacancies in graphene and single-walled carbon nanotubes

Yuchen Ma, P. O. Lehtinen, A. S. Foster and R. M. Nieminen

Laboratory of Physics, Helsinki University of Technology, P.O.Box 1100, Helsinki
02015, Finland
Contact e-mail:yma@fyslab.hut.fi

Spin-polarized density functional theory is used to calculate the properties of vacancies in a graphene sheet and in single-walled carbon nanotubes (SWNTs). For graphene, we find that vacancies are magnetic, and that the symmetry of the sheet is broken by a distortion of an atom next to the vacancy site. We also study vacancies in four armchair SWNTs from (3, 3) to (6, 6) and six zigzag SWNTs from (5, 0) to (10, 0). The calculations demonstrate that vacancies can change the electronic structure of the SWNTs, converting some metallic nanotubes to semiconductors and some semiconducting nanotubes to metals. The metallic nanotubes with vacancies exhibit ferromagnetism or ferrimagnetism, while some semiconducting nanotubes with vacancies show antiferromagnetic order. The magnetic properties depend on the chiralities of the tubes, the configuration of the vacancy and the concentration of the vacancies.

Porosity control of carbon nanotubes using Co-Mo/MCM-41 as a template

A.M. Rashidi [1], *M.M. Akbarnejad* [1], *A.A. Khodadadi* [2], *Y.Mortazavi* [2], *M. A.Attarnejad* [1]

[1]Gas and Catalyst Research Division, Research Institute of Petroleum Industry (RIPI), Tehran, Iran,
[2]Department of Chemical Engineering, University of Tehran, Tehran, Iran
Contact e-mail:rashidiam@ripi.ir

Catalytic MCM-41 was applied as a template for the preparation of ordered nanotubes via thermal decomposition of acetylene at 700°C. A bimetallic catalyst using cobalt and molybdenum with 5-8 wt% was prepared by incipient wetness impregnation method on MCM-41 support as it has been found that these metals are able to produce good carbon nanotube in terms of yield and selectivity. Nitrogen adsorption isotherm and TEM images of the template and nanotube products clearly shows that the shape and pore size of nanotubes exactly reflect the pore size of the template. The result indicates that manipulating the template and thermal conditions during vapor deposition can control the pore size of CNTs. The present investigation is of great interest for synthesis of nanotubes with the defined pore size distribution.

Synthesis of large scale and aligned carbon nanotubes array under an electric field

C.M. Li, C.C. Chiu, N.H. Tai

Department of Materials Science and Engineering, National Tsing-Hwa University,
Hsin-Chu, Taiwan, R. O. C.
Contact e-mail:g913573@oz.nthu.edu.tw

The growth of high-density aligned carbon nanotubes (CNTs) on iron (Fe) film were synthesized by the thermal chemical vapor deposition (CVD) process. The mixture of acetylene/hydrogen/argon was adopted as the carbon precursor, and CNTs were synthesized under a applied electric field in the temperature range 700-900°C. An iron (Fe) catalytic thin film was coated by DC sputter and formed nanoparticles after heat treatment. It was found that the average length and the average diameter of the fabricated CNTs were in the range of 20-50mgm and 20-40 nm, respectively. The height of the nanotube array can be controlled by the deposition period and processing parameters. Images of scanning electron microscopy revealed that a layer of CNT film formed after thermal CVD for 1-5 minutes. The vertically aligned CNTs on Si and SiO_2 substrates were composed, and the area of synthesized CNTs array can extends over several cm^2. Well crystallinity of the fabricated CNTs was detected in the high-resolution transmission electron microscopy analysis.

Use of negative ion source for production of endohedral complexes of fullerene - like structures by ion implantation technique

K.B. Zhogova [1*], *A.G. Zvenigorodskij* [1], *G.A.Domrachev* [2], *B. S.Kaverin* [2], *S.N. Abramovich* [1], *D.S. Kapustin* [1], *B.V. Ferapontov* [1], *V.S.Gritsenko* [1], *Ye.V.Zimin* [1], *M.S. Shtarev* [1]

[1] Russian Federal Nuclear Center - VNII of Experimental Physics, Sarov, Russia;
[2] G.A.Razuvaev Inst.Organometal.Chem., RAS, Nizhny Novgorod, Russia
Contact e-mail:zhogova@online.ru

To product the endohedral complexes of fullerene - like structures there were performed calculation, design and development of an electrophysical facility (implantator). The implantator is a source of pulverizer type with a caesium heating reservoir and a spherical ionizer. Principle of the source operation is the following: positive caesium ions are ionized on the spherical surface of ionizer (anode), the temperature of which is ∼1100 degrees Celsius, then they are accelerated by electric field and atomize the lithium target, encapsulated hollow cylindrical tube (cathode). Being produced negative Li ions are drawn out by magnetic field from the source thorough the hole of ionizer. Li ion beam is analyzed by mass-spectrometer and at an angle of 90 degrees enters into irradiation chamber getting at the thin film of fullerene-like target. While adjusting the implantator there were obtained ion currents of the following ions: C^- =10 micro amps, O^-=20 micro amps, H^-= 1 micro amps, Li^-=0.6 micro amps, Fe^-=2 micro amps, Cu^-=0.75 micro amps. When developing the technique of a thin film evaporation of C60 onto the implantator backing there was determined experimentally the temperature dependence of C60 evaporation rate onto implantator backing. At the temperature range of 300-500 degrees Celsius it is governed by the following dependence $V=0.0005e^{0.0283T}$(molecules/sec).

This work was supported by the ISTC project No.2511.

Ion Bombardment Effects on Carbon Nanotube Formation in Strongly Magnetized Glow-Discharge Plasma

T. Kaneko [1], *H. Matsuoka* [1], *T. Hirata* [1], *R. Hatakeyama* [1], *and K. Tohji* [2]

[1] Department of Electronic Engineering, Tohoku University, Sendai 980-8579, Japan
[2] Graduate School of Environmental Studies, Tohoku University, Sendai 980-8579, Japan
Contact e-mail:hirata@ecei.tohoku.ac.jp

The formation of uniform and well-aligned carbon nanotubes (CNTs) using a magnetron-type rf glow-discharge plasma has been investigated, and it has been reported that the deformation of the CNTs formed on an rf electrode is caused by the bombardment of the high energy ions which are generated by the strong plasma-sheath drop in front of the rf electrode [1]. In order to prevent the high energy ions from directly impinging on the rf electrode, we introduce very strong magnetic field which is externally applied with a superconducting magnet. The rf glow-discharge plasma for the formation of CNTs is generated using a mixture gas of CH_4 and H_2. When the magnetic field is weak (B=0.03 T), the CNTs formed on the rf electrodeare found to be deformed. When the strong magnetic field B=2 T is applied, the CNTs are observed to be well-aligned and not to be deformed. This result can be explained by the reduction of the ion bombardment energy in spite of the existence of the plasma-sheath electric field in front of the rf electrode, which is caused by the magnetization of the ions for B=2 T.

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Self-organization of Fe-C-system with different content of components

G.A.Domrachev [1], *K.B.Zhogova* [2], *L.G.Domracheva* *[3], *A.I.Lazarev* [1], *G.V.Markin* [1], *A.M.Ob'yedkov* [1], *B.S.Kaverin* [1], *E.G.Domracheva* [4], *E.Huipe Nava* [5], *V.L.Karnatsevich* [1]

[1] G.A.Razuvaev Inst.Organometal.Chem., RAS, Nizhny Novgorod, Russia;
[2] Russian Federal Nuclear Center,All-Russ.Research Inst.Experim.Phys.,VNIIEF, Sarov, Russia;
[3] Universidad Michoacana de San Nicolás de Hidalgo, Morelia, Mich., México;
[4] Inst.Phys.Microstructures, RAS, Nizhny Novgorod, Russia;
[5] Technological Inst., Morelia, Mich., México
Contact e-mail:domrachev@imoc.sinn.ru

The MOCVD of Fe-C-system was used in the presence of additives, which can be 1) energy transfer active, 2) mass transfer active, 3) chemically active and 4) catalytic active. The most universal additive is ferrocene. The single Fe-crystals, coated with single-layered carbon film (in presence of 1,2-dibromoethane), the fractal shapes of X-ray amorphous Fe-C-system (in presence of allyl bromide) were obtained on MOCVD from Fe(CO)5 at 300-350 °C. Various aperiodical carbon shapes including single-wall and multi-wall nanotubes (NTs) were produced at 800 °C from benzene in the presence of ferrocene. The single-wall NT growth is discussed on the basis of molecular dynamics calculations. Catalysis and self-organization of multi-wall nanotube growth is proposed on the basis of theoretically predicted the exo-endo-isomerization of iron atom bonded on carbon structure. This isomerization may be a basis for growing the multi-wall nanotubes at high temperatures on continuous deposition of carbon or carbonic fragments. The flow of carbonic material on chemical or physical vapor deposition and on collision with nanotube top carrying iron atom transfers high energy to the nanotube top. This energy amount will be sufficient for the exo-endo-Fe-isomerization. Thus the catalytic center is regenerated at the nanotube top. After this the self-organization of carbonic fragments and systems on Fe-atom and the nanotube surface shape produces next carbonic layer. This work was supported by the ISTC project No.2511 and President grant of RF 1652.2003.3.

Formation of fullerenes under soft oxidation of sh-MWNTs following intercalation with bromine

Vladislav A. Ryzhkov

Rosseter Holdings Ltd, Limassol, Cyprus
Contact e-mail:slava@e-nanoscience.com

Raw deposits of naturally short Multi Wall Nanotubes (sh-MWNTs with median length of 220nm) have been produced in Self-regulated Liquid-phase Arc discharge (SLA) provided in a hydrocarbon liquid. The deposits were powdered, oxidized in air at 535°C, intercalated with bromine, washed with boiling chlorobenzene and then with toluene, dried in vacuum and, finally, softly oxidized in air at 440°C. HR-TEM reveals traces of bromine, uncapping thinner nanotubes, peeling their outer and inner layers and formation of fullerene-like particles (0.7-1.2nm in size) from fragments of the peeled layers (no such particles are seen at the “etched” edges of graphitic carbons). Some of the particles encapsulate bromine. Washing the oxidized nanotube powders with toluene leads to yellowish solutions, yielding after drying in vacuum about 10-3 (0.1%) of black powders, which are re-dissolvable in toluene, i.e., showing a behavior typical for higher fullerenes. The yield is comparable with fullerene yields in flames. We can suggest that the lack of energy (at 440 °C) in comparison with the fullerene formation in flames is covered by high curvature of the peeled fragments. Also presence of bromine can play a crucial role in the fullerenes’ formation.

Gas-Phase Growth of Carbon Nanocoils using Fe-In-Sn-O fine-particle catalysts

Takeshi Nagasaka 1), 2), Hiroyuki Tsuchiya 1), 3), Yugo Higashi 1), 3), Toshiki Goto 1), 4), Keisuke Shiono 1), 5), Nobuharu Okazaki 1), Osamu Suekane 1), 6), and Yoshikazu Nakayama 1), 7)

1) Innovation Plaza Osaka, Japan Science and Technology agency,
2) Taiyo Toyo Sanso Co., Ltd.,
3) Nissin Electric Co., Ltd.,
4) Otsuka Chemical Co., Ltd.,
5) Daiken Chemical Co., Ltd.,
6) Technology Research Institute of Osaka Prefecture,
7) Department of Physics and Electronics, Osaka Prefecture University
Contact e-mail:n.okazaki@osaka.jst-plaza.jp

Carbon nanocoils have attracted interest because of their potential applications for the absorber of electromagnetic wave, reinforced materials, field emission devices, etc. Mass production of nanocoils with high yield is essential to realize these applications. In this work, we first succeeded in nanocoil growth in gas phase using Fe-In-Sn-O fine-particle catalysts.The catalytic particles were prepared by sintering the mixture of Fe_2O_3 fine particles and Indium-tin-oxide solution. These catalytic particles were injected with a carrier gas of helium from the top of a vertical reactor kept at 700°C. Nanocoils were grown in the gas phase at atmospheric pressure from the catalytic particles with a carbon source gas of acetylene. The coil diameter is ranging between 100nm and 500nm, and the length depends on the remaining time of the catalytic particles in the reactor. This result opens the mass production of nanocoils.

E Invited Session (Tuesday Morning)

Chirality-Selective Growth Carbon Nanotubes

(6,5) and (7,5) nanotubes produced by CVD over Co-Mo catalysts

Daniel E. Resasco, Leandro Balzano, Jose E. Herrera, and Olga Matarredona

[1]University of Oklahoma and [2]SouthWest Nanotechnologies
Contact e-mail:resasco@ou.edu

We have optimized a catalytic process to obtain high-quality SWNT over silica-supported Co-Mo catalysts in the temperature range 700-950°C. The excellent performance of this catalyst is based on the formation of a surface cobalt molybdate, in which, the Co-Mo interaction inhibits the Co metal agglomeration that typically occurs at high temperatures. When large Co particles are present, less desirable forms of carbon are produced. By contrast, when the Co clusters are very small, selective growth of SWNT occurs. We propose that the SWNT synthesis requires a nucleation step that precedes the growth of nanotubes. This step involves the disruption of Co atoms from its interaction with Mo oxide when the latter becomes carbidic, and it is followed by formation of metallic Co clusters that are responsible for the nanotube growth. The diameter of the tube is determined by the size of the metal cluster, therefore, we can control the nanotube diameter by controlling the growth rate of the Co clusters (i.e., temperature, pressure and composition). For example, spectroscopic characterization (Raman, TEM, fluorescence) indicate that the nanotubes produced at 750C have diameter in the range 0.75-0.80 nm, in which the (6,5) and (7,5) structures constitute most of the semiconducting nanotubes in the sample. In addition to the selective growth, purification and dispersion methods specific for this type of samples have been optimized.

CVD Synthesis of Single-Walled Carbon Nanotubes from Alcohol

Shigeo Maruyama

Department of Mechanical Engineering, The University of Tokyo
Contact e-mail:maruyama@photon.t.u-tokyo.ac.jp

Developments of catalytic CVD generation of single-walled carbon nanotubes (SWNTs) by using alcohol as the carbon source will be presented. High-purity SWNTs can be generated at relatively low CVD temperatures from metal catalytic particles supported on zeolite or directly dispersed on flat substrates such as meso-porous silica, quartz and silicon. The zeolite support is used for bulk generation and direct growth as film on substrates is useful for optical or semi-conductor applications. By use of the ethanol, the CVD apparatus can be very simple; the cold-wall CVD with in-situ Raman observation is demonstrated. Recently, the vertically aligned SWNTs mat with a couple of micron meters is grown on quartz substrates by employing the most efficient activation of catalytic metals. On the other hand, the chirality distribution of SWNTs determined by the near infrared fluorescence is quite unique for low-temperature CVD condition. The near armchair nanotubes are predominantly generated probably because of the stability of nanotube cap structure for thin nanotubes. The growth process of SWNTs simulated by molecular dynamics method gives an important suggestion about this chirality-selective generation of SWNTs. Perspective of chirality-selective and morphology-controlled CVD growth will be discussed.

F Invited Session (Tuesday Morning)

Characterization of Carbon Nanotubes

Recent Advances in Synthesis and Characterization of SWCNTs produced by laser oven process

Sivaram Arepalli

G. B. Tech. /NASA - Johnson Space Center
Contact e-mail:s.arepalli@jsc.nasa.gov

Results from the parametric study of the double laser oven process indicated possible improvements with flow conditions and laser characteristics (ref. 1). Higher flow rates, lower operating pressures coupled with changes in flow tube material are found to improve the nanotube yields. The collected nanotube material is analyzed using a combination of characterization techniques including SEM, TEM, TGA, Raman and UV-VIS-NIR to estimate the purity of the samples. In-situ diagnostics of the laser oven process is now extended to include the surface temperature of the target material. Spectral emission from the target surface is compared with black body type emission to estimate the temperature. The surface temperature seemed to correlate well with the ablation rate as well as the quality of the SWCNTs. Recent changes in improving the production rate by rastering the target and using cw laser will be presented.

Ref: 1) Sivaram Arepalli, William A. Holmes, Pavel Nikolaev, Victor G. Hadjiev and Carl D. Scott, "A parametric study of single-wall carbon nanotube growth by laser ablation", To be published in Journal of Nanoscience and Nanotechnology (2004).

Nanotubes in B-C-N and other selected inorganic systems as prospective functional materials

D. Golberg, Y. Bando, Y. Li, J. Hu, Y. Zhu, C. Tang

Advanced Materials Laboratory, National Institite for Materials Science, Tsukuba, Japan
Contact e-mail:golberg.dmitri@nims.go.jp

Nanotubes made of Boron Nitride and Boron-Carbon-Nitride were prepared and their electrical behavior, i.e. transport and field emission properties, were analyzed as a function of BN-rich and C-rich layer spatial arrangement and tube overall chemical composition. The I-V curves were measured in transmission and low energy electron point source microscopes. It was found that B-C-N nanotube conductance may be smoothly tuned as a function of these easy-to-control parameters. Inorganic nanotube (BN, MgO, C, In2O3, SiO2) filling with various materials, e.g. wide liquid range metals, oxygen-release compounds, semiconducting and ferromagnetic nanowires, was accomplished. This correspondingly creates: nanodevices for temperature measurements on a sub-micron scale; nanoscale oxygen burners/generators; and insulating nanocables for nanotechnology multi-purposes. Phase transformations, thermal expansion and crystallography of various filled phases confined with a nanotube shape were thor oughly investigated using HRTEM and electron diffraction with a nanosize electron probe. Semiconducting nanotubes made of widely used cubic lattice materials, i.e. GaN and Si were synthesized using templating. Finally, microtubes composed of C or Si were prepared. The latter tubes create new opportunities in performing in-channel nanotube metallurgical and chemical operations.

G Contributed Session (Tuesday Afternoon)

Oral **Poster++** ***Presentation***

A one-dimensional semiconductor crystal with differentially rotating atomic layers encapsulated within a single-walled carbon nanotube

J. Sloan[1,2], *R. Carter*[1,2], *A. I. Kirkland*[2], *R. R. Meyer*[2], *J. L. Hutchison*[2] *and M. L. H. Green*[1]

[1] Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QR U.K.

[2] Department of Materials, University of Oxford, Parks Road, Oxford, OX1 3PH U.K.

Contact e-mail:jeremy.sloan@chem.ox.ac.uk

One-dimensional (1D) nanowires of the semiconductor HgTe formed from stacked Hg_2Te_2 layers can be grown within the capillaries of 1.4 nm diameter single-walled carbon nanotubes (SWNTs) [1]. Some of these 1D wires undergo an unprecedented form of crystal growth in which the alternating constituent Hg_2Te_2 layers rotate differentially along the length of the SWNT capillary. Super-resolved transmission electron microscopy images reveal that static Hg_2Te_2 layers alternates with a secondary mobile Hg_2Te_2 layer that rotates about the axis of the SWNT in an apparently helical fashion. The effect is attributed to differences in packing behaviour between the alternating layers and differential interactions with the encapsulating SWNT and is thus thought to be a unique property of encapsulated nanowires.

[1] R. Carter, J. Sloan, A. I. Kirkland, R. R. Meyer, J. L. Hutchison and M. L. H. Green, 2004, submitted.

G.1 *Raman Charactrization of Nanotubes*

Resonance Raman and optical intensity of isolated single-wall carbon nanotube

R. Saito[1], *A. Gruneis*[1], *J. Jiang*[1], *G. Ge. Samsonidze*[2], *A. Jorio*[3], *M. A. Pimenta*[3], *A. G. Souza-Filho*[4], *G. Dresselhaus*[2], *M. S. Dresselhaus*[2]

[1] Tohoku Univ. and CREST JST, Sendai Japan,
[2] MIT, Cambridge, MA USA,
[3]Univ. Fed. Minas Gerais, MG, Brazil,
[4] Univ. Fed. Cerea, Cerea, Brazil
Contact e-mail:rsaito@flex.phys.tohoku.ac.jp

The resonance Raman intensity and optical absorption and emission of isolated single wall carbon nanotubes (SWNTs) are calculated by using electron-*photon* and electron-*phonon* matrix element calculations made by our groups. Single and double resonance Raman intensities of graphite and SWNTs are calculated in which the relative intensity of Raman spectra to one another is now possible compared with experiment as a function of nanotube diameter and chirality or as a function of excitation laser energy. The calculated results also show (1) optical intensity different between type 1 and type 2 SWNTs, (2) electron recombination rate for a photo-electron for each phonon branch, which are in good agreement with fast optics experiments.

Resonance Raman spectra of isolated single-wall carbon nanotubes

H. Kataura[1], T. Ueno, Y. Miyata[2], S. Okubo[3],S. Suzuki[2], and Y. Achiba[2]

[1] Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, Tukuba 305-8565, Japan
[2] Graduate School of Science, Tokyo Metropolitan Univ., Tokyo 192-0397, Japan
[3] Institute of Multidisciplinary Research for Advanced Materials, Tohoku Univ., Sendai 980-8577 Japan
Contact e-mail:h-kataura@aist.go.jp

We have synthesized well isolated single-wall carbon nanotubes (SWCNTs) embedded in supporting materials and measured resonance Raman spectra. The line width of radial breathing mode (RBM) peak is typically 1.5 cm^{-1} that is much narrower than the previous value of 5 cm^{-1} for the isolate SWCNTs lying on Si surface. Since the narrow RBM peak means that the phonon scattering is well suppressed, it is suggested that SWCNTs in the sample are defect less, well isolated and probably suspended. Each RBM peak showed sharp resonance effect, and then we obtained experimental optical transition energy (Eii) versus diameter plot. We calculated Eii energies by the tight-binding model considering the third neighbors and compared them with the experimental results. In the first and second optical transitions of the metallic SWCNTs, the experimental plot shows good agreement to the calculated ones. Since the chirality assignment by the photoluminescence spectra cannot be applied to metallic SWCNTs, our result will give useful information to the total chirality assignments.

Optical Transitions Energies for HiPco Carbon Nanotubes Measured by Resonance Raman Spectroscopy

C. Fantini[1], *A. Jorio*[1], *M. Souza*[1], *A. J. Mai Jr*[1]., *M. S. Strano*[2], *M. S. Dresselhaus*[3] *and M. A. Pimenta*[1]

[1] Departamento de Fisica, Universidade Federal de Minas Gerais, Brazil
[2] University of Illinois at Urbana, USA
[3] Massachusetts Institute of Technology,USA
Contact e-mail:cfleite@fisica.ufmg.br

Samples of HiPco single-wall carbon nanotubes (SWNTs) within bundles and individual tubes wrapped in sodium dodecyl sulfate (SDS) in aqueous solution are ivestigated by resonance Raman spectroscopy. Stokes and anti-Stokes Raman spectroscopy measurements of the radial breathing modes (RBM) using 76 excitation laser energies between 1.52 and 2.71 eV are reported. For semiconducting nanotubes, the electronic transition energies (Eii) measured by resonance Raman spectroscopy agree with the values measured by optical absorption and photoluminescence. For metallic nanotubes, not observed in photoluminescence experiments, the (n,m) assignment is obtained. Isolated nanotubes in solution and in bundles are observed to exhibit almost the same RBM frequencies while, for nanotubes within bundles, the transition energies are red-shifted. A detailed laser power dependence for SWNTs bundles is presented.

Raman Studies of Individualized, Aggregated, and Ultralong Carbon Nanotubes

Stephen K. Doorn, Michael J. O'Connell, Saujan Sivaram, Michael S. Strano

Los Alamos National Laboratory and University of Illinois
Contact e-mail:skdoorn@lanl.gov

Results from complete NIR (695 nm to 985 nm excitation) resonance Raman enhancement profiles obtained for radial breathing modes (RBM) of individually dispersed solution phase carbon nanotubes will be presented. The data allows definitive assignment of the semiconducting tube types observed, as well as for some metallics. Our results agree well with recently published predictions for transition energies and RBM frequencies. Results demonstrating a chirality dependence of Raman intensities will also be presented with discussion of the origin of the phenomenon. Similar enhancement profile data was obtained on aggregated nanotube samples. Comparison of data between individualized and aggregated nanotubes has allowed us to evaluate recent predictions for the behavior of interacting nanotubes. We discuss expectations for perturbations of electronic states and changes in RBM frequencies. We will also discuss the implications of these results for general Raman characterization of carbon nanotubes, with an emphasis on evaluation of new nanotube separation techniques. Finally, we will present recent results on Raman imaging and characterization of ultralong CVD nanotubes produced by "rapid heating" methods.

Single and Double Resonance Raman G-band Processes in Carbon Nanotubes

M. Souza (1), *A. Jorio* (1), *C. Fantini* (1), *B. R. A. Neves* (1), *M. A. Pimenta* (1),*R. Saito* (2), *A. Ismach* (3), *E. Joselevich* (3), *V. W. Brar* (4), *Ge. G. Samsonidze* (4),*G. Dresselhaus* (4) *and M. S. Dresselhaus* (4).

(1) Departamento de Fisica Universidade Federal de Minas Gerais, Brazil;
(2) Department of Physics, Tohoku University, Japan;
(3) Weizmann Institute of Science, Israel;
(4) Massachusetts Institute of Technology,USA
Contact e-mail:mdesouza@fisica.ufmg.br

Following a recent debate about the resonance nature of the tangential (G) band in the Raman spectra of single-wall carbon nanotubes (SWNT) we measured the Raman spectra of isolated and bundled (aligned and misaligned) SWNT samples, with different excitation laser energies (Elaser). This study shows that the G band can be originated from both single and double resonance mechanisms. By performing Raman spectroscopy using different Elaser, we can separate the contribution from single and double resonance processes. The G band has a single resonance scattering nature with a strong intensity in non-defective nanotubes. These G band spectra present a non-disperse behavior and keep the selection rules of the first-order Raman scattering. However, in defectives samples, the G band spectra is two orders of magnitude lower than the spectra in non-defective sample, and it is composed both by single resonance and dispersive defect-induced double resonance processes.

Step-like dispersive Raman modes in carbon nanotubes

M. A.Pimenta[1], *C. Fantini*[1], *M. Souza*[1], *A. Jorio*[1], *L.O. Ladeira*[1], *A. G. Souza-Filho*[2]

[1] Departamento de Fisica, Universidade Federal de Minas Gerais, Brazil;
[2] Departamento de Fisica, Universidade Federal do Ceara, Brazil;
[3] Tohoku University, Japan;
[4] Massachusetts Institute of Technology,USA
Contact e-mail:mpimenta@fisica.ufmg.br

This work reports observation of selective Resonance Raman scattering of the intermediate frequency modesin carbon nanotubes. The experimental work (Raman spectra with 22 different excitation energies into a 0.8,eV energy range) allowed us to construct a 2D Raman spectra, by plotting the Raman shift in the abscissa and the laser energy in the ordinate. This work reports a new and very unusual phenomenon in Raman spectroscopy, with important new information on the electron-phonon interaction and on acoustic-like waves in a 1D system. Although restrictions on the electron-phonon interaction are not severe in conventional 3D solids, they appear to be strongly selective in single wall carbon nanotubes, due to the presence of van Hove singularities in both the electron and phonon density of states, resulting in a turn-on/turn-off effect for the scattering process. Selection of very special SWNTs, that is those in the family mod(2n+m,3)=1 and with low chiral angle, is shown to be due to quantum confinement of electrons and phonons bounded by symmetry selection rules.

Resonant Raman studies on double-wall carbon nanotubes by high-temperature pulsed-arc discharge

T.Shimada, T.Sugai, C.Fantini, M.Souza, L.G.Cancado, A.Jorio, M.A.Pimenta, R.Saito,A.Grueneis, G.Dresselhaus, M.S.Dresselhaus, Y.Ohno, T.Mizutani, and H.Shinohara

Nagoya Univ, UFMG, Tohoku Univ., MIT, CREST-JST, PRESTO-JST
Contact e-mail:shimada@nano.chem.nagoya-u.ac.jp

High quality double-wall carbon nanotubes (DWNTs), which were synthesized by the high-temperature pulsed-arc discharge (HTPAD) method, have characterized by resonant Raman spectroscopy employing various excitation laser lines (photon energy 1.8-2.8 eV). RBM, D-band, G-band and G'-band have shown salient photon energy dependence. Two distinct peaks for G'-band were observed around 2,450 and 2,650 cm^{-1}. These two peaks have exhibited different dependence on excitation energy. Theoretical considerations indicate that one stems from non-dispersive of phonon frequency and the other from dispersive processes. In fact, experimental results were good agreement with calculation. Such features were also obtained for SWNTs and HOPG.

Growth and Raman spectra of aligned double-walled carbon nanotube long ropes with narrow diameter distribution

Wencai Ren, Hui-Ming Cheng

Shenyang Ntl Lab for Mater. Sci., Inst.of Metal Res., CAS, China
Contact e-mail:cheng@imr.ac.cn

For future applications of double-walled carbon nanotubes (DWNTs) in nanoscale electronics, their aligned long ropes with narrow diameter distributions were selectively synthesized by sulfur-assisted floating catalytic decomposition of methane in the presence of Fe catalyst with the addition of hydrogen. Resonant Raman measurements show that the outer and inner tubes are mostly semiconducting and metallic, with the corresponding diameter in the range of 1.7-2.0 nm and 1.0-1.3 nm, respectively. These special DWNTs with a dominant semiconducting and metallic combination can be expected to have promising applications as molecular cables. Comparing the SWNT bundles with similar outer diameters, about 3% Raman upshifts were obtained in their RBM region. Polarization Raman studies were performed on the aligned DWNT bundles and the results indicated that in addition to the RBM, the G-band, D-band and G'-band profiles all can be well deconvolved into two intrinsic independent single- walled carbon nanotube (SWNT) components constituting a DWNT. According to the G-band mode symmetry assignment results, the diameters and transport properties were obtained, which are in good agreement with those from RBM analysis. All these observations indicate that DWNTs possess unique characteristic Raman spectra different from other sp2 carbon materials.

Fluorescence and Resonant Raman study of double walled carbon nanotubes (DWNTs)

Anna K. Swan, Yan Yin*, Bennett B. Goldberg*, M.Selim Unlu*, Claudio Chamon* , Wolfgang Bacsa+, Revathi Bacsa+*

(*Boston University), (+University of Toulouse)
Contact e-mail:swan@bu.edu

Results from resonant Raman and photoluminescence (PL) measurements of single wall carbon nanotubes (SWNTs) have varied significantly with the nanotube environment. In contrast, the inner tube in DWNTs is shielded by and is only weekly interacting with the outer tube, providing an appealing system for studies of intrinsic properties. The sample is dominated by DWNTs with small inner tube diameters (< 1 nm). Resonant Raman scattering is used to characterize both low density ensembles and individual double wall carbon nanotubes. The variation in frequency with diameter for radial breathing modes allows measurements of narrow line-widths, 1-2 cm^{-1}, even for ensemble data. The range of RBM frequencies demonstrates tube diameters <0.6 nm, in accordance with statistics from TEM data. Several examples of inner and outer pairs are observed for individual DWNTs RBMs. Optical heating of the DWNTs tunes the scattering in or out of resonance, while the linewidths are only weekly depende

ELECTRON ENERGY LOSS AND RESONANT RAMAN SPECTROSCOPY OF SINGLE WALL BORON NITRIDE NANOTUBES

*R. Arenal de la Concha *(1), O. Stephan (2), A. Ferrari (3), D. Taverna (2), S. Reich (3), A. Rubio (4), A. Loiseau (1)*

(1) LEM, CNRS-ONERA, 92322 Chtillon - France
(2) LPS, Universite Paris-Sud, 91405 Orsay - France
(3) Engineering Departement, University of Cambridge, Cambridge UK
(4) DFM, DIPC, Universidad Pais Vasco 20018 San Sebastian - Spain
Contact e-mail:rarenal@onera.fr

Single wall (SW) BN-NTs have been produced in important quantity and with a high degree of crystallinity by a vaporization laser technique [1]. The crystal structure and chemical composition of the collected soot have been characterized by very high resolution transmission electron microscopy (VHRTEM) and electron energy loss spectroscopy (EELS) [2]. EELS measurements in the valence band region have been performed in STEM (Scanning TEM) to obtain information on the electronic structure (band gap, plasmons analysis) of individual tubes. In contrast to C-NTs, BN-NTs are highly polar dielectric material, with a wide band gap close to 5.5 eV,largely independent of helicity and diameter. We thus perform resonant Raman measurements of the raw product [4] and of reference hexagonal BN by exciting with UV ligth in the 5.1-5.4 eV energy range. The experimental results are compared with ab-initio calculations performed by density-functional-theory in local density approximation [5].

[1] R. S. Lee, J. Gavillet, M. Lamy de la Chapelle, A. Loiseau, J.-L. Cochon, D. Pigache, J. Thibault, F. Willaime, PRB 64R, 121405 (2001)
[2] O. Stephan, A. Vlandas, R. Arenal de la Concha, S. Trasobares, A.Loiseau, C. Colliex, Proceedings EMAG (2003) and R. Arenal de la Concha, O. Stephan, A. Vlandas, A. Rubio, A. Loiseau (unpublished)
[3] R. Arenal de la Concha, O. Stephan, D. Taverna, M. Kociak, C. Colliex, A. Rubio,A. Loiseau (to be published)
[4] R. Arenal de la Concha, A. Ferrari, S. Reich, A. Rubio, A. Loiseau (unpublished)
[5] L. Wirtz, R. Arenal de la Concha, A. Rubio, A. Loiseau, PRB 68, 45425 (2003)

The interior of carbon nanotubes studied by Raman spectroscopy and electron spin resonance on N@C_{60}@SWCNT

Ferenc Simon, Rudolf Pfeiffer, Florian Hasi, Matthias Holzweber, Christian Kramberger, Hans Kuzmany

Material Physics Institute, University of Vienna, Austria
Contact e-mail:fsimon@ap.univie.ac.at

The interior of carbon nanotubes was studied using multi-frequency Raman spectroscopy. Peapod structures transformed to double wall carbon nanotubes (DWCNT) were proven to be highly perfect reflecting the catalyst free growth conditions in the nano-clean room environment of the interior of the outer tube. The transformation was followed with a systematical thermal annealing to yield information about the inner tube growth mechanism. The (n,m) indexing of small diameter inner tubes was successfully applied to refine and extend the semi-empirical models of the radial breathing vibrational mode. The identification also allowed to track diameter selectively a range of phenomena such as nanotube closing after annealing, oxidation damage to the inner and outer tubes and many more. This demonstrates that filling with peapod and their subsequent transformation to DWCNT provides an important monitoring tool for nanotube handling procedures such as nanotube separation. DWCNT transforma tion from different carbon sources such as C_{60}, C_{70} peapod fullerenes yield similar inner tube distribution that evidence that the fullerene behaves only as a carbon source and its geometry does not play a role in the inner tube formation. The absence of a few, mid-diameter inner tubes is discussed as an intermediate bottle-neck configuration where C_{70} peapods can not be formed. The range of available spectroscopic methods has been extended to electron spin resonance with the encapsulation of the paramagnetic N@C_{60} inside nanotubes. N@C_{60} is temperature sensitive and its encapsulation in SWCNT requires a low temperature method that is described in detail.

Theory of the tangential G-band feature in the Raman spectra of metallic carbon nanotubes

S.M. Bose[1], *S. Gayen*[1] *and S.N. Behera*[2]

[1] Department of Physics, Drexel University, Philadelphia, PA 19104, USA
[2] Institute of Physics, Sachivalaya Marg, Bhubaneswar 751005, Orissa, India
Contact e-mail: bose@drexel.edu

The tangential G-band feature in the Raman spectra of metallic single-wall carbon nanotube shows two peaks: a higher frequency component having the Lorentzian shape and a lower-frequency component of lower intensity with a Breit-WignerFano (BWF) lineshape [1]. This interesting feature has been analyzed on the basis of phonon-plasmon coupling in a metallic nanotube. It is shown that while the gapless semi-acoustic plasmon cannot account for the observed spectra as claimed by Kempa [2], the low-lying optical plasmon corresponding to the tangential motion of the electrons on the nanotube surface [3] can explain the observed features associated with both the high- and low-frequency components. In particular, this theory gives both the Lorentzian and BWF lineshapes. Furthermore, this theory shows that the BWF peak moves to higher frequency, has lower intensity and lower half width at larger diameters. All these features are in agreement with experimental observations.

[1] S.D.M. Brown et al., Phys. Rev. B 63, 155414 (2001).
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[3] P. Longe and S.M. Bose, Phys. Rev. B 48, 18239 (1993).

G.2 *Characterization of Nanotubes*

NASA-JSC protocol for the characterization of single-wall carbon nanotube material quality

Sivaram Arepalli (1), Pavel Nikolaev (1), Olga Gorelik (1), Victor G. Hadjiev (2), William Holmes (1), Rodrigo Devivar (3), Bradley Files (4), and Leonard Yowell (4)

(1) G.B.Tech Inc. @ NASA-Johnson Space Center, Houston, TX 77058;
(2) Texas Center for Superconductivity and Advanced Materials, University of Houston, Houston, TX 77204;
(3) Bastion Technologies @ @ NASA-Johnson Space Center, Houston, TX 77058;
(4) NASA-Johnson Space Center, Mail Code ES, Houston, TX 77058
Contact e-mail:s.arepalli@jsc.nasa.gov

It is well known that the raw as well as purified single wall carbon nanotube (SWCNT) material always contain certain amount of impurities of varying composition (mostly metal catalyst and non-tubular carbon). Particular purification method also creates defects and/or functional groups in the SWCNT material and therefore affects the its dispersability in solvents (important to subsequent application development). A number of analytical characterization tools have been used successfully in the past years to assess various properties of nanotube materials, but lack of standards makes it difficult to compare these measurements across the board. In this work we report the protocol developed at NASA-JSC which standardizes measurements using TEM, SEM, TGA, Raman and UV-Vis-NIR absorption techniques. Numerical measures are established for parameters such as metal content, homogeneity, thermal stability and dispersability, to allow easy comparison of SWCNT materials. We will also report on the recent progress in quantitative measurement of non-tubular carbon impurities and a possible purity standard for SWCNT materials.

EXAFS study of local structure of Rb in single-walled carbon nanotubes

J-L. Bantignies[1], *R. Aznar*[1], *J-L. Sauvajol*[1], *L. Ducleaux*[2], *L. Alvarez*[3]

1 GDPC, University of Montpellier 2, France2 ESRF, Grenoble, France3 CRMD, University of Orleans, France
Contact e-mail:bantigni@gdpc.univ-montp2.fr

The local structure of intercalated single-walled carbon nanotubes with rubidium ions (Rb-SWNT) produced by electric charge technique and doped in vapour phase has been studied by Rb K-edge extended x-ray-absorption fine structure (EXAFS). The EXAFS spectra have shown the sensitivity of the local arrangement of alkali ions in SWNT. The first coordination shell of Rb ions corresponding to the first carbon neighbours have a clear time doping dependence. The superstructure of alkali is found to be incommensurate with the graphitic layer of the tubes for low time of doping. By contrast, for samples doped at saturation, the superstructure of alkali is found to be commensurate with the graphitic layer and disordered. Comparison between ab initio simulations of EXAFS spectra and experimental data indicates that Rb ions are mainly located inside the tubes and around the bundles. Theses results are in agreement with X-ray and neutron diffraction experiments performed on same samples. These results question the interstitial site as the preferential absorption site.

Nanoauger spectroscopy study of thin film metal catalyst transformation for the production of multi-wall and single-wall carbon nanotubes by chemical method deposition

R. G. Lacerda[1], *K. B. K. Teo*[1], *F. Wyczisk*[2], *P. Legagneux*[2], *A. S. The*[1], *M. H. Yang*[1], *S. H. Dalal*[1], *D. A. Jefferson*[1], *N. L. Rupesinghe*[1], *D. Roy*[1], *M. Chhowalla*[3],*G. A. J. Amaratunga*[1] *and W. I. Milne*[1]

[1] Engineering Department, University of Cambridge, Trumpington Street, Cambridge, CB2 1PZ, UK,
[2] Thales Research and Technology France, Domaine de Corbeville, 91404 Orsay, France,
[3] Rutgers University, Ceramic and Materials Engineering, Piscataway, New Jersey 08854
Contact e-mail:rgl26@eng.cam.ac.uk

The aim of this work is to study in detail the growth process of multi-wall and single-wall carbon nanotubes from thin metal catalyst by using Nanoauger spectroscopy. The growth is performed by CVD using a thin film triple metal (Al/Fe/Mo) catalyst, by a rapid growth process (gas C2H2, 1000 °C, 5 s) directly on silicon substrates [1]. Recently, a considerable amount of work has been performed using thin film metal layers as the catalyst for nanotube growth, however, the physical phenomena of transforming a thin metal layer into nanosize particles has not been fully understood. We intend to show how the catalyst is transformed and how it diffuses at different growth temperatures. A surface elemental map study is also presented providing a clear view of the distribution of the catalyst on the surface. We observe that during the formation of SWCNT's at high temperatures ($\sim$ 1000 °C), the initial Fe layer ($\sim$ 1 nm) is transformed into nano-size particles at the surface. In addition, the Al layer also plays a critical role as a suitable under-layer by being altered into Al2O3 particles. Finally, we will show how Nanoauger spectroscopy can also be used to directly observe single-wall carbon nanotubes.

[1] R. G. Lacerda et al., Appl. Phys. Lett. 84, 269 (2004).

Microscopic and spectroscopic studies of highly nitrogen-doped carbon nanotubes

M. Castignolles[1,2], *M. Glerup*[2,3], *S. Enouz*[1],*P. Bernier*[2], *A. Loiseau*[1], *and O. Stéphan*[4]

[1] Laboratoire d'eEtudes des Microstructures, CNRS-ONERA, Chatillon, France
[2] Groupe de Dynamique des Phases Condensées, Université Montpellier II, Montpellier, France
[3] Grenoble High Magnetic Field Laboratory, MPI-CNRS, Grenoble, France
[4] Laboratoire de Physique des Solides, Université Paris
Contact e-mail:casti@onera.fr

We will present a detailed study of highly-nitrogen doped multi-walled nanotubes, with nitrogen concentration up to 25 %. These tubes were synthesized using an aerosol method which is described in ref. [1].

The tubes were characterized by high-resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS). Particular attention will be given to the evolution of the fine structure of the carbon and nitrogen K-edges in the EEL spectra. This is correlated to the concentration and electronic environment of nitrogen in the tubes.

Also, it will be demonstrated that there exist a close relation between the tube morphologies and the spatial distribution of the carbon and nitrogen atoms.

These information have given insight to the growth of these highly-nitrogen doped multi-walled nanotubes and a mechanism will be discussed.

[1] M. Glerup, M. Castignolles, M. Holzinger, G. Hug, A. Loiseau and P. Bernier, Chem. Comm., 2542-2543 (2003)

Image simulation of carbon nanotubes

T. Hayashi, H. Muramatsu, Y.A.Kim*, H.Kawakami*, M. Kobayashi*, and M. Endo**

General Information Processing Center, Shinshu University,
*Faculty of Engineering, Shinshu University
Contact e-mail: hayashi@endomoribu.shinshu-u.ac.jp

Since carbon nanotube is a nanoscale material, we need some special tools such as TEM, SPM, Raman, and photoluminescence, etc. to understand the nanostructure. Since TEM is one of the most intuitive tool to observe the nanostructure, it is widely used in lots of scientific studies. Although TEM is a powerful tool, it is not that easy to understand the image especially when there is a overlapping matter such as amorphous carbons films or obstructing tubes. In this presentation, TEM image simulation is used to simulate many situations that could lead to the misinterpretation of the actual TEM image by changing the defocus value. The results are compared with the TEM images that appears to be obtained at the inappropriate defocus conditions.

G.3 *Nanotube Dispersion and Purification*

Manipulating SWNTs via Dielectrophoresis: Separation and Deposition

R. Krupke

[1] Forschungszentrum Karlsruhe, Institut frür Nanotechnologie, 76021 Karlsruhe, Germany.
Contact e-mail:krupke@int.fzk.de

We have demonstrated recently that metallic SWNTs can be separated from semiconducting ones by their opposing movement in a solvent when interacting with an external alternating electric field[1]. The effect is based on the different, electric-field induced polarisabilities of the two tube types. Now, we have performed a comprehensive study to get a full description of the separation scheme over a range of experimentally acessible parameters. Our new results reveal the existence of a finite surface conductance of suspended semiconducting SWNTs, which gives rise to a unique frequency dependence of the dielectrophoretic separation. As a result dielectrophoresis can be used for both, the separation and the selective deposition of metallic and semiconducting SWNTs, which makes dielectrophoresis a viable method for device fabrication.

[1] R. Krupke, F. Hennrich, M. M. Kappes, H. v. Léhneysen, Science 301, 344-347 (2003)

Dielectrophoretic separation of metallic and semiconducting SWNT

T.Lutz and K.J.Donovan

Physics Department, Queen Mary, University of London
Contact e-mail:t.lutz@qmul.ac.uk

Using dielectrophoresis, and taking advantage of the very high polarisability of metallic SWNT, the latter are extracted from mixtures of semiconducting and metallic nanotubes, the separation process being followed by resonant Raman spectroscopy. Different types of dispersing agent were used, and different electrode geometries were tested where the electric field lines are either in the same direction as or perpendicular to the field gradient. The advantages and disadvantages of these different geometries are discussed. The fraction of tubes driven toward the high field gradient region shows an enrichment in metallic nanotubes, as can be deduced from the intensity variations of the radial breathing modes of the two types of tubes in the initial and fractionated product.

Extraction of semiconducting CNTs by repeated dielectrophoretic filterings

D. S. Lee[1], *D. W. Kim*[1], *H. S. Kim*[1], *S. W. Lee*[1], *S. H. Jhang*[1], *E. E. B. Campbell*[2], *Y. W. Park*[1]

[1] School of Physics and Condensed Matter Research Institute, Seoul National University, Seoul 151-747, Korea
[2] Department of Experimental Physics, Göteborg University and Chalmers University of Technology, SE-41296 Göteborg, Sweden
Contact e-mail: dwater@phya.snu.ac.kr

We have separated semiconducting carbon nanotubes from as-grown batch material (HiPco production). A special configuration of electrodes which generates a 3-dimensional electric field gradient was used to filter out and deposit metallic carbon nanotubes by dielectrophoretic method, leaving the remaining dispersion enriched in semiconducting nanotubes. The efficiency of filtering was determined by Raman spectroscopy. Using repeated deposition cycles, the ratio of semiconducting to metallic tubes was increased. After seven cycles, the proportion of semiconducting tubes in the remaining dispersion reached 94%.

Multi-Step Purification of Single Wall Carbon Nanotubes

Ya-Qiong Xu, Haiqing Peng, Zhenning Gu, Yuhuang Wang,
Robert H. Hauge and Richard E. Smalley

Department of Chemistry and Department of Electrical & Computer Engineering,
Rice University.
Contact e-mail:yqxu@rice.edu

A scalable multi-step purification method is developed to remove metal catalysts and non-nanotube carbon from raw material produced by the High-Pressure CO (HiPco) process. In this study, the iron catalysts, coated by non-nanotube carbon, are exposed and oxidized by oxygen at successively higher temperatures. To avoid the catalytic effect of iron oxide on carbon nanotube oxidation, after each oxidation, the exposed and oxidized metal catalysts are inactivated by the reaction with $C_2H_2F_4$ orSF_6. Finally, inactivated iron compounds are removed by concentrated HCl soxhlet extraction. The purity and quality of each sample are documented by thermo-gravimetric analysis (TGA), Raman spectrometry, ultraviolet-visible-near-IR (UV-vis-near-IR) spectrometry, environmental scanning electron microscope (ESEM), and transmission electron microscope (TEM) spectroscopy. The purity (Fe < 1wt%) and yield (70%) are better than those of conventional methods and little side wall damage is found.

Novel Methods of Processing Carbon Nanotubes

Walter V. Cicha, Yun Li, Patrick Malenfant, and Davide Simone

Global Research Center, General Electric Company
Contact e-mail:cichawa@crd.ge.com

See next section please.

Dissolution of carbon nanotubes

Alain Penicaud

Centre de Recherche Paul Pascal - CNRS - U. Bordeaux
Contact e-mail:penicaud@crpp-bordeaux.cnrs.fr

Upon chemical reduction, it is found that carbon nanotubes are rendered solubles in polar organic solvents without functionnalization and without the aid of ultrasounds, thus keeping both the true chemical structure of carbon nanotubes and their length. We will present the synthesis method and will describe the nanotube solutions thus obtained. Solubilities are as high as a few mg/ml . These solutions may have a number of applications such as organic functionnalization of carbon nanotubes, purification, obtention of thin films and composites and so on.

Characterization and Processing of Single-Walled Carbon Nanotubes Dispersions

Yael Dror[1], *Wael Salalha*[2], *Rafail L. Khalfin*[1], *Yachin Cohen*[1],*Alexander L. Yarin*[2], *Eyal Zussman*[2], *Rachel Yerushalmi-Rozen*[3], *Wim Pyckhout-Hintzen*[4]

[1]Chemical and [2]Mechanical Engineering Departments, Technion, Haifa, Israel
Contact e-mail: ceyael@techunix.technion.ac.il

Dispersion of carbon nanotubes in fluid medium is a crucial step in the successful production of applicable products that may exhibit their superior properties. We study the interactions of stable aqueous dispersions of single-walled carbon nanotubes using three different dispersing agents: a linear amphiphilic alternating ionic copolymer, a nonionic surfactant and highly branched natural (ionic) polysaccharide. The dispersions were characterized using cryo-transmission electron microscopy and small angles neutron scattering with contrast variation. The objective is to recognize different modes of structural associations between the dispersing agent and the nanotubes and to evaluate quantitative parameters of the dispersions such as mean diameter of the dispersed bundles, thickness of the adsorbed layer etc. The electrospinning process was used successfully to fabricate nanofibers of poly(ethylene oxide) in which carbon nanotubes are embedded. The degrees of orientation of polymer, dispersant and nanotubes were studied using X-ray diffraction and transmission electron microscopy. The results show that the quality of the dispersion has a key roll in the ability of the electrospinning process to incorporated individual nanotubes in an oriented manner into the nanofibers.

Effects of Solubility Parameters on Ultrasonic Dispersions of Singlewall Carbon Nanotubes

Hyeong Taek Ham, Yeong Suk Choi, Mu Guen Chee, In Jae Chung

KAIST
Contact e-mail:hamlet79@kaist.ac.kr

The ultrasonicated dispersions of singlewall carbon nanotubes (SWNTs) in various solvents and aqueous surfactant emulsions were investigated to correlate the degree of dispersion states of SWNTs with Hansen's solubility parameters (δt2= δd2+ δp2 + δh2). It was found that SWNTs were dispersed or suspended very well in the solvents with certain value of the dispersive component (δd). They were precipitated in the solvents with high polar component (δp) and hydrogen bonding component (δh). The solvents in dispersed group occupied a certain region in 3-dimensional space of three components. The surfactants with lipophilic group equal to and longer than decyl, containing 9 methylene groups and 1 methyl group, contributed to the dispersion of SWNTs in water. The surfactant in dispersed group had a lower limit in the dispersive component (δd) of Hansen parameter.

G.4 *Chemical Modification of Nanotubes*

Electrochemical modification of individual carbon nanotubes

Kannan Balasubramanian, Alicia Maroto, Roman Sordan, Marko Burghard, Klaus Kern

Max-Planck-Institut fuer Festkoerperforschung, Heisenbergstrasse 1, D70569
Stuttgart, Germany
Contact e-mail:b.kannan@fkf.mpg.de

Chemical modification is an effective tool for broadening the application spectrum of carbon nanotubes (CNTs). We have developed this tool into an efficient procedure utilizing electrochemistry to achieve electronic structure modification and tailoring of surface properties of individual single-wall nanotubes (SWCNTs). Specifically, individually selected SWCNTs can be coated with ultrathin layers of functional moieties with a controllable thickness in a covalent or non-covalent manner [AdvMat]. Furthermore, with gate voltage tuning, the metallic SWCNTs in an ensemble have been selectively modified to eliminate their current carrying capability. As this approach results in a purely semiconducting channel between electrodes, a generic route towards fabrication of high-performance field-effect transistors has been established [NLett]. Moreover, the transport properties of SWCNTs modified with functional groups sensitive to specific ions or pH are studied for potential applications as sensors.

[*AdvMat*] K. Balasubramanian et al., Adv. Mat 15, 1515 (2003)
[*NLett*] K. Balasubramanian et al., Nano Lett. (submitted).

FUNCTIONALIZATION AND BINDING TECHNIQUES FOR ALIGNMENT USING OF CARBON NANOTUBES

Sandeep Kumar, Dr. Lalit M. Bhardwaj, Dr. R.P. Bajpai

Central Scientific Instruments Organization
Contact e-mail:

Carbon nanotubes are wonderful nanostructures with perfect atomic structure having different diameters and chiralities and have unique electrical and mechanical properties. The impurities present in the carbon nanotubes during their synthesis are amorphous carbon soot, fullerenes, and catalyst particles. Their purification is necessary for different applications. Also, these are produced in random fashion and need to be aligned properly. Our main focus is to create different functional groups on carbon nanotubes and their binding with biomolecules like proteins, DNA etc. Molecular modeling has shown binding of DNA to carbon nanotubes. CNT adhered to DNA can be separated by biotechniques like electrophoresis and chromatography. Binding of biomolecules to carbon nanotubes will help in the alignment of carbon nanotubes. Due to their extreme flexibility and regular structure, carbon nanotubes open up the exciting possibility of fabricating devices approximately 1000 times smaller(NEMS) than current MEMS, thus allowing for unique applications in healthcare, nanodevices sensors etc.

Covalent Attachment of DNA Oligonucleotide and Hybridization on the Patterned Single-Walled Carbon Nanotube Film.

Dae-Hwan Jung[1], *Byung Hun Kim*[1], *Young Koan Ko*[1], *Sang Yup Lee*[1] *Soung Hee Park*[2], *Hee-Tae Jung*[1]

[1] Department of Chemical & Biomolecular Engineering, Korea Advanced Institute of Science & Technology,
[2] Department of Advanced Materials Engineering, Woosuk University
Contact e-mail:heetae@kaist.ac.kr

The immobilization of DNA oligonucleotides on single-walled carbon nanotube (SWNT) multilayer films is a crucial step for any application in the field of DNA microarrays. It determines the efficacy of hybridization and influences the signal strength for the detection. For the immobilization of DNA, we used SWNT multilayer films made from the chemical reaction using the cut SWNTs and the chemical reagents onto an amine-terminated glass. These SWNTs multilayer films were constructed via consecutive condensation reactions that created stacks of SWNT layers linked together with the aid of a linker molecule 4,4'-oxydianiline (ODA) and a condensation reagent. The aminated or carboxylated DNA oligonucleotides were covalently immobilized to the carboxylated or aminated SWNTs multilayer films via amide bonds by 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride-catalyzed amidation reaction. Absorbance spectrophotometry (UV-vis-NIR) analysis indicated that the surface density of SWNT films increased uniformly according to the number of reaction cycles. Scanning electron microscopy measurements results showed that the SWNT multilayer film thoroughly and uniformly covered the substrate surface. The DNA oligonucleotide probe attached onto SWNT multilayer films and subsequent hybridization has been investigated using X-ray photoelectron spectroscopy and fluorescence-based measurements of DNA hybridization. The resultant DNA-attached SWNT multilayer films were shown to exhibit excellent specificity and chemical stability under the conditions of DNA hybridization.

Optical Studies of GT-DNA-Nanotube Hybrids

S. G.Chou, H. B. Ribeiro, A.. P. Santos, C. Fantini, Ge. G. Samsonidze, A. Jorio, F. Plentz, G. Dresselhaus, M. S. Dresselhaus, Y-M. Chiang, M. Zheng, A.. K. Swan, M. S. Unlu, B. B. Goldberg

Chemistry, MIT; Physics, UFMG, Brazil; CDTN, Brazil; Physics, UFMG, Brazil; EECS, MIT; Physics, UFMG, Brazil; Physics, UFMG, Brazil, F. B. Magnet Lab, MIT; Physics and EECS, MIT; Material Sciences and Engineering, MIT; Dupont; ECE, Boston Univesity; ECE, Boston University; ECE and Physics, Boston University.
Contact e-mail:grace@mgm.mit.edu

Optical studies were carried out simultaneously using both fluorescence and resonance Raman scattering techniques on isolated DNA-nanotube hybrids that are prepared by the sequence dependent wrapping of single stranded DNA, around CoMoCAT nanotubes (NT) ($d_t \sim 0.75$nm). The optical measurements are carried out on the same NT after the DNA is removed. The study at the single nanotube level gives insights into how the charge transfer between biomolecules and the NT alters the electronic structure. At the same time, the two complementary optical techniques provide a good assessment of the tight binding approximation (TBA) for the interband transition energy, E_{ii}, in the small diameter regime. The authors acknowledge the support from NSF, Dupont-MIT Alliance, NIRT-0210752, CNPq-Brazil, and Renishaw Inc.

Formation of Carbon-Nanotube/DNA Composite Materials

T. Okada[1], *T. Kaneko*[1], *R. Hatakeyama*[1], *and K. Tohji*[2]

[1]Department of Electronic Engineering, Tohoku University
[2]Graduate School of Environmental Studies, Tohoku University
Contact e-mail:okada@ecei.tohoku.ac.jp

Recently, the investigations on novel properties of carbon-nanotube/biomolecule composite materials have rapidly progressed [1]. Especially, DNA is one of the most interesting materials because of their unique properties such as 1D nano structure and highly selective binding among many bio-molecules. In this study, we have demonstrated the formation of carbon-nanotube/DNA composite materials using novel plasma technique, i.e., arc discharge in DNA solution. When the formation of carbon nanotube is performed in the DNA solution, Raman spectrum of the carbon nanotubes has a broad peak in the region of the 500-1200 cm^{-1}, which is expected to originate from carbon-nanotube/DNA composite materials. Furthermore, based on the emission measurement during the discharge, the C_2 radical is considered to play an important role in the carbon nanotube formation process in DNA solution.

[1] M. Zheng et al., Science 302 (2003) 1545.

Identification and characterization of a peptide aptamer for single-wall carbon nanohorn

D. Kase[1], *J. L. Kulp III*[2], *J. Zhu*[3], *M. Yudasaka*[3], *J. S. Evans*[2], *S. Iijima*[4], *K. Shiba*[5]

[1] Department of Protein Engineering, Cancer Institute.(Tokyo),
[2] Laboratory for Chemical Physics, New York University(New York),
[3] NEC and SORST, JST, c/o NEC(Tsukuba),
[4] Meijo University and AIST(Nagoya),
[5]CREST, JST c/o Cancer Institute(Tokyo)
Contact e-mail:dkase@jfcr.or.jp

With the long-term goal of developing nevel nano-composites consisting of single-wall carbon nanohorns(SWNHs) and artificial proteins, we report here the use of peptide phage display methodology to select peptide motifs that specifically recognize the surfaces of SWNHs. Starting from 10^9 population, the phage clone displaying DYFSSPYYEQLF has been concentrated via 6 cycles of bio-panning. The synthetic peptide showed an conformational variations: at neutral pH, the sequence adopts a random-coil-like structure, but at low pH, the sequence prefers an α-helical structure.

We will introduce our efforts to construct artificial proteins by using this motif.

Derivatization of Hydroxyl Groups Attached to Carbon Nanotube Surface

C. A. Furtado1, F. N. Paschoal1, A. A. Okuma1, A. P. Santos1, L. P. S. Pimenta2, R. P. F. Gil2, R. B. Alves2, U. J. Kim3, P. C. Eklund3

1 CDTN/CNEN - Brasil,
2 UFMG - Brasil,
3 The Pennsylvania State University - USA
Contact e-mail:clas@cdtn.br

Chemical derivatization of carbon nanotubes is the main approach to increase nanotube solubility, change optical and electronic properties, improve nanotube-matrix interaction in composite materials, sort nanotube filaments by size, chirality and electronic properties and arrange them on patterned substrates. In this work, we explore experimentally the reactivity of hydroxyl groups toward long chain alcohol derivatives in order to get ether-bonded carbon nanotubes-alkyl systems (CN-O-R). These systems may further undergo to self-organization. In addition, by theoretical studies, the oxygen-alkyl bonds of CN ends-O-R systems are stronger for armchair nanotubes than zigzag tubes [1]. This might open a new route for chirality-based bulk separation of carbon nanoutbes.

[1] S. Gustavsson, A. Rosn, K. Bolton, Nano Lett. 3/2, 265 (2003).

Structural and Vibrational Properties of Alkali-metal Atoms Adsorbed Single-walled Carbon Nanotubes: A Density Functional Study

Brahim Akdim [1], *Xiaofeng Duan* [2], *and Ruth Pachter* [1]

[1]Air Force Research Laboratory, Materials & Manufacturing Directorate,
Wright-Patterson Air Force Base, Ohio
Major Shared Resource Center for High Performance Computing, Aeronautical
Systems Center, Wright-Patterson Air Force Base, Ohio
Contact e-mail:brahim.akdim@wpafb.af.mil

In this study, we present a theoretical examination of the effects of K, Rb, and Cs adsorbed on single-walled carbon nanotubes. As previously shown, alkali-metal atoms doping results in the downshifts of the radial breathing and G-band modes, rationalized in terms of charge transfer between the adsorbates and the SWCNTs (Rao et al. Nature 1997). Applying first principles density functional theory within the generalized gradient approximation calculations, we report on the structural, energetics, and Raman modes of armchair and zigzag doped SWCNTs. Assorted models, representing possible adsorption mechanisms, are considered, and changes in the Raman modes are quantified. Furthermore, a charge transfer from the alkali metal to the carbon nanotube is shown in our results, supporting the previously suggested experimental work. However, in addition to such charge transfer, a lowering of tube symmetry due to alkali-metal intercalation may play a role in the modes softening. Finally, the correlation of mode softening with tube diameter will be discussed.

How and where lithium atoms are adsorbed on carbon nanotubes

Juan S. Arellano

Universidad Autonoma Metropolitana Azcapotzalco
Contact e-mail:jsap@correo.azc.uam.mx

Some results are presented for the adsorption of a lithium atom inside or outside a (6,6) carbon nanotube. The results includes besides the static calculations a few more with relaxation of the lithium atom. Other results are given for the simultaneous approach of two or four lithium atoms in perpendicular direction to the axis nanotube. The FHI96MD code was used with the LDA (local density approximation) for the exchange and correlation contributions to the energy to do the calculations. The distance between the axis of adjacent carbon nanotubes has been fixed to almost 27 a.u. to study the interaction of one lithium atom with only a unit cell along the axis of the carbon nanotube. The preferable sites for lithium adsorption are shown in each case.

Attachment of Metal Nanoclusters to Single-Walled Carbon Nanotubes

Valerie C. Moore, Christopher A. Dyke, Michael P. Stewart, Elizabeth A. Whitsitt, Robin E. Anderson, Douglas C. Ogrin, Ramon Colorado, Andrew R. Barron, James M. Tour, Robert H. Hauge, Richard E. Smalley

Department of Chemistry, Rice University, 6100 Main Street, Houston, TX 77005
Contact e-mail:vcmoore@rice.edu

The attachment of metal nanoclusters to purified single-walled carbon nanotubes (SWNTs) has been investigated. By preparing nanotubes with different end and sidewall functionalities, an iron/molybdenum polyoxometalate nanocluster can be attached to the open ends of SWNTs. The degree of attachment is dependent on the end and sidewall functionalities and the attachment conditions. AFM and TEM were used to analyze the degree of attachment under the various conditions.

Iodine adsorption in carbon nanotubes and hypervalence.

Jean-Pierre Gaspard and Celine Otjacques

University of Liege, B5, 4000 Sart-Tilman, Belgium
Contact e-mail:jp.gaspard@ulg.ac.be

Carbon is amphoteric: electronic charge can be transferred from and to carbon. The case of iodine is particularly interesting as the increased electronic charge of iodine atoms stabilizes molecular ions I3- and I5-. This is a particular case of hypervalence. Using simple arguments, we demonstrate that the molecule I2 becomes unstable by charge transfer and we discuss the departures from the octet rule called hypervalence.

Binding energies to nanotube sidewalls

Holger F. Bettinger

Lehrstuhl fuer Organische Chemie 2, Ruhr-Universitaet Bochum, Germany
Contact e-mail:Holger.Bettinger@rub.de

Density functional computations (PBE and B3LYP) in conjunction with 3-21G and 6-31G* basis sets are used to determine the energy of fluorine atom and CH2 addition to the sidewall of (5,5) C30+10nH20 (n = 0,1,2,?,18) carbon nanotube slabs as well as infinite tubes with increasingly larger units cells. Using the cluster approach, a pronounced oscillation of the addition energy is found for fluorine atom addition, while oscillations are significantly damped for carbene addition the due to insertion into CC bonds.

Functionalisation of carbon nanotubes in a plasma

N. O. V. Plank and R. Cheung

School of Engineering and Electronics, The University of Edinburgh
Contact e-mail:natalie.plank@ee.ed.ac.uk

Single walled carbon nanotubes (SWNTs) have been exposed to fluorinated plasma mixtures in a standard reactive ion etching (RIE) system. The nature of the fluorination of SWNTs has been investigated using X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and transmission electron microscopy (TEM). The mechanism of the fluorine attachment has been studied using Langmuir probe and optical emission spectroscopy (OES). It is observed that the different plasma parameters influence the nature of fluorination of the SWNTs, which is determined by XPS with emphasis on the F1s peaks. It is believed that the mechanism of the fluorine attachment is dependent upon both the ions incident to the SWNTs and the radical concentrations within the plasma. Raman spectroscopy and TEM have shown that the tube structure has not been broken by the ion bombardment and XPS studies have confirmed that limiting stochiometries of the fluorination have not been reached. The versatility of us ing fluorinated plasma to accurately control the behaviour of the SWNTs will be discussed.

Two phases of Ar and Kr confined inside open single walled carbon nanotubes.

Zygmunt J. Jakubek and Benoit Simard

Steacie Institute for Molecular Sciences, National Research Council, Ottawa,
Ontario, Canada
Contact e-mail:Zygmunt.Jakubek@nrc.ca

Isothermal adsorption of Ar and Kr on single walled carbon nanotubes (SWNT) have been studied at 77 and 87 K. The nanotubes have been prepared for gas adsorption measurements by prolonged outgassing of as-grown material in vacuum at the room temperature (295 K) and at elevated temperatures up to 475 K and by oxidization for 2 hrs in dry air at 470 K. Formation of two condensed phases of Ar in the interior of SWNT has been observed at 77 K. The low-density phase is formed at 0.155(5) mtorr, while the high-density one at 0.120(5) mtorr. At 87 K, only single phase has been observed at 0.185(5) mtorr. Condensation at both 77 and 87 K appears to be the first order phase transition. Onset of the quasi-one-dimensional linear (one-channel) phase and the quasi-two-dimensional monolayer (six-channel) phase formation on the external surface of bundles has been observed at 77 K near 0.0017 and 0.8 torr, respectively, and at 87 K near 0.018 and 5 torr, respectively. The low-density and high-density phases of Kr are formed at 77 K at 0.175(5) mtor

Functionalisation of Open Ends in Single-Wall Carbon Nanotubes.

Andrei Gromov, Raluca E.Morjan, Staffan Dittmer and Eleanor E. B. Campbell

School of Physics and Engineering Physics, Chalmers University of Technology &
Gothenburg University , 41296 Gothenburg, Sweden.
Contact e-mail:gromov@fy.chalmers.se

Single-wall carbon nanotubes (SWNT) are found to be extremely promising materials for various fields of nanoelectronics, material science and biological applications due to their unique electronic and mechanical properties. Significant numbers of applications require the use of dispersions of purified individual SWNTs. Chemical functionalisation, especially side-wall modification, is known to promote dispersion of carbon nanotubes in solvents, but also alters (usually worsens) their electronic properties. Contrary to rather rich side-wall chemistry of SWNTs, the chemistry of tube open ends has been limited only to various substitution reactions on the carboxylic groups, which appear during oxidative purification of SWNT as-produced material. We have carried out the four-step synthesis of SWNT-NH2 from purified SWNT-COOH via intermediate formation of acyl chloride, ester and amide in series. The initial material, intermediate and final products have been characterised by IR and Raman spectroscopy and AFM. The possible applications of the obtained product will be discussed.

Mechanical properties and melt-state rheology of polymer-grafted single-wall nanotube composites

G. Viswanathan, H. Yang, C. Y. Ryu and P. M. Ajayan

Rensselaer Polytechnic Institute, Troy NY
Contact e-mail:viswag@rpi.edu

Polystyrene-grafted single-wall carbon nanotubes (SWNTs) were synthesized according to a method reported recently1. The polymer-grafted nanotubes were incorporated into a polystyrene matrix. Optical micrographs reveal better dispersion for functionalized nanotubes in polymer compared to unfunctionalized SWNTs. Static tensile tests and melt-state rheological studies were performed on the composites. The composite containing only 1% of functionalized SWNTs exhibit ~30% increase in tensile strength and ~ 50 % increase in toughness compared to both pure polymer and the composites containing unfunctionalized nanotubes. Melt-state rheology performed on these composites indicates higher activation energies for terminal flow for the composites containing functionalized nanotubes. The low frequency-storage modulus was close to two orders of magnitude higher, and the divergence of dynamic viscosity observed at low frequencies suggests the onset of a percolated network-filler structure e ven at low nanotube loadings.

Polystyrene-grafted in N-dopped multi-walled carbon nanotubes by nitroxide-mediated radical polymerization.

M. Dehonor[1,2], M. Terrones[1], A. González-Montiel[2],K. Masenelli-Varlot[3], J.Y. Cavaillé[3], Ana Laura Elias-Arriaga[1], Julio Rodríguez-Manzo[1], Adalberto Zamudio[1], Samuel Baltazar[1] and H. Terrones[1].

[1] Advanced Materials Department, IPICYT, San Luis Potosi, México.
[2] CID, Centro de Investigación y Desarrollo Tecnológico, S.A. de C.V., Lerma, Mexico.
[3] GEMPPM, Groupe d'Etudes de Métallurgie Physique et de Physique des Matériaux, INSA de Lyon, France.
Contact e-mail:mdehonor@mail.girsa.com.mx

Polystyrene (PS) chains were grafted in bamboo type nitrogen-dopped multiwall carbon nanotubes (CNx-MWNT) to form novel nanotube polymer nanocomposites. Nanocomposite synthesis method include the free radical "controlled/living" functionalization of CNx-MWNT with initiator and several nitroxides, and the consequent in situ styrene solution polymerization by Nitroxide Mediated Radical Polymerization (NMRP).
The first reaction step of the functionalization of CNx-MWNT was analyzed by Electron Paramagnetic Resonance (EPR) to determine the association of initiator and nitroxide radicals with the CNx-MWNT.
The nanotube polymer nanocomposites after purification and separation processes were studied by several microscopy techniques like HR-TEM, HR-EELS, elemental line scans, elemental mapping, as well as GPC and TGA. The synthetized nanocomposites were compared with the correspondent physical blend of CNx-MWNT and polymer. Preliminary results show that the polymerization reaction and the grafting from techniques proceeds successfully over CNx-MWNT when the method NMRP is used. Also, the characterization techniques give important differences of the PS over the nanotubes between the reaction and physical blend samples.

Raman and XPS analysis of dielectric barrier discharge (DBD) func-tionalisation of pre-chemical-activated and non-activated MWCNTs

T.I.T Okpalugo, P. Papakonstantinou, H. Murphy, J. McLaughlin, N.M.D Brown*

NIBEC, University of Ulster, Shore Road, BT37 0QB, Northern Ireland, UK
Contact e-mail: tit_okpalugo@yahoo.com

We examine atmospheric pressure DBD technique as a non wetting alternative to chemical functionalisation of CNT and also examine the bonding of certain functional groups via this technique to both pristine and pre-chemical functionalised CNT in order to as-certain bonding information. We looked at the bonding of N from concentrated liquid ammonia vapour atmosphere, Cl and F atoms from trichlorotrifluoroethane vapour in DBD atmosphere. The surface pre-activated (in nitric acid) chemical functionalised CNTs treated in DBD-NH3 atmosphere attracted four times (x4) more N atoms compared to the non-functionalised (un-activated, non chemical treated) counterparts treated in the same DBD-NH3 atmosphere. Whereas, the same pre-activated samples treated in trichlorotrifluoroethane-DBD atmosphere attracted eight times (x8) less F and more than three times less (>3x) Cl atoms under similar conditions when compared to the non-chemical [O] activated counterparts. Raman preliminary examination of the non-functionalised and oxygen chemical functionalised (treated with nitric acid only) CNT, revealed defect induced dispersive-D band ~ 1345.5 cm^{-1}, the graphite related mode-G band ~ 1572.1 cm^{-1}, the highly dispersive defect induced D-band overtone-G' (or 2D) ~ 2691.6 cm^{-1} and the radial displacement, radial breathing mode, RBM (non-functionalised MWCNT) ~ 142.9 to 169.1 cm^{-1}, compared to RBM (functionalised MWCNT) ~ 113.1 cm^{-1} to 116.6 cm^{-1}. The estimated nanotube diameter from the shown RBM frequency is $\sim$ 1.5-2.8 nm. Also other Raman second order modes (2D or G' and 2E2g), third order modes (2D + E2g), the second-order combination (D + E2g) and the third-order combi-nation (2D + E2g) frequencies were detected. There seems to be a remarkable difference between the functionalised and non-functionalised MWCNT. This include a downward shift in the RBM after functionalisation, pronouncement of the second order dispersive disorder peaks (2D) and its third order combination frequency (2D + E2g) following functionalisation with nitric acid. However, there seems to be a slight forward Raman shift in both the D- and G-peak position following functionalisation, a decreased FWHM-G which could imply increased purity, an increase in FWHM-D and a slight de-crease in the ID/IG ratio following acid treatment indicative of increased defects states and/or possible decrease in crystallinity. This work is fundamental to nanotube functionalisation for various nano-applications.

H Contributed Session (Tuesday Afternoon)

Oral Poster++ *Presentation*

$Mo_6S_{4.5}I_{4.5}$ Nanowires: High Resolution TEM Observations and Electronic Structure Calculations

Valeria Nicolosi[1], *Savas Berber*[4], *Jonathan N. Coleman*[*,1], *Jeremy Sloan*[5], *David Tomanek*[4], *Dragan Mihailovic*[2,3], *and Werner J. Blau*[1]

[1] Materials Ireland Polymer Research Centre, Department of Physics, University of Dublin-Trinity College, Dublin 2, Ireland
[2] Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
[3] Mo6, Teslova 30, 1000 Ljubljana, Slovenia
[4] Physics and Astronomy Department, Michigan State University, East Lansing, MI 48824, USA
[5] Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QR U.K.
Contact e-mail:nicolosv@tcd.ie

In the last few years Carbon Nanotubes have attracted a great deal of attention because of their interesting properties, including dependence of their chemical and electronic behavior on their small dimension, high anisotropy and tube-like structure. Since nanotubes are difficult to process, one-dimensional inorganic nanowires have been receiving growing attention as a viable alternative to nanotubes. The most promising of these are the $Mo_6S_{9-x}I_x$ family. Easy fabrication, easy dispersability and processability, and uniformity in terms of metallic character as well as diameter, makes $Mo_6S_{9-x}I_x$ nanowires one of the most promising one-dimensional materials. We present an Atomic Resolution Transmission Electron Microscopy study of the atomic structure of $Mo_6S_{4.5}I_{4.5}$ nanowires. Combination of electron microscopy, crystallographic and electron microscopy-simulated studies reveals that this system has a trigonal symmetry, with the spatial group 148. These detailed structural studies are complemented by *ab initio* Density Functional calculations of the structural stability and electronic structure of this unique system.

H.1 *Non-Carbon Nanotubes*

Single-walled hetero carbon nanotubes

M. Glerup (1,2), V. Krstic (2), S. Roth (3), J. Steinmetz (1), P. Bernier (1), O. Stéphan (4)

(1) GDPC (UMR5581), Université Montpellier II, 34095 Montpellier, France,
(2) Grenoble High Magnetic Field Laboratory, MPI / CNRS, 38042 Grenoble, France,
(3) Max-Planck-Institut für Festkörperforschung, 70569 Stuttgart, Germany,
(4) LPS, Université Paris-Sud, 91405 Orsay, France
Contact e-mail:glerup@gdpc.univ-montp2.fr

The electronic properties of single-walled carbon nanotubes (SWNTs) vary between semi-conducting and metallic. Doping carbon nanotubes with other chemical elements such as nitrogen and boron can be envisioned to be an efficient way for tuning both electronic and optical properties. To shed light on these predictions, systematic experiments have been performed.
A novel synthesis method has been developed for the direct production of doped single-walled nanotubes [1]. Comprehensive characterisation of these tubes has been carried out using several spectroscopic and microscopic methods, such as HRTEM coupled with EELS and Raman spectroscopy. Transport measurements on individual tubes have been performed for probing changes in their conductivity behaviour.

[1] M. Glerup, J. Steinmetz, D. Samaille, O. Stéphan, S. Enouz, A. Loiseau, S. Roth and P. Bernier, Chem. Phys. Lett., 387, 193-197 (2004)

Endohedral Silicon Nanotubes as the Thinnest Silicide Wires?

Traian Dumitrica, Ming Hua, and Boris I. Yakobson

Rice University
Contact e-mail:traian@rice.edu

Along with carbon nanotubes, semiconductor-based nanowires seamless solid rods with nanometer size widths and micrometer lengths) represent the most critical components of molecular electronics assemblies. It is known that silicon cannot form fullerene-like stable cage-clusters, unless a guest atom (metal) is introduced inside the cage. Based on density functional theory calculations, we propose new metal-encapsulated silicon nanoclusters, which can be extended to the thinnest (2,2) and (3,0) - using standard nanotube notation - silicide nanowires. Next, we will discuss their stability in comparison with other 1D structures of similar stoichiometry and show that they represent the limit of small-diameter, rigid one-dimensional atomic structures that can be experimentally grown by employing novel techniques such as the kinetic and thermodynamic control of the deposition process [1].

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Synthesis and characterisation of SiC- nanorods by CVD

A. Leonhardt, H.Liepack, J. Thomas, K.Biedermann

Leibniz Institut for Solid State and Material Research Dresden,P.O. Box 270116,
D-01171 Dresden,Germany.
Contact e-mail:a.leonhardt@ifw-desden.de

SiC is one of the most important semiconductors as it is a wide band gap material, suitable for high temperature, high frequency, and high power applications.In particular, nanorods of SiC could possess some properties that might be distinctive from their bulk,i.e. they exhibit a unique blue photoluminescence emission at room temperature, they show a Young-modulus of 600GPA and an excellent electron field emission. In this presentation we describe a new method for the synthesis of pure SiC- nanorods by using the chemical vapor deposition. Similar to the growth of single and multi-walled carbon nanotubes, SiC nanorods grow about a catalytically controlled process. Suitable catalyst are Fe, Ni or Co. For the deposition we used metallocenes of these metals, a hydrocarbon (CH4 or hexane) and as the precursor for silicon the liquid SiCl4. HRTEM-investigations with EEL and EDX- analysis show the well- developed SiC-nanorods with a C/Si-ratio of 1. The yield of SiC is depended on the gas phase composition, the deposition temperature and the deposition time. The process is up-scable and a deposition on templated or prestructured substrates is possible.

Structure and stability of AlP nanotubes

Sergey Lisenkov

Institute of Biochemical Physics of RAS, 119991, Moscow, Russian Federation
Contact e-mail:lisenkov@sky.chph.ras.ru

Using density functional theory, we predict the stability and electronic structure of aluminum phosphorus nanotubes. All the AlP nanotubes are semiconductors with band gaps ranging from 2.2 to 3.6 eV. The zigzag nanotube is a semiconductor with a direct band gap, whereas the armchair nanotube has an indirect band gap. In contrast to the cases of carbon nanotubes, the band gap of AlP nanotubes increases with the increasing diameter of the tubes and saturates at a value corresponding to the calculated band gap of an AlP hexagonal sheet.

Sedimentation and Purification Studies on $Mo_6S_{4.5}I_{4.5}$ Nanowire Bundles in solution

Valeria Nicolosi[1], *Seán O'Flaherty*[4], *Daniel Vrbanic*[2], *Ales Mrzel*[2], *Dragan Mihailovic*[2], 3, *Jonathan N. Coleman*[1] *and Werner J. Blau*[1]

[1] Materials Ireland Polymer Research Centre, Department of Physics, University of Dublin -Trinity College, Dublin 2, Ireland.
[2] Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia.
[3] Mo6, Teslova 30, 1000 Ljubljana, Slovenia.
[4] European Synchrotron Radiation Facility ESRF, Grenoble, France
Contact e-mail:nicolosv@tcd.ie

Recently carbon nanotubes have generated a great deal of attention because of their interesting properties. Their one-dimensional nature results in exciting electrical, mechanical and optical properties. While these materials can now be produced in large quantities, purification, dispersability and processability have always been serious issues. Recently, alternative one-dimensional inorganic nanowires have been demonstrated. The most promising of these are the $Mo_6S_{9-x}I_x$ family. These materials have the advantage that they are easy to fabricate, all nanowires are metallic and all have the same diameter. In addition they can easily be dispersed in various solvents. These properties suggest $Mo_6S_{9-x}I_x$ to be one of the most promising one-dimensional nano-materials. However, issues such as the optimum solvent, maximum solubility, polymer stabilisation and nanowire bundling have not been studied. Here we present a quantitative study of the dispersion properties of $Mo_6S_{4.5}I_{4.5}$ nanowires. Optical absorption based sedimentation studies have been carried using a large range of solvents showing Isopropanol to be the best. To clarify the sedimentation process we propose a theoretical model to correlate the local nanowire concentration with sedimentation time. Combining experiment with theory, these sedimentation studies show three phases to be present in the as produced material: approximately one third impurity material, one third insoluble nanowire bundles and one third soluble nanowire bundles. In addition sample purification can be attained by controlling the sedimentation time. The soluble fraction can also be increased by addition of small amounts of suitable polymers. Futhermore, TEM studies show a variation of the mean bundle diameter with dispersion concentration. This highlights the possibility of controlling the mean diameter of the nanowire bundles by controlling the initial concentration of the solution.

Study and Formation to Molybdenum Disulfide Nanotubes

V. Lavayen[1], *N. Mirabal*[1], *M. A. Santa Ana*[1], *E. Benavente*[2], *G. Gonzalez*[1]

[1] Department of Chemistry, School of Science, Universidad de Chile, PO Box 653,
Santiago de Chile, Chile.
Contact e-mail:vlavayen@ciq.uchile.cl

Template-directed synthesis represents a route to 1-D nanostructures, In this kind to approach the template (long primary amines) act like a structural direct agent, also the mainly function is to generated in situ nano structured [1]. Some reports described the chemistry to intercalation of MoS2 [2, 3], also the formation the nanocomposites of molybdenum disulfide- long primary amines [3]. Here we present some results the synthesized to nanotubes and microfibers to MoS2 by hydrothermal treatment of lamellar MoS2-long-chain primary amine (e.g. hexadecylamine) intercalated, Products are mainly characterized by powder X-ray diffraction analysis, scanning electron microscopy, and transmission electron. The molybdenum disulfide nanotubes have length in the range to 2-12.5 μm and diameter in the range 400-60 nm (outer), 100-25 nm (inner). Microtubes have length in the range to 70-2 μm.

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H.2 *Nanotube-Based Composites*

Preparation and Characterisation of Carbon Nanotube/Polycarbonate Composites

V. Aboutanos, M. Holzinger, K. Schierholz and P. Bernier

GDPC, University of Montpellier, France
Contact e-mail:*unknown*

The high young's modulus and tensile strength of carbon nanotubes makes them ideal candidates as reinforcements for structural composites. The high conductivity of carbon nanotubes combined with their large aspect ratio allows for electrically conductive composites to be prepared with a low carbon nanotube loading. We present in this study the results obtained for polycarbonate/single wall carbon nanotube (PC/SWNT) composites. The PC/SWNT composites were prepared using solution processing techniques and characterised by transmission electron microscopy. The electrical and mechanical properties of these composites were determined.

Investigation of Carbon Nanotubes/Polyester Composites

Yi Huang, Zhifei Li, Dongliang Tao, Xiuqin Qi, Weiping Zhou, Guohua Luo, Fei Wei

Department of Chemical Engineering, Tsinghua University, Beijing, 100084, Peoples Republic of China
Contact e-mail:yihuang2001@tom.com

Carbon nanotubes (CNTs) are long, thin cylinders of carbon. Intrinsic van der Waals attraction among CNTs often leads to significant agglomeration. Many research showed that the homogeneity of the composite is a critical point for the mechanical and electrical properties of the nanocomposite.In this contribution, Poly(ethylene terephthalate) (PET) and Poly(butylene terephthalate) (PBT) resin has been compounded with carbon nanotubes. Two kinds of coupling agents were introduced to promote the distribution of carbon nanotubes in the polyester matrix. Scanning electron microscopy was used to characterize the microstructure of the composites. The results showing that it was highly efficient to use a special coupling agent to disaggregate and improve the dispersion of CNTs. We also detected the electrical performance of the composites. The volume resistance of the composites decreased from 10E14Ω·cm to 10E1Ω·cm with the addition of CNTs which related to the interface an the microstructure of the composites. The thermas stability of the composites was detectes by TGA.

Nanotube Dispersion in Nanotube Composites

Silvia Giordani[1], *Shane D. Bergin*[1], *Anna Drury*[1], *Éimhín Ní Mhuircheartaigh*[1], *Alexander Fleming*[1], *Andrew I. Minett*[1], *Janos B. Nagy*[2], *Hans Kuzmany*[3], *Daniel E. Resasco*[4], *Jonathan N. Coleman*[1] *and Werner J. Blau*[1]

[1] Department of Physics, Trinity College Dublin, Dublin 2, Ireland
[2] Laboratoire de Rsonance Magntique Nuclaire, Fac. Universit N.D. de la Paix, Namur, Belgium
[3] Institut fuer Materialphysik, Universitaet Wien, Wien, Austria
[4] School of Chemical Engineering and Materials Science, University of Oklahoma, US
Contact e-mail:giordans@tcd.ie

Single-wall carbon nanotubes are severely restricted in their applications, as they exist in rope-like bundles. It has been shown that these bundles dissociate in low concentration NT-polymer composites, via a spectroscopic method [1]. This method measures the ratio of free polymer to the nanotube-bound polymer in the SWNT-polymer solutions. However, the concentration at which the bundles dissociate into individual NT is very low and their use in other applications is again restricted. We have designed and synthesized different polymers as well as PPV-analogous short-chain compounds [2] in order to improve the interactions with the nanotubes and therefore to increase the concentration at which individual nanotubes become stable. We have investigated, using the same spectroscopic technique, the response of the different dispersant molecules with single-wall, double-wall, and thin multi-wall nanotubes. We found that as we increase the diameter of the NT the bundles dissociate into individual NT at higher concentrations of the nanocomposites. Our results were supported by AFM and HRTEM data.

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Achieving electrical percolation in polymer-carbon nanotube composites

M. Shaffer1, Jan K.W. Sandler2, Alan H. Windle2, Christian A. Martin2,3,Wolfgang Bauhofer3, Karl Schulte4, S. Rahatekar2, J. A. Elliott2

1 Department of Chemistry, Imperial College, South Kensington, London, SW7 2AZ, UK.
2 Department of Materials Science and Metallurgy, University of Cambridge, UK.
3 Materials in Electrical Engineering and Optics, TU Hamburg-Harburg, Germany.
4 Polymer Composites, TU Hamburg-Harburg, Germany
Contact e-mail:shaffer@imperial.ac.uk

The addition of carbon nanotubes (CNTs) to insulating polymer matrices can yield electrically percolating networks. Simple processing can lead to charge-stabilised dispersions of carbon nanotubes in epoxy resin. Under suitable conditions, nanotube agglomeration produces electrically conductive composites at extremely low loading fractions. Both percolation threshold and conductivity can be adjusted through processing parameters and nanotube aspect ratio. Comparisons can be made between a variety of different nanotube types and surface functionalities; the use of aligned multiwall nanotubes seems to allow lower percolation thresholds than have been reported in other systems. Furthermore, the application of electric fields during processing induces the formation of aligned nanotube networks. Such composites show electrical conductivity above the anti-static level and retain a degree of optical transmissivity. On the other hand, in some nanotube-polymer systems, relatively high percolation thresholds are observed. The challenge is to understand how the choice of nanotube, matrix, and processing route influence the percolation behaviour. Mesoscale simulation of packed assemblies of suspended CNTs can be used to explore these questions. Computer simulation has been carried out to study the effect of processing conditions, CNT aspect ratio, and electric field strength.

Mechanism for mechanical reinforcement in nanotube-polymer composites

A. Wall, J. N. Coleman and M. S. Ferreira

Physics Department, Trinity College Dublin, Ireland
Contact e-mail:ferreirm@tcd.ie

The significant increase in the Young's modulus of nanotube-polymer composites is often correlated with the formation of a crystalline layer of polymers surrounding the nanotubes. Although this has been attributed to an improved stress transfer between the stiffer nanotubes and the softer polymer matrix, the actual physical mechanism for this transfer is still unclear. To clarify this matter, we model the polymer-nanotube composite by harmonic chains interacting with a rigid periodic potential, an extension of the so-called Frenkel-Kontorova model. We identify the origin of the reinforcement with the occurrence of a pinning transition, in which sections of the polymer are trapped by the periodic potential of the templating nanotube.

Thermal Conductivity of Aligned Carbon Nanotube-Polymer Composites

I.N. Ivanov, A. A. Puretzky, G. Eres, M. J. Lance, H. Wang, S. Jesse, and D. B. Geohegan

Oak Ridge National Laboratory, Oak Ridge, TN 37831-6056
Dept. of Materials Science and Engineering, University of Tennessee
Contact e-mail: qy1@ornl.gov

Structural and thermal properties measurements were performed for millimeters-long, vertically aligned multiwall carbon nanotubes (VA-MWNTs) and micron-long aligned singlewall carbon nanotubes (VA- SWNT and) and their polymer composites. As-grown bundles of VA-NTs were tested on an Instron universal testing machine for breaking load and elongation, in order to understand and test their continuity. Polymer composites were obtained by infiltrating VA-MWNT and VA-SWNT arrays with aminoepoxy resin, preserving their alignment. The thermal properties of these composites were tested using a Xenon flash lamp thermal diffusivity system and NIR camera. Aligned VA-MWNT in aminoepoxy at less than 2 wt.% loading were found to have higher thermal diffusivities than randomly-oriented CNT fibers at loadings of 40 wt.%, and thermal diffusivity improvements by a factor of 20 compared to the pure polymer.

Directional thermal conductivity of VA-MWNT and VA-SWNT was extracted from the results of these experiments for the direction parallel and perpendicular to nanotube axes. Similar experiments were done with the non-aligned mats of raw, purified, surfactant coated SWNTs. Effect of nanotube treatment on their thermal conductivity was investigated.

Atomic Scale Characterisation of Carbon Nanotubes and Interfaces in their composites

N.Y. Jin-Phillipp[1], *M. Kelsch*[1], *M. Sycha*[1], *C. Scheu*[1], *K. Hahn*[1], *F. Lupo*[1], *N. Grobert*[2], *and M. Ruehle*[1]

[1] Max-Planck-Institut fuer Metallforschung, Heisenbergstr.3, D-70569 Stuttgart, Germany;

[2] Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, U.K.
Contact e-mail:nyjin@mf.mpg.de

The structure and composition of, and bonding among multiwalled carbon nanotubes (MWCNT) grown by pyrolysis of different organometallic precursors have been studied by various techniques of transmission electron microscopy, including high-resolution transmission electron microscopy (HRTEM), elemental mapping, and electron energy loss spectroscopy (EELS). Various crystal structures of metal filling in CNT cores have been identified. In particular, the atomic, as well as electronic structure of interface between CNT and the metal filling has been studied for the first time by using cross-sectional specimen of Fe-filled MWCNTs. The combination of HRTEM and high-spatially resolved EELS demonstrates an interfacial bonding of CNT with Fe.

Aligned nanotube composites

KKK Koziol[1], *S Boncel*[1], *MSP Shaffer*[2], *AH Windle*[1]

[1] Department of Materials Science & Metallurgy, University of Cambridge,
Pembroke Street, Cambridge CB2 3QZ, UK
[2] Department of Chemistry, Imperial College Science Technology & Medicine,
Imperial College Road, London SW7 2AZ, UK
Contact e-mail:kk292@cam.ac.uk

Carbon nanotubes promise significant advances in a large variety of applications (including materials, electronics, medicine and displays) due to their unique combination of mechanical, thermal, electrical and chemical properties. It is possible to make highly uniaxially oriented carbon nanotubes films of different thickness by controlling the growth substrate and the ratio of the catalyst to hydrocarbon in the chemical vapour deposition process. A variety of polymers can then be introduced into these films to produce composites with a high nanotube loading and anisotropic properties.

Reinforcement of polymers with carbon nanotubes: the role of nanotube surface area

M. Cadek[1], *J. N. Coleman*[1], *K. P. Ryan*[1], *V. Nicolosi*[1], *A. Fonseca*[2], *J. B. Nagy*[2], *F. Beguin*[3] *and W. J. Blau*[1]

[1] Materials Ireland Polymer Research Centre, Department of Physics, Trinity College Dublin, Dublin 2, Ireland,
[2] Lab. de Résonance Magnétique Nucléaire, Fac. Universite. N.D. de la Paix, rue de Bruxelles 61, 5000 Namur, Belgium,
[3] Centre de Recherche sur la Matiére Divisée, CNRS, 1b, rue de la Férollerie, Cedex 02, F-45071 Orléans, France
Contact e-mail:cadekm@tcd.ie

Due to their extraordinary mechanical properties and very low densities, carbon nanotubes are seen as the future reinforcement agents for high-tech polymers. In addition to their mechanical properties they show excellent thermal and electrical properties. Tensile tests were carried out on free-standing composite films of polyvinyl alcohol and seven different types of carbon nanotubes. Furthermore, polymer functionalised carbon nanotubes were included in a polypropylene matrix. Significant increases in Young's modulus and strength by up to a factor of five were observed in all cases. Known theories for polymer/carbon fibre reinforcements such as Krenchel's rule-of-mixtures or the Halpin-Tsai-theory could not explain the relative differences between composites made from different tube types. However, it is possible to show that the reinforcement scales linearly with the total nanotube surface area in the films. In addition, in all cases crystalline coatings around the nanotubes were detected by calorimetry suggesting similar polymer-nanotube interfaces. This supports the fact that the reinforcement is critically dependent on the polymer-nanotube interfacial interaction.

Synthesis and Properties of Polyaniline - Carbon Nanotube Composites

D.A. Makeiff, M.N. Diep, M.C. Kopac, and T.A. Huber

Defence R & D Canada - Atlantic
Contact e-mail:trisha.huber@drdc-rddc.gc.ca

Carbon nanotube-polymer composites have enjoyed much attention in the literature due primarily to the ability of the nanotubes to impart electrical conductivity and mechanical reinforcement to the composites at very low loading. The electrical properties of the composite are particularly interesting when the polymer itself is also electrically conductive. There is evidence in the literature for an enhancement in electrical behaviour of such composites, relative to the parent components. We have prepared polyaniline-carbon nanotube composites under a variety of synthetic conditions. The composites were subject to electronic characterization, as well as traditional characterization techniques. It was found that the composites did indeed exhibit enhanced electrical conductivity relative to the parent materials; the results will be presented.

Molecular dynamics simulations of boron-nitride nanotubes embedded in amorphous silicon-boron-nitride matrices

M. Griebel and J. Hamaekers

Department of Numerical Simulation, University of Bonn, Germany
Contact e-mail:hamaekers@ins.uni-bonn.de

The elastic properties of BN-nanotubes embedded in amorphous Si-B-N ceramics are examined by molecuar dynamics simulations. To derive stress-strain curves for various tensile and compressive load cases at given temperature and pressure, we use the Parrinello-Rahman approach to apply external stress to a periodic system. In addition to Young moduli and Possion ratios, we compare radial distribution functions, average coordination numbers, ring statistics and self-diffusion coefficients, in order to characterize the short-range, medium-range and long-range order of Si_3BN_5, $Si_3B_2N_6$ and $Si_3B_3N_7$ matrices. Here, our results show that $Si_3B_3N_7$ exhibits the highest Young modulus and the largest elastic range. Furthermore, we calculate stress-strain curves for capped BN-nanotubes and infinite BN-nanotubes embedded in Si-B-N matrices to compare the derived Young modul i with different macroscopic rule-of-mixtures predictions. Here, the influence of the nanotube/matrix ratio and of the temperature on the elastic modulus is examined. Our results show a good agreement with the rule-of-mixtures predictions. In particular, all systems are modeled with a reactive many-body bond order potential due to Tersoff.

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Microstructural Investigations on Zirconium Oxide-Carbon Nanotube Composites

F. Lupo, R. Kamalakaran, C. Scheu, M. Rüle

MPI
Contact e-mail: F.Lupo@mf.mpg.de

Zirconium oxide (ZrO2)/carbon nanotube composites were prepared by hydrothermal crystallisation of zirconium hydroxide [(Zr(OH)4 nH2O; n = 8-16] in the presence of carbon nanotubes. The hydrothermal crystallisation of zirconium oxide, under autoclave conditions, occurred on the walls of the tubes. The process yielded a homogeneous, composite powder consisting of microcrystalline ZrO2 and multi-walled nanotubes, hence representing an alternative route for the synthesis of ceramic-nanotube composites. Microstructural and qualitative characterisations were performed using different electron microscopy techniques.

Carbon nanotube/Polymer composite from ATRP polystyrene grafted CNx MWNT

Benjamin Fragneaud[1,2,3], *Karinne Massinelly-Varlot*[2], *Alfonso Gonzales*[3], *Mauricio Terrones*[1], *Jean Yves Cavaille*[2], *Ana Laura Elias-Arriaga*[2], *Julio Rodrguez-Manzo*[1], *Adalberto Zamudio*[1], *Samuel Baltazar*[1] *and H. Terrones*[1]

[1] Advanced Materials Department, IPICYT, San Luis Potosi 78216, Mexico.
[2] GEMPPM, Groupe déEtudes de Métallurgie Physique et de Physique des Matériaux, INSA de Lyon, France.
[3] CID, Centro de Investigación y Desarrollo Tecnológico, S.A. de C.V., Lerma, México
Contact e-mail: bfragneaud@yahoo.com

Since the year 1991 [1], the discovery of the carbon nanotubes many research focused his effort in nanotubes technologies. Nanotubes show very good physical and electronic properties (semi conducting) they are an important focus of interest in the scientific community. Multiwalled carbon nanotubes nitrogen doped were grafted with polystyrene using Atomic Transfer Radical Polymerization. All the functionalization process was analyzed using TGA, Coupled gas chromatography-mass spectrometry, HREELS, XPS and HRTEM. EPR analysis was used to know the behavior of the ATRP macroiniciador grafted on the external layer of the CNx MWNT. The grafted tubes were introduced in a poly (styrene-butadiene, co) in order to study mechanical and electrical behavior of the composite material. First results are presented in this exposition: DMA, traction, DSC.

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H.3 *Morphology and Application of Modified Nanotubes*

Hydrogen Molecule in a Single Walled Nanotube: H-H Bond Length Analysis

Raul Perez-Enriquez (1,2), German Campoy G. (2), Raul Riera (2)

(1) Departamento de Fisica, Universidad de Sonora,
(2) Departamento de Investigacion en Fisica, Universidad de Sonora.
Contact e-mail:rpereze@fisica.uson.mx[

In order to contribute to the knowledge of the process of hydrogen physisorption in single walled nanotubes, we made "ab initio" calculations on a system consisting in a hydrogen molecule confined inside a SWNT. After optimizing the nanotube geometry, we obtained SCF Hartree-Fock energies, considering in each calculation the variations on the H-H bond length, an important parameter usually taken as fixed in most molecular dynamics calculations. A change of about 5% in the H-H bond length with respect with its value for the free molecule, was observed when the molecule is placed off the center of the zigzag (9,0) nanotube. Furthermore, limiting values for the relative position of the molecule with respect to the center of the nanotube were obtained, before the occurrence of chemisorption.

Morphology of PEO Nanofibers Embedded by MWNTs through Electrospinning

Weiping Zhou, Fei Wei, Guohua Luo*

Department of Chemical Engineering, Tsinghua Unversity, Beijing 100084, China
Contact e-mail:weifei@flotu.org

Poly Ethylene Oxide (PEO) Nanofibers embeded by multiwalled carbon nanotubes (MWNTs) were successfully produced by electrospinning process. The influences of nanotube concentration, nanotube tortuousity and PEO concentration on the morphology of nanofibers have been investigated. HRTEM analysis showed that the nanotube tortuousity has significant effect on the alignment of MWNTs in naofibers. Three kinds of nanofibers composite were found: straight nanofibers with straight MWNTs , curved nanofibers containing irregular curved MWNTs , and branched nanofibers with MWNTs coated with several nanometers of thin films PEO and pulled out from main fiber. The formation mechanism of above third nanofibers during the electrospining process will be discussed.

Fullerene Oligomer Peapods as Evidence for a Nanotest-tube

*David A. Britz, Andrei N. Khlobystov, Kyriakos Porfyrakis,
Arzhang Ardavan, G. Andrew D. Briggs*

University of Oxford, Department of Materials and Clarendon Laboratory,
Department of Physics
Contact e-mail:david.britz@materials.ox.ac.uk

We report the first evidence of a controlled organic reaction inside a carbon nanotube. C120O fullerene dimers were inserted into SWNTs in 30% yield, indicating a large energetic barrier for encapsulation.A heated C60/C60O/SWNT mixture formed oligomers composed of up to five fullerenes inside SWNTs in 60% yield. Such oligomers should have a very large energetic barrier to encapsulation, indicating that C60 and C60O entered as monomers and reacted inside the nanotube via epoxide ring opening. Mechanisms of filling and oligomer formation are discussed.

ELECTRIC DETECTION OF KINASE ASSAY USING MWCNT NANOELECTRODE

Jae Shin Lee, Seok Jae Lee, Jong Pil Park, Tae Jung Park, Do Hyun Kim, Sang Yup Lee, Jin Hee Kim, Seong Ku Kwon and Jeong O Lee

1.Korea Advanced Institute of Science and Technology,
2. Korea Research Institute of Standard and Science,
3. Electronics and Telecommunications Research Institute,
4. Korea Research Institute of Chemical Technology
Contact e-mail:ljs1@kaist.ac.kr

Semiconducting single-walled carbon nanotubes(SWCNT) are known to be used to detect biomolecules in FET. In this study, metallic multi-walled carbon nanotubes(MWCNT) are shown to be used as electrode for kinase assay. kinase assay is important because phosphorylation of proteins by kinases plays a central role in regulating cellular processes and is involved in many diseases like cancer, diabetes, and inflammation.

First step of our experiment produce is the fabrication of MWCNT nanoelectrode plate. The second step is a series of biological reaction such as immobilization of peptide substrates on MWCNT, phosphorylation of the peptide by protein kinase A and dephosphorylation. In each step, two probe conductance was measured by biological groups on MWCNT nanoelectrode. We can find that amide bond is formed first by the protonization on the surface of MWCNT, where the density of free charge carriers is decreased. In the next step, phosphate group with two negative ionic active sites interacts with the surrounding ions of the MWCNT and conductance is changed. Conductance decrease is the result of a change in the capacitance of the MWCNT. After dephosphorylation, conductance was almost restored. Due to this recovery property, metallic MWCNT can be used as the biosensor for kinase assay.

Virtual Nanomanipulator with Carbon Nanotube Nanotweezers

Shigenobu Yamanaka[1], *Seiji Akita*[2], *Shotato Mizooka*[1], *Takashi Okawa*[1], *Yoshikazu Nakayama*[2]

[1] Daiken chemical Co., Ltd., [2] Department of Physics and Electronics, Osaka Prefecture University
Contact e-mail: yamanaka@daiken-chem.co.jp

Nanomanipulation is one of strong tools for Nanoscience today. But conventical techniques cannot move nano size materials to vertical direction. Nanotweezers witch can build up nano-structures form nano size particles are strong requested by researchers. Nanotweezers are made by Carbon nanotubes at a tip of an AFM cantilever witch has electrodes. When the tweezers close, Carbon nanotubes are attracted by electro static force to another tube. The voltage to close tweezers is 4.5V, when nanotubes distance is 780nm and length is 2500nm. This voltage is close to calculated value in condition that nanotubes diameter is 13nm and Yangs modulus is 1TPa. We have developed a virtual manipulator for Nanotweezers, which is, connected AFM by ether net. The manipulator displays 3D AFM image from AFM controller and manipulates nano size materials in 3D virtual space, for the nanotweezers is both an AFM cantilever tip and a nanomanipuletor device. And we have developed an algorithm for 3D manipulation with the nanotweezers. These results open a next generation nanomanipulation.

Controlled placement of single-walled carbon nanotubes for device applications

Indhira O. Maciel, Adelina P. Santos**, Clascidia A. Furtado**, Flavio Plentz**

* Dept of Physics - UFMG - Brazil,
** CDTN/CNEN - Brazil
Contact e-mail: adelina@cdtn.br

Electric transport properties measurements in isolated single wall carbon nanotubes (SWNTs) and SWNT's junctions are an important tool for the investigation of the basic electronic and structural properties of this promising nanomaterial and for applications in novel nanodevices and sensors. This work focuses on the fabrication of carbon nanotube-based electronic devices by patterning metallic pads onto individual which were either deposited from stable suspensions or growth directly on catalytic templates. Recently it has been shown that stable suspensions of SWNT's can be obtained and separation methods that explore the rich covalent chemistry of SWNT's have been demonstrated. This opens up the possibility of having suspensions of isolated semiconducting or metallic SWNT's with controlled diameters and known electric transport properties. In order to successfully create metallic contacts to the SWNT's it is essential to be able to manufacture samples with control over the SWNT's deposition where clear AFM images can obtained upon patterning the samples. In this work we address the study of methods for in making reproducible and clean depositions of SWNT from surfactant-suspended nanotubes onto amino-silane functionalized surfaces. The role of heat treatments and washing steps in the removal of the surfactant from wafer and nanotubes will be discussed.

Carbon Nanotube Probed Positioning Encoder with Nanometer Resolution: Design and Kinematics

Y. C. Lin, U. Y. Lin, C.C. Su, J.H. Hsu, N. K. Chang, S. H. Chang, Y. M. Chu, J. H. Wu, W. H. Wang

National Taiwan University and MIRL, ITRI
Contact e-mail:shchang@ntu.edu.tw

The single walled carbon nanotube (CNT) is adapted as a probe for the nanometer resolution displacement measurement. The system includes an oscillating CNT tip scanning in contact across a grating which contains the periodic pattern of metal and dielectric layers and is moving at a constant speed. The concept of the encoder design is to record contact trajectory between the tip and the grating would provide the kinematics displacement information. The amplitude of the tip oscillation is intentionally different from that of the grating pitches. Therefore the contact trajectory between the tip and grating can be divided into several components. In this study, the tip size of the single-walled CNT is 2∼4 nm. The grating pitch is varied from 100 nm to 1 micron. The system design is presented by dynamic kinematics analysis using commercial software, MSC ADAMS. The analysis of the contact trajectory during the scanning under different design parameters has been conducted. The design parameters include the tip geometry, displacement amplitude and frequency of the probe, grating pitch and its speed. The analysis data show that during the scanning, the discontinuously contacts between probe and the grating surface have been strongly speed and oscillation dependent. The signal processing involving the pulse width modulation is applied for improvement of the displacement measurements. The simulation results illustrate the optimal design of the system using non-dimensional parameters as following: tip diameter η= 0.02, tip oscillation amplitude A*=0.9, and grating speed V*=0.02. The non-dimensional parameter is based on the metal pitch of the grating.

Electroplating of Carbon Nanotubes

Ryo Tomuro, Yoshiaki Abe, Masahito Sano

Department of Polymer Science and Engineering, Yamagata University
Contact e-mail:mass@yz.yamagata-u.ac.jp

Carbon nanotubes (CNTs) were successfully electro-deposited on a conducting substrate from their dispersion. It is well known that CNTs possess negative charges in solution. By applying electric potential across two electrodes that are immersed in an organic dispersion of CNTs, they are deposited only on the anode surface. Once deposited, CNTs are tightly bound to the substrate surface and cannot be removed without scraping the substrate materials. After removal of solvents, the film consists only of CNTs which become a part of the electrode surface. This property allows us to grow CNT films layer-by-layer by repeating deposition-rinsing-drying cycles. The present method can coat conducting objects of various shapes and sizes, with CNT thickness ranging from nanometer to millimeter scales. It requires only a few volts and lasts within about 10 minutes. Since electro-deposition occurs without any chemical reaction, no current flows during the process. An ordinary 1.5 V dry cell is enough to coat large surfaces. Furthermore, we have found that CNTs are not deposited on the anode regions that are pre-coated with dielectric materials. CNTs are deposited only on patterned conducting regions. The present electroplating is a versatile method to produce CNT films without any residual catalysts or binders by extremely simple and cost effective set-up.

H.4 *Photo-Induces Reactions in Nanotubes*

Selective Cap Opening in Carbon Nanotubes Driven by Laser-Induced Coherent Phonons

Traian Dumitrica, Martin E. Garcia, Harald O. Jeschke, and Boris I. Yakobson

Freie Universität Berlin and Rice University
Contact e-mail:traian@rice.edu

We show the ability of coherent phonons to forcibly drive precise ultrafast transformations in carbon nanotubes (CNTs). Performing molecular dynamics simulations based on a microscopic electronic model, which also accounts for the interaction with an external e.m. field, we obtain that the laser induced ultrafast structural changes differ dramatically from the thermally induced ones. In the ultrafast nonthermal regime, we show that bond weakening and a simultaneous excitation of two coherent phonons modes, localized in the spherical caps and cylindrical nanotube body, lead to a selective cap opening. Our finding is of a broader fundamental interest since it provides a unique way of manipulating lattice structures and shapes at the nanoscale level. The transformation achieved here, of CNT cap opening with little loss of material, is a challenging technological issue motivated for example by the perspective of nano-confinement of molecular species inside CNTs.

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Light-Assisted Oxidation for Selective Removal and Remaining of Single-Wall Carbon Nanotubes

M. Yudasaka, M. Zhang, Y. Miyauchi, S. Maruyama, S. Iijima

[1] JST, NEC (Tsukuba, Japan)
[2] University of Tokyo (Tokyo, Japan)
[3] Meijo University (Nagoya, Japan)
Contact e-mail: yudasaka@frl.cl.nec.co.jp

We previously reported that irradiation of light on SWNTs during the oxidation has an effect of enhancing the oxidation-disappearing of SWNTs [1]. It was also found that the diameters of the disappearing SWNTs were predicted from the wavelength of the irradiated light by using the Kataura-plot, which, in turn, was useful to make SWNTs with certain diameters to remain. These results indicate that the light-assisted oxidation would be a basic technique for photo-engineering of SWNTs. We also clarified the chiral index of oxidation-disappearing or remaining SWNTs with supporting information from optical absorption-spectrum, however, the chiral index thus clarified did not coincide with those determined by the fluorescence spectra. In addition to this, we noticed several unusual phenomena, a part of which are supposed to be caused by the SWNT bundling or surfactant-SWNT interaction. The details will be presented in the talk.

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H.5 *Thermal and Mechanical Properties of Nanotubes*

Computer simulation of the thermal conductivity of carbon nanotubes

Masamitsu Kobayashi[1], *Hideyuki Kawakami*[1], *Syogo Tejima*[2], *Yoong Ahm Kim*[1], *Takuya Hayashi* [1], *David Tomanek*[3], *Morinobu Endo*[1]

[1] Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano, 380-8553, Japan

[2] Research Organization for Information Science & Technology, 2-2-54, Nakameguro, Meguro-ku Tokyo, 153-0061, Japan

[3] Physics and Astronomy Department, Michigan State University, East Lansing, MI 48824-2320, USA

Contact e-mail:kobayashi@endomoribu.shinshu-u.ac.jp

Using a parallelized version of the Carbon Recursion Technique Molecular Dynamics (CRTMD) code, we investigate the thermal conductivity of carbon nanotubes as a function of tube diameter and unit cell size. Specifically, we evaluate the thermal conductivity of small-diameter carbon nanotubes, including the (3,3) nanotube, which is known to be the smallest free-standing carbon nanotube, and other nanotubes narrower than ∼1nm, and compare our results with those for wider nanotubes. Due to the long phonon mean-free path, we find the thermal conductivity to depend sensitively on the length of the unit cell. We discuss the effect of changing sp^2 bonding, chirality, and low dimensionality of nanotubes on their thermal conductivity in terms of phonon transport [1].

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Thermal Measurement on a Multi Wall Carbon Nanotube

L. Hao1, L. Brown1, J. Gallop1, J. Macfarlane2, L. Cohen3

1National Physical Laboratory, Teddington, TW11, 0LW, UK
Contact e-mail:ling.hao@npl.co.uk

Unlike electrical and mechanical properties,the thermal properties of carbon nanotubes have not been measured at the mesoscopic scale. We have recently begun thermal measurements on a multi wall carbon nanotube (MWNT) using a temperature sensing scanned microscope probe. An MWNT bundle produced by the arc discharge method is attached to a thermal probe with several individual MWNTs protruding from the end of the bundle. The system is operated in high vacuum and the temperature of one end of the nanotube may be controlled between 100K and 500K. Under piezo displacement, the MWNT is brought into contact with the heated or cooled substrate surface and the heat flow down the MWNT recorded as a function of the temperature difference. To ensure that we are observing thermal conductance through a single nanotube we measure electrical and thermal conductance simultaneously. When the signature of quantum electrical conductance is seen it is clear that only one tube is involved. We present the results for thermal and electrical conductance of a number of different nanotubes as both temperature and force applied between nanotube and substrate are varied. This confirms the predictions of exceptional thermal conductivity of MWNTs and may in future allow observation of quantised thermal conductance in single wall carbon nanotubes.

Ion-irradiation-induced load transfer in single-walled carbon nanotube bundles and multi-walled carbon nanotubes

M. Huhtala-Sammalkorpi[1], *A. Krasheninnikov*[2], *K. Nordlund*[2], *J. Aittoniemi*[1], *A. Kuronen*[1], *S. Stuart*[3] *and K. Kaski*[1]

[1] Laboratory of Computational Engineering, P.O. Box 9203, FIN-02015 HUT, Finland,
[2] Accelerator Laboratory, P.O. Box 43, FIN-00014 University of Helsinki, Finland,
[3]Department of Chemistry, Clemson University, Clemson, South Carolina 29634
Contact e-mail:maria.huhtala@hut.fi

During production single-walled carbon nanotubes clamp together to form bundles. In these bundles the tubes are bound weakly together through van der Waals interactions which results in a low shear modulus. Similarly, the shells of multi-walled nanotubes provide low-friction surfaces. Besides enabling low-friction based devices, this can also be detrimental when slippage is undesirable, for example in some composite structures or parts of nanomachines.

Electron and ion irradiation should improve load transfer by inducing defects that can bridge the shells in a multi-walled tube or the tubes in a rope. This is supported by a recently published work [1] which provided experimental evidence that electron irradiation increases the bending modulus of a nanotube rope and thus increases the shear modulus.

Here we present simulation based results of how irradiation induced defects affect the onset of sliding in multi-walled tubes and how the stiffness of a nanotube rope is affected by the defects as a function of the defect density. Covalently bonding intershell and intertube defects are found to improve the mechanical load transfer significantly.

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High-Q Mechanical Oscillators Based on Carbon Nanotubes*

Brian Hunt, M. Bronikowski, D. Choi, J. Davis, L. Epp, D. Hoppe, E. Wong#, L. Guo, K. Hanson, A. Yin, M. Tzolov, J. Xu∧, D. Adam, R. Young+

#JPL/Caltech, ∧ Brown University, +Northrop Grumman
Contact e-mail: bdhunt@jpl.nasa.gov

Mechanical resonators based on carbon nanotubes offer the possibility of high-Q oscillators operating at GHz frequencies for signal processing and sensing applications. This work describes progress in developing two novel and complementary nanotube-based high-Q resonator devices: a tunable resonator using a horizontal suspended nanotube bridge; and a narrow-band RF filter based on a vertical nanotube array integrated with an RF waveguide structure. We have fabricated suspended lateral nanotubes with lengths down to 100 nm using prepatterned coplanar waveguide (CPW) molybdenum electrodes and liftoff-defined Fe nanoparticle catalysts with methane CVD growth. We have also developed a process for integration of ion-mill-patterned, highly ordered, vertical nanotube arrays (1) with thin film CPW RF electrodes. Both the lateral and vertical nanotube devices exhibit the expected dc electrical properties. RF testing of prototype vertical array devices with unpatterned nanotubes shows a strong narrow-band resonance near 0.84 GHz. Additional RF testing is in progress on second-generation vertical array devices with patterned nanotube active areas and an improved electrode design.

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Mechanical properties of undulating long nanotubes under axial strain

Syogo Tejima[1], *Noejung Park*[1], *Savas Berber*[2], *Hisashi Nakamura*[1], *David Tomanek*[2]

[1] Research Organization for Information Science & Technology (RIST)
[2] Michigan State University
Contact e-mail: tejima@tokyo.rist.or.jp

The unusually tensile strength of carbon nanotubes exceeds that of any other known fiber because of the inherent strength of the sp^2 carbon-carbon bond. This has beneficial consequences for the application of nanotubes in composite bulk materials and for high mechanical stability of individual elements in nanometer-scale devices and sensor chips. Due to the narrow diameter of nanotubes, however, their mechanical properties are expected to be depend sensitively on their structure and presence of defects. In spirt of the importance of this topic, current microscopic understanding of mechanical properties of nanotubes, including their Young's modulus and stress-induced deformations, is based on computer simulations with a relatively small number of atoms per unit cell and mainly bond-order potentials. Here we present results of large-scale simulations of stress-induced undulations in nanotubes as a function of the unit cell size using a parameterized Linear Combination of Atomic Orbitals approach. Our study focusses on structural deformations of (10,10) nanotubes subject to axial pressure, with up to 2,200 atoms per unit cell, ten times larger than considered in previous simulations. With significantly fewer structural constraints, implied by the larger unit cell, our results differ significantly from those published previously [1]. We also present analogous results for more complex carbon nanostructures, including double wall nanotubes and peapods with different chiral indices.

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Incipient Mechanical Yield in Carbon Nanotubes: Two Competing Atomistic Routes

Traian Dumitrica, Ming Hua, and Boris I. Yakobson

Rice University
Contact e-mail:traian@rice.edu

Fullerene nanotubes yield to tension in two basic ways: (i) At a high temperature or in a long time limit a single bond rotation creates a Stone-Wales (SW) dislocation-dipole, favored thermodynamically under large stress. (ii) At zero temperature chemical bonds break directly (without SW bond rotation) with the formation of a microcrack, whose growth is governed by the phenomenon of "lattice trapping" [1]. In general, the two yield mechanisms are in competition and the occurrence of one or the other depends mainly on temperature and applied strain rate. How do carbon nanotubes yield to mechanical tension in real laboratory conditions of room temperature and finite experiment duration? The competition of the main failure routes will be discussed based on ab initio transition state calculations [2] and tight-binding molecular dynamics simulations. A complete map of the mechanical response with temperature and applied strain rate as parameters, obtained from theoretical considerations and computer simulations, will provide a clear connection between atomistic behavior and inherently mesoscopic phenomena such as plasticity and fracture.

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Tribological performances of nanotubes

F.Dassenoy [1], *L.Joly-Pottuz* [1], *J.M.Martin* [1], *D. Mihailovic* [2], *T.Mieno* [3]

[1] LTDS, Ecole Centrale de Lyon, 69134 Ecully cedex, France
[2] Jozef Stephan Institut, Jamova 39, SI-1000 Ljublana , Slovenia,
[3] Shizuoka University, Department of physics, 836 Ooya, 422-8529 Shizuoka, Japan
Contact e-mail: fabrice.dassenoy@ec-lyon.fr

Graphite and layered material made from metal disulphides (MoS2, WS2) are known to be very good lubricants. The weak bond strengths between the layers allow for easy shearing of the crystal, resulting in a lamellar mechanism of lubrication. Therefore they are widely used as solid lubricant or as additives dispersed in oil. However, the use of these additives is at the origin of some problems of toxicity and pollution. Recently, the application of nanoparticles and nanotubes in tribology has received considerable attention. The reason comes from the chemical stability of these spherical and cylindrical crystal shapes (absence of dangling bonds) in contrast to flat geometry. In this paper, we describe the tribological performances of some carbon and Mo-S-I nanotubes used as additives in lubricating oil. Our results show that nanotubes are potential additives for lubricating oil. They can be used as friction modifiers and/or antiwear additives in lubricating oils. The wear and friction characteristics of the pure oil can be significantly enhanced by dispersing only 1 wt % nanotubes. Such improvement is due to the formation of a deposit film in the contact area (DLC like coating and MoS2 respectively for carbon and Mo-S-I nanotubes) which reduce the frictional force.

Structural stability of carbon Y-shaped rings

D. Grimm, P. Venezuela, and A. Latgé

Instituto de Física, Universidade Federal Fluminense, 24210-340 Niteroi, Rio de Janeiro- Brazil
Contact e-mail:daniel@if.uff.br

Y-shaped junctions and rings composed of single wall carbon nanotubes are proposed as possible nanosized electronic devices exhibiting quantum interference mechanisms. The defect consists of six heptagons, according to the Crespi's rule, localized exactly at the bifurcation area. The thermal and structural stability of the Y-structures are investigated by Monte-Carlo simulations, using the Tersoff many-body potential. Structures with small diameters are quite stable for temperatures below 700 K, whereas bigger sized are stable up to 1300 K. At higher temperatures one finds a type of coalescence process between the two equal arms composing a symmetric Y-shaped ring. In the case of asymmetric Y-shaped rings, a formation of localized defect in the longer kinked arm is observed. When mechanically stretched along the tube axis, the Y-shaped rings exhibit yield strains a few percent lower compared to the pristine nanotube counterparts. Under high strain the a rupture process starts at the heptagon defects. Local electronic properties of a variety of metallic and semiconducting Y-junctions and Y-rings are calculated by adopting a single band tight binding model. Remarkable changes in the electrical conductance are found by varying the length of one of the junction's arm acting as a resonance cavity, whereas asymmetric Y-shaped rings show a complete downfall of the transport channels due to the destructive quantum interference effects associated with the two distinct nanotube paths.

Deformation of a Carbon Cell under Hydrostatic Pressure using an Empirical Interatomic Potential

G. Nieto Malagón, J. Orozco Velazco, P. Rosendo Francisco

Facultad de Ciencias, UAEM. Instituto Literario 100, Col. Centro, C. P. 50000,
Toluca, Estado de México, México.
Contact e-mail: rosendop@uaemex.mx

We performed a molecular dynamic simulation to determine changes in shape of a carbon cells, under hydrostatic pressure, using an empirical potential and the Parrinello-Rahman formalism. The interatomic potential is a classic one that explicitly incorporate the dependence of the bond order on local environment, and gives a convenient and relatively accurate description of the structural properties and energetics of carbon. Its simplicity and good results make it adequate for molecular simulation. The Parrinello-Rahman formalism is appropriated to conduct simulations under conditions of constant pressure or stress, rather than constant volume. This allows the simulation of a change in symmetry or unit cell size. We present the changes of the volume cell and the radial distribution function versus applied pressure.

Single walled carbon nanotubes under pressure

S. Baltazar-Rojas[1], *A. H. Romero*[1], *J. L. Rodríguez-López*[1], *K. Lindenberg*[2], *R. Martonak*[3]

[1] Instituto Potosino de Investigación Científica y Tecnológica, SLP, Mxico
[2] Chemistry Department, University of California, USA
[3] Computational Science, Department of Chemistry and Applied Biosciences, ETH Zurich, Switzerland.
Contact e-mail: sbaltaza@ipicyt.edu.mx

The study of systems under extreme conditions like high pressures can give us novel structures and/or configurations that are metastables under normal conditions. These transitions could be associated to new electronical and mechanical properties. In this work we introduce a new method to simulate finite systems under pressure by using a classical interparticle potential. This method could be applied to different physical systems, and it is an extension of the Lagrangian by a thermodynamical term 'PV'. We have applied this method to study finite single walled carbon nanotubes (SWCNTs). We find structural transitions in nanotubes (10,10) and (5,5). Our results are in partial agreement with a recently reported calculation[1]. Our main difference with that work is basically a non-universal transition in SWCNT. The cross section changes from circular to oval is not a critical behaviour compared with a critical transition from an oval to a peanut. These observed transitions have important implications on changes of the electronic properties of SWCNT as function of pressure.

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H.6 *Atomic Structure of Carbon Nanotubes*

Atomic Structures of Carbon Nanotubes

N.Y. Jin-Phillipp[1], *M. Rühle*[1], *A. Fonseca*[2] *and J.B. Nagy*[2]

[1] Max-Planck-Institut fuer Metallforschung, Heisenbergstr.3, D-70569 Stuttgart, Germany
[2] Laboratoire de RMN, Facultes Universitaires Notre-Dame de la Paix, Rue de Bruxelles 61, B-5000 Namur, Belgium
Contact e-mail:nyjin@mf.mpg.de

Direct atomic imaging of carbon nanotube (CNT) can be achieved by atomic resolution microscopy (ARM). We report the study on atomic structure of single wall carbon nanotubes and their defects by comparing experimental images of high-resolution transmission electron microscopy (HRTEM) with image simulation

Should BN nanostructures have line defects?

S. Azevedo (2), M. S. C. Mazzoni (1), R. W. Nunes (1), H. Chacham (1)

(1) Departamento de Fisica, ICEX, Universidade Federal de Minas Gerais, CP 702,
30123-970,Belo Horizonte, MG, Brazil.
(2) Departamento de Fisica, Universidade Estadual de Feira de Santana, Km 3
BR-116, 44031-460, Feira de Santana, BA, Brazil.
Contact e-mail:mazzoni@fisica.ufmg.br

Boron nitride (BN) and carbon can be found in similar structures. However, unlike carbon, BN structures can contain three types of covalent bonds. In BN, fullerene-like structures are usually formed from disclinations that minimize the formation of “wrong” bonds, namely B-B and N-N bonds. Recently, however, such a “no-wrong-bond” rule has been challenged by at least two experiments[1,2] which show disclinations that would imply the existence of line defects with a large number of non-BN bonds. In this work, we investigate the stability of boron nitride nanocones, using first-principles calculations. Our results indicate, surprisingly, that “defective” nanocones with an antiphase boundary [3] (a line defect that contains either B-B or N-N bonds) can be more stable than those without one. This arises from a competition between the elastic energy (associated with the curvature) and the energy cost of non-BN bonds. We also find that modifications in the antiphase boundaries by carbon atom substitutions can further stabilize the nanocones, even though the defect induces localized states in the bandgap that can present a significative spin splitting.

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The atomic structure of carbon nanohorn dahlia particle at the core: Numerical simulations for Y-junctions formation

Takazumi Kawai and Yoshiyuki Miyamoto

NEC fundamental and environmental research laboratories
Contact e-mail:t-kawai@da.jp.nec.com

The carbon nanohorn core has very complicated atomic structure. From TEM images, the core part seems to consist of planer graphitic network for the most part. The core part structure is so stable that one cannot separate it even after ultrasonication in a solvent or thermal treatment. Then core part is supposed to be constructed not only with weak interlayer interaction of planar network but also with relatively tight covalent bonding. In that sense, three-dimensional junction structures constructed from two-dimensional graphene sheets are strong candidates for units of nanohorn core.

We focused on some junction structures consist of graphene sheets, which are thermally very stable. The junction structures are easily formed from the coalescence of two graphene sheets at right angles. Since these junction structures have "Y" section, we call these structures as 'Y-junction'. DFT-LDA calculations show that expected formation processes need no activation barrier or significantly low barrier. Tight-binding molecular dynamics simulations show that the formation processes do not depend largely on initial atomic configurations or temperature.

We expect that nanohorn dahlia particle have Y-junction structures at the core and may reveal interesting phenomena due to specific properties of Y-junction electronic states.

Intensity problem in singe-walled carbon nanotubes

S. Reich(1) and C. Thomsen(2)

(1) University of Cambridge, Department of Engineering, Cambridge CB2 1PZ, UK;
(2) Institut fuer Festkoerperphysik, Technische Universitaet Berlin, Hardenbergstr. 36, 10623 Berlin, Germany
Contact e-mail: sr379@cam.ac.uk

Samples of isolated carbon nanotubes have a photoluminescence intensity that depends strongly on chiral angle. Tubes close to the armchair direction have the highest luminescence intensity, whereas zigzag tubes are not detected at all. We show that this systematic dependence is due to an exciton resonance. Depending on the chiral indices of a tube the second-subband exciton can resonate with the two-electron-hole state of the first subband. By calculating the absorption line shape we show how this process broadens and weakens the photoluminescence intensity. The intensity problem thus reflects the luminescence of the individual tubes and not a particular chirality distribution in the sample.

A REVIEW ON THE PROPERTIES (MECHANICAL, OPTICAL, ELECTRICAL) AND THE EFFECT OF CHIRALITY ON THE BEHAVIOR OF CARBON NANOTUBES

Katya Marinova SIMEONOVA and Ganka Marinova MILANOVA

Institute of Mechanics, BULGARIAN ACADEMY OF SCIENCES and UNIVERSITY OF ARCHITECTURE, CIVIL ENGINEERING AND GEODESY
Contact e-mail:katyas@bas.bg or katyageorge@abv.bg

Paper, presented is an attempt to generalize, to analyse and suumarise, some recent publications - in a period of 1999-2003, devoted to investigation of different properties and the effect of chirality of carbon nanotubes. The work has been developed in some sections. Nanotechnologies and nanomaterials, are new era of nanoscince, has been pointed out into the introduction. Both types of carbon nanotubes have been considered- single walled carbon nanotubes (SWNT) and multi walled carbon nanotubes (MWNT). Regarding elastic behaviour of carbon nanotubes, it is found that Young's Modulus of MWNTs and SWNT are about 1.28 and 1.22 TPa. Considering some other mechanical properties - it must be mentioned, that these nanomaterials have as well high stiffness, high strength and good buckling resistance. Studies of optical properties, showed that carbon nanotubes could behave as metallic or semiconducting ones. Electrical transport properties (ballistic conductance, resistivity and maximum current density) have been analysed as well. SWNTs has been characterized, by the chiral vector(n,m) and at given chiral vector the diameter of carbon nanotube can be determined. In conclusion could be pointed out that the paper presented may be used as a good tool for investigation of carbon nanotubes for engineers, physists, chemists, scientists at all in advancement of nanotechnologies.

Geometric constraints in the growth of nanotube-templated polymer monolayers

M. S. Ferreira and J. N. Coleman

Physics Department, Trinity College Dublin, Ireland
Contact e-mail:ferreirm@tcd.ie

The large increase in the mechanical response of nanotube-polymer composites is directly correlated with the formation of a crystalline layer of polymers surrounding the nanotubes. Motivated by this correlation, we present a simple model that describes the ordered assembly of polymer strands on nanotube surfaces. Energetically favourable coiling angles are identified based on geometric constraints that limit the maximum coverage of polymers on the walls of the nanotubes. The coiling angles can be controlled by selecting the appropriate nanotube diameters, opening the possibility of engineering the strength of composite fibers.

I Invited Session (Thursday Morning)

Interaction of Nanotubes with Photons

Keynote Lecture

Carbon Nanotube Photophysics and Some Grand Challenges

M.S. Dresselhaus

Department of Physics and Department of Electrical Engineering and Computer
Science, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.
Contact e-mail:millie@mgm.mit.edu

Single wall nanotubes provide a benchmark for new phenomena that might be possible in 1D (one-dimensional) systems, originating from their well defined 1D density of states, whereby every structurally distinct *(n,m)* nanotube has its own unique and characteristic 1D electron and phonon density of states spectra. One of the special phenomena of 1D physics is the large enhancement in signal from spectral probes that depend on the van Hove singularities in the density of states associated with 1D systems. This phenomenon allows a variety of photophysical phenomena to become observable, such as Raman scattering and luminescence from one individual nanotube, and leads to the identification of the nanotube geometrical structure from measurement of its diameter and energy eigenvalues. This talk will both review some recent advances in nanotube photophysics and discuss some related grand challenges to future research directions for carbon nanotube science.

Characterization of carbon nanotubes by Raman and novel spectroscopic techniques

A. Jorio

Depto de Física, Univ. Federal de Minas Gerais and Instituto de Nanociencias
Contact e-mail:adojorio@fisica.ufmg.br

We report our latest results on the Raman characterization of carbon nanotubes and discuss novel spectroscopic techniques, placing them in the context of the general progress in the field of characterization techniques. Raman scattering has been used to characterize both bundles and individual SWNTs, and provides unique information about nanotube structure, i.e. diameter, chiral angle and handedness, as well as electronic properties through the resonance effect, and chemically/physically-induced phenomena. Optical absorption, photoluminescence and fast optics techniques are also discussed, addressing how they have been used to help the general progress in the field of characterization techniques.

Photo-Cleaning and Carrier Decay in Nanotubes Explored by First-Principles Simulation tool for Electron Ion Dynamics

Yoshiyuki Miyamoto

Fundamental and Environmental Research Labs, NEC, Tsukuba, Japan.
Contact e-mail:y-miyamoto@ce.jp.nec.com

Can nanotubes be electronic-devices superior to silicon devices? The answer depends on intrinsic properties of nanotube beside its contact nature with electrodes. Although nanotubes are tolerant to presence of vacancies [1], control of oxygen (O) impurities is still demanded for device reliability since the O impurities strongly interact with carbon (C) atoms in the chemisorption stage [2]. On the other hand, time-constant of carrier decay in nanotubes [3] is a key factor for the frequency of device operation.

To theoretically attack above issues, we have performed the molecular dynamics (MD) simulations under electronic excitations with use of the computer code FPSEID^{T}M (First-Principles Simulation tool for Electron Ion Dynamics) [4], which is on the basis of the time-dependent density functional theory (TDDFT) [5]. Thus we simply call this type of simulation as TDDFT-MD simulation.

Present TDDFT-MD simulation shows one possible way to eliminate O impurities from nanotube without damaging remaining C-C-bond networks in a very short time constant. We expect this result gives a hint of a future purification technique for nanotube-devices. Meanwhile, as for the carrier dynamics, the TDDFT-MD simulation shows feasibility to theoretically determine the mechanisms of hot-carrier decay by highlighting microscopic scattering processes.

The present calculations are extremely time-consuming, but are feasible when we use massively parallelized vector processors; **the Earth Simulator** in Yokohama, Japan.

Present works are in collaborations with Professors A. Rubio and D. Tomanek. The author is indebted to N. Jinbo for his technical assistance.

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J Invited Session (Thursday Morning)

Nanotubes for Optoelectronics

Optical and time-domain spectroscopy of single- and double-wall carbon nanotubes

Tobias Hertel

Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235, USA.
Contact e-mail:tobias.hertel@vanderbilt.edu

Carbon nanotubes with their unique combination of electronic, thermal and mechanical properties hold promise for nano-electronic as well nano-optical devices. Beneficial for application in such devices is the tuneability of optical band gaps by tube structure throughout almost the entire near infrared range. A careful look at optical absorption and photoluminescence spectra reveals the nature of optical excitations in CNTs and the role of the detailed tube structure for transition energies and band gaps. In double-wall CNTs, the addition of a 'second skin' makes studies of the dynamics of optical excitations of the inner core-tubes particularly fascinating. We present time-resolved photoluminescence studies of SWNTs and DWNTs and discuss the observed carrier dynamics and relaxation processes in different environments.

Voltage-Translatable Infrared Source in a Carbon Nanotube Field-Effect Transistor

Marcus Freitag[1],[2], *Jia Chen*[1], *James C. Tsang*[1],*Qiang Fu*[3], *Jie Liu*[3] *and Phaedon Avouris*[1]

[1] IBM Research Division, T. J. Watson Research Center, Yorktown Heights, NY 10598;
[2] Carbon Nanotechnologies, Inc., Houston, TX 77084;
[3] Department of Chemistry, Duke University, Durham, NC 27708
Contact e-mail:mfreitag@us.ibm.com

We present a novel infrared emitting device based on an ambipolar carbon nanotube field-effect transistor with long channel length. Electrons and holes are injected into the nanotube from opposite contacts and recombine in a small segment of the carbon nanotube. The gate-control in 1D allows us to move the ambipolar domain and the nanoscale light source between the two contacts along the carbon nanotube. At high bias we also observe local minority carrier generation through Zener tunneling or Avalanche breakdown. Most importantly, the spatially resolved electroluminescence provides valuable insight into the nanotube transistor behavior.

K Challenges and Future of NT Research and Technology. (Thursday Afternoon)

Nanotube Research and Technology

Kiyoshi Shishido

Senior Manager, Technology & Business Development Dept
Mitsubishi Corporation, Japan

Computational Nanotechnology: The Next Frontier

Hisashi Nakamura

Director, Division of Computational Science and Technology
RIST, Japan

Due to the quantum nature of phenomena dominating the behavior on the nanometer scale, even the most advanced experimental observations are subject to being fundamentally influenced by the measurement itself. Especially when addressing novel nanostructures and their properties, large-scale computer simulations emerge as an indispensable complement to the experiment. Recent progress in High Performance Computing technology allows us to perform such predictive computer simulations involving large numbers of atoms. This contribution will summarize recent trends and perspectives in the rapidly evolving field of Computational Nanotechnology, especially in the field of Nanotubes.

Funding Nanoscience and Technology in the USA

Thomas Weber

Director of Division of Materials Research
National Science Foundation, USA

Funding Opportunities for Nanoscience and Nanotechnology

Jaime Parada Avila

General Director, CONACyT, México

Manuel Méndez Nonell

Director of Science, CONACyT, México

L Invited Session (Friday Morning)

Functionalized Nanotubes

Manipulating Carbon Nanotubes with Nucleic Acids

Ming Zheng

DuPont Central Research and Development
Contact e-mail:ming.zheng@usa.dupont.com

Single-stranded DNA (ssDNA) forms stable complex with CNT and effectively disperses CNT into aqueous solution. We found that a particular ssDNA sequence (d(GT)n, n = 10 to 45) self-assembles into an ordered supramolecular structure around individual CNT, in such a way that the electrostatic properties of the DNA-CNT hybrid depend on tube type, enabling CNT separation by anion-exchange chromatography. Optical absorption and Raman spectroscopy showed that the separation is bimodal based on both electronic properties and the diameters of CNTs: early fractions are enriched in the smaller diameters and metallic tubes, whereas late fractions are enriched in the larger diameters and semiconducting tubes. In this talk, I will show the separation of single (n, m) type carbon nanotubes and use of the material in novel solution chemistry and device applications. This work comes from the Molecular Electronics group at DuPont CR&D.

Polymer-nanotube composite materials: From interactions to Applications.

JN Coleman, M Cadek, V Nicolosi, K Ryan, R Murphy, A Fleming, M Ferreira, WJ Blau

Physics Dept, Trinity College Dublin, Ireland
Contact e-mail:colemaj@tcd.ie

A detailed study of the physical and chemical properties of selected polymer-nanotube composites has been carried out. We have studied composite formation and polymer-nanotube interactions for a range of nanotube types from SWNT to large diameter MWNT and both conjugated and non-conjugated polymers. Certain polymers such as polyphenylenevinylene derivatives, and vinyl based polymers such as polyvinylalcohol and polyvinylpyrrolidone tend to disperse nanotubes while rejecting other carbon based impurities. In many cases interaction with nanotubes tends to nucleate the formation of a crystalline polymer coating in the solution phase. This coating has a strong influence on the physical properties of the subsequent solid state composite materials.

We have modeled the formation of the first mono-layer and found that that the energy is minimized as the polymer coating on the nanotube is maximized. Geometric constraints mean that the coverage can only be maximized for ordered coatings at some magic angles.

In addition we have developed a new spectroscopic method the study the adsorption/desorption kinetics for organic molecules in SWNT composite solutions. This work shows that as the nanotube concentration is lowered in these solutions, the SWNT bundle size tends to decrease until individual nanotubes are stable at low concentration. The concentration at which individual SWNT become stable is strongly dependent on the nature of the dispersant molecules. In addition, larger diameter NT such as DWNT and MWNT can be isolated at higher concentrations as expected. In addition, tensile tests were carried out on free-standing composite films of polyvinyl alcohol and six different types of carbon nanotubes for different nanotube loading levels. Significant increases in Young's modulus by up to a factor of two were observed in all cases. Theories such as Krenchel's rule-of-mixtures or the Halpin-Tsai-theory could not explain the relative differences between composites made from different tube types. However, it is possible to show that the reinforcement scales linearly with the total nanotube surface area in the films. In addition, in all cases crystalline coatings around the nanotubes were detected by calorimetry suggesting comparible polymer-nanotube interfaces. Thus, the reinforcement appears to be critically dependent on the polymer-nanotube interfacial interaction as previously suggested. Furthermore, additional polymer-multiwall nanotube composite films were fabricated using polyvinylalcohol and chlorinated polypropylene. As observed previously polyvinylalcohol formed a crystalline coating around the nanotubes, maximising interfacial stress transfer. In the second case the interface was engineered by covalently attaching chlorinated polypropylene chains to the nanotubes, again resulting in large stress transfer. Increases in Young's modulus, tensile strength and toughness of ‘3.7, ‘4.3 and ‘1.7 respectively were observed for the polyvinylalcohol based materials. Similarily for the polypropylene based composites, increases in Young's modulus, tensile strength and toughness of ‘3.0, ‘3.9 and ‘4.4 respectively were observed. In addition a model to describe composite strength was derived. This model shows that the tensile strength increases in proportion to the thickness of the interface region. This suggests that composite strength can be optimised by maximising the thickness of the crystalline coating or the thickness of the interfacial volume partially occupied by functional groups.

Non covalent functionalization of carbon nanotubes for potential nanobiotechnology applications

C. Mioskowski, S. Rickling*

Laboratoire de synthese bioorganique - Faculté; de Pharmacie 74 route du Rhin
F-67401 Illkich - France & CEA/Saclay, SMMBC - bat. 547 F-91191 Gif sur Yvette -
France
Contact e-mail:mioskow@aspirine.u-strasbg.fr

New photo polymerisable amphiphilic lipids, which self organize around carbon nanotubes have been obtained. These lipids form half-micelles around nanotubes leading to nano-rings which can easily be polymerized by photo-irradiation. The supramolecular structures that are obtained are stable, water soluble and allow purification and shortening of single walled carbon nanotubes. Furthermore, the polymerized rings can be removed from the nanotubes by application of an electical field to form new nano-objects that are called nanosomes. The structure and some properties of these new nanosomes will be presented and applications for the solubilization and vectorization of hydrophobic molecules including drugs, membrane proteins, dyes, pheromones and fullerenes will be discussed.

M Invited Session (Friday Morning)

Transport in Nanotubes

Flow Induced Voltage and Current in Carbon Nanotubes

A. K. Sood

Department of Physics, Indian Institute of Science,Bangalore-560 012, India.
Contact e-mail:asood@physics.iisc.ernet.in

Our recent experiments (1) have shown that voltage/current is induced in single walled carbon nanotubes by the flow of water and other liquids. The induced voltage depends logarithmically on the flow velocity. The magnitude of the voltage depended sensitively on the ionic conductivity and on the polar nature of the liquid. This suggests that the dominant mechanism responsible for this highly sub-linear response involves a direct forcing of the free charge carriers in the nanotubes by the fluctuating Coulombic field of the liquid flowing past the nanotubes. Most interestingly, the direction of the induced current with respect to the flow direction can be controlled by the nature of the liquid and by voltage gating the nanotubes (2). In these experiments, the nanotubes are biased with respect to another reference electrode, thereby controlling the ions brought near the nanotubes. It is shown that when positive (negative) ions are brought closer to the tubes, the flow induced current is parallel (antiparallel) to the flow direction. A general semi-phenomenological model will be presented involving dissipative coupling of charge carriers in the nanotubes to the fluidic Coulomb fluctuations with their correlations made spatially asymmetric by the flow. The main reason for the logarithmic dependence is that the flow not only drags the carriers in the nanotube, but also contributes to their friction. Recent applications using the flow-induced voltage generations will be discussed.

I thank S. Ghosh, S. Ramaswamy and N. Kumar for collaboration. It is a pleasure to thank Prof. C.N.R. Rao for the fruitful interactions and for providing the nanotube samples.

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[2] S. Ghosh, A.K. Sood, S. Ramaswamy and N. Kumar (to be published)

Quantum transport in defected and doped nanotubes

Jean-Christophe Charlier

Université Catholique de Louvain, PCPM & CERMIN,
Place Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium.
University of Louvain (Belgium)
Contact e-mail:charlier@pcpm.ucl.ac.be

Early theoretical works predicted that the electronic properties of ideal carbon nanotubes depend on their diameter and chirality. The presence of topological defects such as 5/7 pairs, Stone-Wales (5775), vacancies, does strongly modify their electrronic and transport properties. In this account, a novel class of perfect crystals, consisting of layered sp2-like carbon and containing periodic arrangements of pentagons, heptagons and hexagons, has been proposed [1]. The cohesive energies of these phases suggest the possible synthesis of such carbon arrangements, in comparable conditions as for C60. These sheets, called Haeckelites, are rolled up so as to generate SWNTs with intriguing electronic properties. Ab initio local density of states calculations of all sheets and tubes revealed an intrinsic metallic behavior, independent of orientation, tube diameter, and chirality. Particularly, an unusual high intensity LDOS peak at the Fermi level is noticed for a crystal with an hexagonal symmetry and its respective nanotubes, thus suggesting the possible existence of superconductivity. The predicted ab initio IR and Raman frequencies allow us to distinguish unambiguously these structures [2]. STM images and quantum conductances of various tubular Haeckelite structures are calculated within a tight-binding framework. The three investigated Haeckelite structures are shown to be good candidates as conducting wires in nanoelectronics. The results presented here provide a catalog of properties that could be helpful for the identification of other Haeckelite structures as well as systems presenting pentagon and heptagon defects.

In order to tailor the electronic properties of CNTs, the Fermi level can be tuned by chemical doping. Electronic quantum transport is investigated in boron and nitrogen doped carbon nanotubes using tight-binding methods correlated to ab initio calculations [3]. Within such a technique, both the effect of dopants on the charge transfer and the random scattering are accurately taken into accounts. The generic transport properties such as conduction mechanisms, mean-free-paths and conductance scalings are derived for various concentration of boron and nitrogen dopants which are randomly distributed within the honeycomb network of the single-wall carbon nanotubes. Our calculations display that a small amount of dopants can drastically modify the electronic transport properties of the tube, which is certainly a key effect for future nanoelectronics.

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N Contributed Session (Friday Afternoon)

Oral Poster++ *Presentation*

Environment effects on optical properties of carbon nanotubes

J.S. Lauret, C. Voisin, S. Berger, G. Cassabois, Ph. Roussignol, C. Delalande, A. Filoramo, L. Cape

ONERA (Chatillon, France); LPA Ecole Normale Supérieure (Paris, France); LEM CEA (Saclay, France)
Contact e-mail:jean-sebastien.lauret@onera.fr

Optical properties of single wall carbon nanotubes are related to their quasi one-dimensional nature. Their absorption spectra consist in a set of lines in the near infrared, the lowest one corresponding to the transitions between the first pair of Van Hove singularities in the semiconducting tubes. However, for standard samples consisting in deposited nanotubes on a glass substrate no photoluminescence is observed.

We have studied the dynamics of the electronic interactions on a femtosecond time scale after a selective and resonant excitation of the semiconducting tubes. We have observed a transient photobleaching due band filling effects with a recovery time of about 1 ps. We propose a mechanism based on a carrier tunnelling between nanotubes within a bundle that accounts for the fast electronic relaxation and consequently for the quenching of the photoluminescence [1].

We have also investigated a new class of samples that show photoluminescence even at room temperature. They consist in a suspension of quasi-isolated nanotubes encased in a micelle [2]. Indeed our pump-probe measurements show that the electronic dynamics is qualitatively modified. A non-exponential dynamics is observed with a long lived component persisting up to a few hundreds of picoseconds.

[1] Lauret Phys. Rev. Lett. 90, 057404-1 (2003)
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N.1 *Transport in Nanotubes*

Quantum transport in multiwall carbon nanotubes

B. Stojetz[1], *E. Thune*[1], *E. Ljubovic*[2], *L. Forro*[2], *and Ch. Strunk*[1]

[1] Institute for Experimental and Applied Physics, University of Regensburg, Germany,
[2] Institute of Physics of Complex Matter, FBS Swiss Federal Institute of Technology, Switzerland
Contact e-mail:ethune@gwdg.de

We report on magnetoresistance measurements for individual multiwall carbon nanotubes in a magnetic field perpendicular to the tube axis. Al backgates provided strong electrostatic coupling of the nanotube to the gate and allowed for a considerable variation of the doping level of the tube. Gate voltage sweeps were performed for many values of the magnetic field and over a wide temperature range. At very low temperatures we observed Coulomb blockade from which we could infer the ratio between gate voltage and the shift of the Fermi level. After subtraction of the zero-field fluctuations, which can be attributed to both universal conductance fluctuations and Coulomb charging, the data show clear weak localization features. Our analysis also reveals an unusual suppression of the magnetoresistance at certain gate voltages, which are grouped symmetrically around the estimated position of the charge neutrality point of the tube. We attribute the quenching of the magnetoresistance to the population of subbands of the outermost nanotube shell, which is supported by band structure calculations.

Electronic spectrum of carbon- nanotubes rings under electric fields

M. Pacheco1, Z. Barticevic1, C. Rocha2, A. Latgé2

[1] Universidad Técnica F. Santa María,
[2] Universidade Federal Fluminense do Niteroi
Contact e-mail:monica.pacheco@usm.cl

In this work, we analyze the electronic properties of a carbon-nanotube ring under an external electric field applied perpendicular to the plane of the structure [1]. Our calculations are based on the π-electron single-orbital tight binding approximation, and the effect of the electric field is included into the on-site energies of the carbon atoms along the ring [2]. An interesting electric-field effect is found for zigzag/armchair toroids. By considering a dephasing angle between the electric field direction and the position of the carbon atoms along the toroid one finds a clear modification of the energy spectra deriving essentially from the lattice symmetry of the graphite sheet. Actually, for an even number of atoms along the zigzag nanotube, certain eigenenergies in the toroid spectrum oscillate as a function of a dephasing angle. The range and position of those particular energies, and the amplitude and period of the oscillations, may be conveniently modulated by changing the strength and direction of the electric field. We will present here a detailed analysis of this effect including analytical expressions for the oscillating energies as a function of the electric-field dephasing angle.

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Electronic properties of suspended carbon nanotubes

A. Hassanien[1], *M. Tokumoto*[1], *T. Shimizu*[1], *H. Tokumoto*[1]

[1]AIST, Tsukuba Japan
Contact e-mail:Abdou.Hassanien@aist.go.jp

We have performed STM measurements on suspended single wall carbon nanotubes at room temperature in order to probe their intrinsic electronic properties. We find that substrate-nanotube interactions influence the electronic properties. On supported semiconducting nanotubes bands are shifted toward higher energies while they are more symmetric around the Fermi level in the unsupported ones. For metallic tubes we observed that interference patterns of electron waves caused by defects and edges are more pronounced on suspended nanotubes than the supported nanotubes. These results highlight the role of substrate-nanotubes interactions and shed some light on their influences on nanotube devices.

Transport properties of multiwalled carbon nanotubes synthesized with plasma-enhanced CVD

M. Ahlskog, P. Hakonen, A. Koshio, M. Yudasaka, S. Iijima

University of Jyväskylä, Helsinki University of Technology, NEC Research Center
Contact e-mail:ahlskog@phys.jyu.fi

We have studied low temperature transport properties of multiwalled carbon nanotubes grown without catalyst by a plasma-enhanced CVD method. The diameter of our nanotubes varies from 3 to 8 nm. At low temperatures we observe a gap in the IV-curves at positive gate voltages in all of our measured tubes. Regular Coulomb oscillations are also seen in the data.

Effect of increasing curvature in the electronic structure of carbon nanotubes: In situ UV-photoemis

T. de los Arcos [1], *M. G. Garnier* [2], *J. W. Seo* [3], *L. Forré* [3], *P. Oelhafen* [1], *C. Domingo* [4], *J. V. Garcia Ramos* [4], *and S. Sanchez Cortes* [4]

[1]Institute of Physics, University of Basel, Switzerland
[2] Institute of Physics, University of Neuchatel, Switzerland
[3] Institute of Physics of Complex Matter, EPFL, Switzerland
[4] Instituto de Estructura de la Materia, CSIC, Madrid, Spain
Contact e-mail:t.arcos@unibas.ch

The electronic structure of carbon nanotubes has been investigated in situ with UV-photoemission spectroscopy (photon energies of 21.2 and 40.8 eV). The investigated samples correspond to CNTs with different diameters grown by CVD either onto bare Si substrates or onto Si covered with buffer layers of Al_2O_3, TiN or TiO_2. Since there was no exposure to air, no cleaning procedure was necessary before the measurement. Although the diameter distributions of the CNTs are broad the samples analyzed belong to clearly separated CNT families: nanotubes around 7 nm diameter onto Si and Al_2O_3, and nanotubes around 20-30 nm diameter onto TiN and TiO_2 layers. Since the diameter distributions were not overlapping, we could identify features in the spectra that were clearly dependent of CNT curvature, like for example a progressive decrease in the intensity of p-states around 3 eV binding energy, in dicative of higher degree of s-p hybridization with decreasing radius. Surprisingly, a curvature dependence was also observed in other spectral features, which to our knowledge have not been reported before. The observed effects will be discussed and compared with structural information obtained from high-resolution TEM and micro-Raman measurements of the nanotubes.

Tunabel Electric Property of Small-Radius Double-Walled Carbon nanotube

Youngmi Cho[1], *Gunn Kim*[1], *Hyoung Joon Choi*[2], *and Jisoon Ihm*[1]

School of Physics, Seoul National University, Seoul, Korea[1],
School of Computaional Sciences, Korea Institute for Advanced Study, Seoul
130-722, Korea [2]
Contact e-mail: cym68@phya.snu.ac.kr

Based on first-principles calculations, we study the electronic structure of double-walled carbon nanotubes(DWCNTs), especially when the diameter of the inner tube is less than 5.5 A. Our model system, (7,0)@(17,0), may be grown exothermically and is composed of two semiconducting nanotubes. Large curvature of the inner tube induces s^*-p^* hybridized band near the Fermi level and the DWCNT becomes metallic by band-crossing of the s^*-p^* inner-tube band and the p outer-tube band. We investigate the changes of electronic structure near the Fermi level by the adsorbates on the outer tube. We also find that the energy gap of composite double-walled nanotube, which consists of boron nitride nanotube and carbon nanotube(CNT), is modified from that of the original CNT due to radial distortion.

The Electrical Properties of Cs encapsulated Single-Walled Carbon Nanotubes

T. Izumida[1], *G. -H. Jeong*[1], *T. Hirata*[1], *R. Hatakeyama*[1], *Y. Neo*[2], *H. Mimura*[2], *K. Omote*[3], *and Y. Kasama*[3]

[1] Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan¡BR¿
[2] Research Institute of Electronics, Shizuoka University, Hamamatsu, Japan¡BR¿ [3]
Ideal Star Incorporation, Minami-Yoshinari 6-6-3, Sendai, Japan¡BR¿
Contact e-mail:hatake@ecei.tohoku.ac.jp

One of the most attractive properties of single-walled carbon nanotubes (SWNTs) is the electric transport property. Therefore, extensive researches have been reported concerning the application to electronic devices such as field effect transistor (FET). Because pristine SWNTs have been found to behave only as a p-type FET, n-type FET formation method becomes a key factor for further development. Recently, the method such as alkali-metal doping has been developed in order to realize n-type FET. However, usual vapor deposition method used for the alkali-metal intercalation has the inherent problem of air-stability. For this reason, we have carried out an interdisciplinary experimental approach using plasma ion irradiation to create cesium-encapsulated SWNT (Cs@SWNT)[1]. Moreover, we now start to experimentally investigate electric transport of this individual Cs@SWNT. At first, we made Cs@SWNTs suspension in N,N-dimethylformamide. After then, supersonic treatment was carried out in order to disperse heavily tangled Cs@SWNTs bundles. Sonicated Cs@SWNTs were dripped on a FET substrate. According to the gate-bias (V_G) dependence of current-voltage characteristics between the source-drain electrodes measured at 293 K, we can clearly confirm the V_G dependence that source-drain currents increase with decreasing V_G. In addition, Cs@SWNTs are found to show both the p- and n-type semiconducting properties.

[1] G. -H. Jeong *et al.*, Chem. Commun. (2003) 152; Phys. Rev. B **68** (2003) 075410.

Electronic Properties of Nitrogen-Doped Carbon Nanotubes

L.G. Bulusheva, A.V. Okotrub, A.G. Kudashov

Nikolaev Institute of Inorganic Chemistry SB RAS, pr. Ak. Lavrentieva 3,
Novosibirsk 630090, Russia
Contact e-mail:bul@che.nsk.su

Nitrogen-containing multiwall carbon nanotubes were produced by a chemical vapor deposition (CVD) technique. Acetonitrile was decomposed over Ni/Co nanoparticles at temperature of 850^{o}C. X-ray photoelectron spectroscopy revealed a splitting of N 1s line measured for the sample produced. The interpretation of spectral features was made by the results of ab initio calculation on different nitrogen doped graphite fragments. Theoretical binding energies were computed using specially evaluated correction factor. The low-energy maximum of N 1s spectrum was assigned to pyridinic like nitrogen (structure with three nitrogen atoms located at the edges of atomic vacancy), while the high-energy maximum corresponds to three-coordinated nitrogen atoms, substituted carbon ones in the graphite lattice. Relative intensity of the N 1s spectral maxima was found to depend on the catalyst composition and nanotubes synthesized using catalyst with the ratio Ni/Co 1:1 contain the greatest proportion of pyridine-like nitrogen. The quantum chemical calculations demonstrated the inserting of three-coordinated nitrogen atoms into graphitic network lowers the ionization potential of carbon nanotube. This result explains the field emission characteristics measured for set of samples. The voltage threshold was shown to decrease with increasing of content of three-coordinated nitrogen.

Electrical conducting CNT/metal-interfaces

Joachim Glatz-Reichenbach, Jan-Henning Fabian, Eric Wapelhorst, Markus Abplanalp, Henning Fuhrmann,Sami Kotilainen

ABB Schweiz AG, Corporate Research, CH-5405 Baden-Dättwil
Contact e-mail:joachim.glatz-reichenbach@ch.abb.com

It is still challenging to optimize the interfacial resistance between physically touching contacts, and to reduce the impact of electrical arcing, always present when switching electrical power circuits. Today electrical switches or relays comprise a metal contact system. Such metal contacts show erosion and material loss during and after multiple switching cycles due to heavy thermo-electrical load. In order to keep the lifetime of electrical contacts as high as necessary or even possible, erosion of the contact material must be minimized while an optimum in performance must be guaranteed, i.e. low contact resistance, and reduced tendency to contact welding, respectively. Furthermore metal contacts show a certain surface roughness, which may lead to high and inhomogeneous current density at the contact area. In order to reduce the current density at the interface of touching electrical contacts, the transition area can be enlarged and reduced in micro-roughness by covering The electrical characterization of such CNT-covered contacts has been done by determination of IV-characteristics. Also the change of the interfacial transition resistance between two CNT-covered contacts was studied by variation of the gap distance in between. A quantitative analysis of the three different major contributions to the overall electrical resistance of CNT/metal interfaces has been performed, and they are identified to belong to (-1-) the interface between CNT and metal substrate, (-2-) the CNT-body itself, and (-3-) the interfacial contact resistances between touching CNT.

Conducting properties of chemically doped single wall carbon nanotubes

Urszula Dettlaff-Weglikowska[1], *Viera Skakalova*[1], *Ralf Graupner*[2], *Sung Ho Jhang*[3], *Lothar Ley*[2], *Yung Woo Park*[3], *Siegmar Roth*[1], *Savas Berber*[4], *and David Tomanek*[4]

[1] Max-Planck-Institute for Solid State Research, D-70569 Stuttgart, Germany
[2] Institute of Technical Physics, University Erlangen, D-91058 Erlangen, Germany
[3] School of Physics, Seoul National University, Seoul 151-747, Korea
[4] Physics and Astronomy Department, Michigan State University, East Lansing, MI 48824, USA
Contact e-mail:U.Dettlaff@fkf.mpg.de

Purified single wall carbon nanotubes have been treated by $SOCl_2$. We observed that $SOCl_2$ reacts readily with the nanotube sample, forming a homogenous dispersion. Entangled networks obtained after filtration show an increase in the electrical conductivity up to factor of 5. EDX and XPS identify presence of sulphur after the reaction with $SOCl_2$. Thus, we assume that S containing groups, such as -SO-, -SOCl, $-SO_2Cl$ or $-SO_3H$ are attached to the nanotubes. The charge transfer due to the doping reaction was investigated by XPS. The carbon 1s peak is shifted by 0.4 eV towards lower binding energy, suggesting p-type doping. This is consistent with ¡i¿ab initio¡/i¿ calculations of $SOCl_2$ interacting with nanotube fragments, where we observe a down-shift of the Fermi level into the next van Hove singularity in the nanotube density of states. Clear evidence for the electronic structure modification after $SOCl_2$ exposure is also found in optical absorption spectra. The absorption band at 0.75 eV, related to semiconducting tubes, vanishes in the modified SWNT sample. In agreement with the calculated electronic structure, this finding suggests a shift of the Fermi level into the valence band, thus converting semiconducting tubes into conductors. The difference in the conductivity between the pristine and functionalized sample is even more pronounced at low temperatures. The pristine sample shows a semiconducting character in the temperature dependent conductivity, whereas metallic behavior is observed in the functionalized material. The positive temperature dependence of the thermopower confirms holes as majority carriers in the chemically doped system.

Functionalised carbon nanotubes: Transport properties

A. Latgé[1], *D. Grimm*[1], *R. B. Muniz*[1], *and M. S. Ferreira*[2]

[1] Instituto de Fisica, Universidade Federal Fluminense, 24210-340 Niteroi - RJ, Brazil;
[2] Trinity College, Physics Departament, Dublin, Irland
Contact e-mail:latge@if.uff.br

Functionalised carbon nanotubes are certainly interesting systems due to the possible changes on their mechanical and electronic properties. As expected, the extent of the modifications will certainly depends on the nature and size of the attached systems. Chemists are presently capable of synthesizing larger molecules in a controlled fashion and producing compounds with tailor-made chemical and physical properties. In particular, polymers are one of the different structures that can interact with a carbon nanotube. Those long quasi one-dimensional molecules can adhere to a nanotube in different ways, depending on the type of polymers and on the solutions in which they are immersed. In the case of a carbon nanotube with a conducting polymer coiled around its walls along the axial direction , higher values for the conductance are expected since conducting polymers contribute with extra electron channels. Measurements confirm this picture displaying clear enhancement of the conductivity. By adopting a simple tight-binding model we investigate the conductance of functionalized carbon nanotubes in the presence of a varied number of polymers attached on their walls. Randomic distributions for the set of grafted polymers are considered and the percolation problem is studied. We determine the critical concentration of added molecules for which the electronic transport is completely suppressed. The quantum conductance is calculated via the Kubo-Landauer formalism expressed in terms of the single-particle Green function. Potential use of carbon nanotubes as chemical sensors and nanometer-scale electronic devices has already been envisaged.

Extraordinary Mobility in Semiconducting Carbon Nanotubes

M. S. Fuhrer, T. Durkop, T. Brintlinger, S. A. Getty and E. Cobas

University of Maryland
Contact e-mail:cobas@eng.umd.edu

We have developed a voltage-contrast scanning electron microscopy technique to locate conducting nanotubes on insulating substrates[1]. Using this technique we have located and made electrical contacts to individual nanotubes with lengths up to 800 microns, in order to determine the intrinsic conduction properties of the SWNTs. From the gate-voltage dependence of the conductance, we determine the charge carrier mobility which exceeds 100,000 cm2/Vs at room temperature[2], greater than that of the best known semiconductors.

Full conductance distribution and fluctuation of disordered carbon nanotube

Wei Ren and Jian Wang

Physics Department, The University of Hong Kong, Hong Kong
Contact e-mail:wren@nano.physics.hku.hk

We investigate the full distribution and sample-to-sample conductance fluctuations, using the tight binding Anderson Hamiltonian to model quantum scattering (ballistic and diffusive) in disordered carbon nanotubes. The quantum transport calculation are found to be in good agreement with results from random matrix theory (RMT). For instance, the root mean squared (rms) values of onductance fluctuation reach the universal quantum limit of RMT for 1D systems. For the metallic nanotubes, large conductance G ($\gg G_0$) has a Gaussian distribution; while in the small G regime, it would be a log-normal distribution. The universal conductance fluctuations dominate over a wide range of disorder strength. When expressed as a function of disorder strength, the metal-to-insulator crossover is clearly presented by the mean values of conductance. Detailed investigation on the evolution of G distribution is shown in this work. Furthermore we present the third and fourth order cumulants of the disordered nanotubes, which could be explored by experimental distribution measurements.

High-bias Electrical Transport in Semiconducting Single-wall Carbon Nanotubes

Yung-Fu Chen, Gokhan Esen and M. S. Fuhrer

Department of Physics and Center for Superconductivity Research, University of Maryland, College Park, MD 20742-4111, USA
Contact e-mail: yfuchen@physics.umd.edu

Transport in semiconducting single-walled carbon nanotubes tens of microns in length at high source-drain bias is investigated. Both hole-like and electron-like carriers can contribute to the current, with efficient recombination in the nanotube. The electron and hole currents can significantly exceed 25 microamps per nanotube, the limit in long metallic nanotubes due to optical phonon emission. The transconductance is half of the limit expected for a ballistic field effect transistor, and the origin of this transconductance limitation will be discussed.

In situ TEM observation of carbon nanotubes under electric field

Makoto OKAI[1], *T. FUJIEDA*[2], *K. HIDAKA*[2], *T. Muneyoshi*[1], *T. Yaguchi*[1].

Hitachi Displays, Ltd.[1], Hitachi Research Laboratory, Hitachi, Ltd.[2]
Contact e-mail:okai@crl.hitachi.co.jp

We observed carbon nanotubes under electric field by transmission electron microscope in order to clarify the mechanisms of field emission from carbon nanotubes. Lying carbon nanotubes start to stand along the electric field vector under the electric field of 0.5V/mm. Standing carbon nanotubes return to their original positions when the electric field becomes zero.

Electron transmission through a carbon nanotube perturbed by a time varying potential

P. Orellana1, M. Pacheco2

[1]Universidad Católica del Norte
Contact e-mail:monica.pacheco@usm.cl

We investigate the electronic transport through a single-wall carbon nanotube connected to leads in the presence of a transversal ac-potential. We have calculated the density of states at zero temperature for semiconductor zigzag nanotubes via the equation of motion approach for the Greens functions and we have found an interesting dependence of the gap with the frequency and amplitude of the external time-varying potential. We studied the feasibility that this effect can be observed in transport measurements by calculating the coherent conductance within the Landauer-Bütikker formalism [1].

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Electronic properties of individual defects in carbon nanotubes and semiconductor nanowires by Scanning Probe Microscopy

V. Meunier, S. V. Kalinin, J. Shin , A. P. Baddorf, R. J. Harrison

Oak Ridge National Laboratory
Contact e-mail:vm2@ornl.gov

Using Scanning Gate Microscopy (SGM), individual atomic defects in a nanotube can be visualized as a decrease in the current through the nanocircuit, since defects are depleted for tip voltages that are related to the local electronic structure of the defect. Here, the interaction between a carbon nanotube and a point charge is studied using both atomistic first principles modeling and continuum electrostatic methods. Results are compared and extrapolated to real tip geometries to simulate the interaction of the scanning tip with an adjacent nanotube. Comparison with experiment suggests that the gate voltage dependence of the image contrast is a direct measure of the difference in Fermi energies at these defects. A crucial factor in SGM is the tip radius and an approach for the unambiguous determination from SPM data is presented. This analysis is extended to SGM measurements on semiconductor and oxide nanowires and relative contributions of surface states and bulk dielectric screening to SGM response are determined.

Engineered Multiwalled Carbon Nanotubes

B. Bourlon[1], *C Miko*[2], *L. Forro*[2],*D.C. Glattli*[1,3], *A. Bachtold*[1]

[1] Laboratoire Pierre Aigrain, Ecole Normale Superieure, 24 rue Lhomond, 75231
Paris 05, France.
[2] EPFL, CH-1015, Lausanne, Switzerland.
[3] CEA Saclay, F-91191 Gif-sur-Yvette, France.
Contact e-mail: bourlon@lpa.ens.fr

We have studied the high-bias transport properties of the different shells that constitute a multiwalled carbon nanotube(MWNT). In order to probe the current in the different shells, the MWNTs are engineered using the electrical-breakdown method which allows to selectively remove the shells. Different electrodes are attached on a same MWNT with different electrode separations. We find that the current per shell saturates at high bias and varies between 10 and 60 microA. For the shortest separation (200 nm), the current is shown to increase as a function of diameter. For longer separations (1000 nm), the diameter dependence is much weaker and more difficult to observe. We propose that this geometrical dependence is due to a weak variation of the number of current carrying subbands within each shell that results from the competition in the electron transmission between the electron-phonon scattering process and Zener tunneling. The electrical-breakdown method is then used to fabricate a nanoelectromechanical system consisting of a plate rotating around a multiwalled nanotube bearing. The motion is possible thanks to the low intershell friction. Indeed, the nanotube has been engineered so that the sliding happens between different shells. The plate rotation is activated electrostatically with stator electrodes.

N.2 *Field Electron Emission*

Carbon nanotubes as electron sources in electron microscopes

Maya Doytcheva, Niels de Jonge

Philips Research, Eindhoven, The Netherlands
Contact e-mail:maya.doytcheva@philips.com

The research is aimed at developing a new type of electron source for electron microscopes to improve their resolution. Electron sources were constructed from individual carbon nanotubes by mounting them on tungsten tips using a nano-manipulator [1,2]. The electron emission of thin multi-walled nanotubes, as well as nitrogen-doped multi-walled carbon nanotubes has been studied and important parameters such as energy spread of the emitted electron beam, emission pattern, angular current density, current stability and brightness were measured. It was found that upon thorough cleaning of the nanotube surface, the emission process is field emission as described by the Fowler Nordheim theory. A workfunction of 5 eV was determined. Compared to the state of the art commercial sources, the nanotube source shows a lower energy spread than the Schottky emitter and a better current stability than the cold-field emission gun (CFEG). The source provides an extremely high brightness: $3\text{x}10^{\ 9}$ $\text{Asr}^{-}1\text{m}^{-}2\text{V}^{-}1$ - an order of magnitude larger than that of the Schottky emitter and the CFEG [1,3].

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Field emission properties of cup-stacked-type carbon nanofiber

D. Yoshizawa, Y.A. Kim, T. Hayashi, T. Yanagisawa, M. Kobayashi, K. Osada, M. Endo

Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nangano-shi
380-8553, Japan
Contact e-mail:yoshizawa@endomoribu.shinshu-u.ac.jp

Cup-stacked-type carbon nanofiber obtained by a chemical vapor deposition method, especially using the floating reactant method, has been introduced as functional materials due to their peculiar morphology such as their stacking morphology of truncated conical grapheme layers [1,2]. In this study, we performed various post-treatment on this type of carbon nanofiber such as air oxidation and also heat treatment, basically in order to remove the deposited carbon on the outer surface of carbon nanofiber, characterized the structural changes using various techniques such as high resolution transmission electron microscope and Raman spectroscopy, and then evaluate the emission properties of these modified carbon nanofibers. Carbon nanofibers heat treated at 3000∘C exhibited lower threshold voltage as compared with those of the pristine and oxidized carbon nanofibers. This study will try to understand the variation of emission properties in relation with structural changes such as loop formation.

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High Electron Field Emission from Side Wall decorated MWNT

M. Sveningsson, R- E. Morjan, O. Nerushev, E. E. B Campbell.

Department of Experimental Physics, School of Physics and Engineering Physics,
Göteborg University and Chalmers University of Technology, SE-412 96 Gteborg,
Sweden.
Contact e-mail: f3amsv@fy.chalmers.se

Films of long and aligned multi-walled carbon nanotubes with side-wall decorations are grown by plasma enhanced chemical vapour deposition [1]. The field emission measurements show that these films have excellent field emission properties with very high emission current densities. These tube wall decorations are extremely sharp with a thorn like structure and seems to have a big influence on the enhancement of the applied electric field.

In addition to these experiments we have theoretically investigated the ohmic heating process of multi-walled carbon nanotubes that will occur during high electron field emission. Having emitter temperatures above 2000 K, which have experimentally been observed [2], gives an enhancement of the emission current leading to a non-Fowler-Nordheim emission behaviour that instead assumes electron emission from a zero Kelvin surface. The enhanced field emission current has also been observed from experiments on individual MWNT.

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High Current Density Field Emission from Carbon Nanotube Bundles

Michael J. Bronikowski, Harish Manohara, Brian D. Hunt, Peter Siegel

Jet Propulsion Laboratory/California Institute of Technology, Pasadena, CA, USA
Contact e-mail:Michael.J.Bronikowski@jpl.nasa.gov

The field emission behavior of bundles of multiwalled carbon nanotubes (CNT) arranged in a variety of array geometries has been investigated. We have found that such arrays of CNT bundles perform significantly better in field emission than arrays of isolated nanotubes or dense, continuous mats of CNT, and that the field emission performance depends strongly on the bundle diameter and inter-bundle spacing. In particular, arrays of 1 - 2 micron diameter CNT bundles spaced 5 - 10 microns apart produced the largest emission densities, routinely giving 1.5 - 1.8 A/cm2 at electric fields of 4 V/micron, and > 6 A/cm2 at 20 V/micron. Studies of the optimization of field emission from such CNT bundle arrays with respect to various array and process parameters will be presented and discussed.

Field emission properties of capped and open-ended carbon nanotubes

Hiroyoshi Tanaka, Yasumoto Konishi, Seiji Akita, Lujun Pan and Yoshikazu Nakayama

Department of Physics and Electronics, Osaka Prefecture University, 1-1
Gakuen-cho, Sakai, Osaka 599-8531, Japan
Contact e-mail:nakayama@pe.osakafu-u.ac.jp

Field emission properties of standalone carbon nanotubes have been investigated experimentally in terms of the capped and open-ended tip shapes. The capped multiwall nanotube with a tip curvature of ∼2.5 nm is compared with the open-ended single wall nanotube with a diameter of ∼5 nm. An arc-discharge-produced capped nanotube was attached to a tungsten tip by using a scanning electron microscope manipulator in the same manner as that for preparing nanotube probes and nanotube tweezers. To obtain the open-ended nanotube emitter, a nanotube was cut by an excess current to have a bamboo-shoot-like shape and then an inner layer was extracted to form an open ended tip of a single wall nantoube with a diameter of 5 nm. These samples have almost the same current-voltage characteristics but show different field-emission-microscope images. The capped one shows some bright spots and in contrast the open-ended one shows twelve bright stripes with a spindle shape. These images are related to the electron emission from the pentagons of carbon atoms at the tip and from the standing wave of electrons along the circumference on the nanotube, respectively. The magnification of the images is larger for the capped one than for the open-ended one.

Carbon Nanotubes as Thermionic Emitters

R. O. Loutfy, M. Samandi, A. Moravsky, and S. Strange

MER Corporation
Contact e-mail:rloutfy@mercorp.com

Thermionic converters are an interesting option for lightweight and long-life power generators due to a number of compelling advantages, including all solid construction, no moving parts, and waste heat rejection at high temperature. An experimental set up has been built that allows the screening of thermionic coatings and new nano-materials from room temperature to 2000 K in high vacuum and at gap sizes as small as 1 mm. A new class of very high temperature compatible materials, carbon nanotubes, has been investigated for their performance as cathodes. Seven different types of carbon nanotubes have been screened as thermionic emitter cathodes and compared to tungsten and nitrogen doped diamond. It has been found that some carbon nanotubes combine excellent temperature stability with good thermal emission performance. Yet other carbon nanotubes exhibited exceptional combined thermal and field enhanced emission performance.

Carbon Nanotubes/Nanofibers and Metallic Nanowires for field emission applications

P. Legagneux[1], *K.B.K. Teo*[2], *L. Vila*[3] *and O. Groening*[4]

[1]THALES, France
[2]University of Cambridge, UK
[3]University of Louvain-La-Neuve, Belgium
[4]EMPA, Thun, Switzerland
Contact e-mail: pierre.legagneux@thalesgroup.com

According to T. Utsumi(1), vertically aligned cylindrical columns presents the ideal shape for field emission. For these emitters, the geometrical electric field enhancement at the emitter apex is close to the aspect ratio (height/radius). We have studied arrays of two different types of aligned columns : first, metallic Nanowires(2) grown at room temperature by electrodeposition into nanoporous templates; second, carbon Nanotubes/Nanofibers(3) (CNs) grown by catalytic plasma enhanced chemical vapour deposition.

The fabrication process of arrays of 2 m height and 20 nm diameters Cobalt Nanowires and arrays of 5 m height and 50 nm diameter carbon Nanotubes/Nanofibers (CNs) will be presented. Due to their exceptional aspect ratios, these Nanocolumns exhibit excellent field emission properties. For example, a 0.5 x 0.5 mm2 CN based cathode emits a 2mA current corresponding to a current density of 0.8A/cm2. The use of such Nanocolumn arrays for different field emission applications will be discussed.

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Dispersion Method of Carbon Nanotubes for Field Emission Electron Source

Masahiro FUJIKAWA, Toshio KOBAYASHI, Shuhei NAKATA, Takao SAWADA and Soichiro OKUDA

MITSUBISHI ELECTRIC CORPORATION,Advanced Technology R & D Center
Contact e-mail:Fujikawa.Masahiro@wrc.melco.co.jp

Recently carbon nanotubes have been studied as an field emission electron source. Because it is possible to make a large screen display by an easy process : the printing method using a carbon nanotubes paste. One of serious problems for the printing method is the rugged surface of a carbon nanotubes layer due to the aggregation of the CNT degraded in the paste. If the surface of printed layer is rough, the emission uniformity becomes degraded. To remove the aggregation and to form a flat carbon nanotubes layer, the carbon nanotubes should be well dispersed in the paste.

Therefore, we have been developed carbon nanotubes paste what includes the amino group dispersion agent and the alcoholic group solvent which can disperse carbon naotubes effectively. The surface roughness (Ra) of a Carbon nanotubes layer was improved from 1.0μm to less than 0.2μm, the excellent emission property was obtained.

Camphor-pyrolyzed carbon nanotubes may be efficient field emitters

Mukul Kumar[1*], *Keita Kakamu*[1], *Tsugio Okazaki*[1], *Yoshinori Ando*[1], *Mineo Hiramatsu*[2]

[1] Department of Materials Science and Engineering, Meijo University, Tempaku-ku, Nagoya 468-8502, Japan
[2] Department of Electrical and Electronic Engineering, Meijo University, Tempaku, Nagoya 468-8502, Japan
Contact e-mail:mukul@ccmfs.meijo-u.ac.jp

Vertically aligned nanotubes were grown by thermal decomposition of a tree product - camphor - on various substrates for field emission (FE) application. In a parallel plate (∼500 mm apart) FE device, as-grown CNTs exhibited appreciable emission current densities in the range of 1-20 mA/cm^2 at applied fields of 6-8 V/4mm at an ordinary vacuum of 10^{-5} torr; i.e. ultrahigh vacuum is not essential! Best results were observed from CNTs on a cobalt-coated silicon substrate with a turn-on current density of 1 mA/cm^2 at a low applied field of 2 V/mm, and maximum current density of 20 mA/cm^2 at 8 V/mm. Field enhancement factor was on the order of 10^3. The effect of the thickness of the cobalt film on field emission was studied. It was observed that the conductive cobalt film overrides the underlying resistive SiO_2 layer, thereby improving the FE characteristics of as-grown CNTs. Utilizing such an emission efficiency of camphor-grown nanotubes, a model FE microscope was fabricated with isolated nanotube emitters and informative emission patterns were observed on a fluorescent screen (placed at a working distance of 5 cm) at low applied voltages of 300-1000 V. Presence of localized density of states corresponding to pentagons at the emitter tip was identified. Emission patterns obtained from isolated nanotubes were considerably stable; for instance, a constant emission current of 10 mA was recorded for 6 h at 1000 V. These features suggest that camphor-pyrolyzed CNTs may be efficient field emitters.

Field Emission of Carbon Nanotubes Grown on Carbon Cloth

J. Y. Huang[1], *S. H. Jo*[1], *D. Z. Wang*[1], *W. Z. Li*[2], *K. Kempa*[1] *and* *Z. F. Ren*[1]

[1] Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467
[2] Department of Physics, Florida International University, Miami, Florida 33199
Contact e-mail: huangje@bc.edu

Field emission from carbon nanotubes grown on carbon cloth has been studied. An extremely low electric field of less than 0.4 V/um is required to reach an emission current density of 1 mA/cm2. This ultra-low operating electric field of carbon nanotubes grown on carbon cloth is mainly due to a very high field enhancement factor of 1.882×10^4, which is the result of geometrical configuration of the carbon nanotubes and the substrate. This field enhancement factor is even higher than that of the macroscopic tungsten tip, even though the carbon nanotubes grown on carbon cloth are planar field emitters. In addition to the field enhancement, the highly disordered microstructure of carbon nanotubes grown on carbon cloth plays an important role to field emission. This unexpected result indicates that the roughness of the substrates on which carbon nanotubes grow is very important. This result also brings us significantly closer to practical applications such as highly efficient lamps,field emission displays, micro vacuum electron sources, etc.

N.3 *Optical Properties and Optoelectronics*

Circular Dichroism Spectra of Chiral Single-Wall Carbon Nanotubes

A. Sanchez-Castillo, Carlos E. Roman-Velazquez**, Cecilia Noguez**, L. Meza-Montes**

Instituto de Fisica UAP**, **Instituto de Fisica UNAM
Contact e-mail:asanchez@venus.ifuap.buap.mx

Effects of chirality on optical properties have been observed in molecules, clusters and other entities. Circular Dichroism (CD) Spectroscopy has been extensively used to detect chirality in these systems. Therefore this technique can be applied to study chiral nanotubes In this work, theoretical CD spectra of single-wall chiral carbon nanotubes have been calculated and their dependence on chirality has been analyzed. We first optimized atomic structures of carbon nanotubes using first-principles total-energy calculations. Then we calculated the CD spectra within the dipole approximation [1]. Chiral single-wall carbon nanotubes with different radii and chiralities were considered. Results reveal that the CD spectra of nanotubes with similar radius and different chiral angles show similar shape but relative intensities strongly depend on the chiral angle.

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Polarized Incandescent Light Emission from Carbon Nanotubes

Peng Li, Kaili Jiang, Ming Liu, Qunqing Li, Jialin Sun and Shoushan Fan

Department of Physics and Tsinghua-Foxconn Nanotechnology Research Center,
Tsinghua University, Beijing 100084, P. R. China
Contact e-mail:jiangkl@tsinghua.edu.cn

Polarized light emission from multi-walled carbon nanotube (MWNT) bundles due to current heating is observed. The spectra of the emitted light fit well with the blackbody radiation distribution. And the emitted light is partially polarized with a degree of 0.33 along the axis of MWNT bundle, which is qualitatively explained in terms of one-dimensional (1-D) structure of carbon nanotubes (CNTs). Negative temperature dependent resistance is also observed, which is different from normal metal filaments. The MWNT bundles are very stable at high temperature in vacuum during light emitting, indicating that CNTs can be a good candidate as polarized incandescent light sources.

Low temperature photoluminescence of surfactant-suspended SWNT's

Henrique B. Ribeiro, Marcos A. Pimenta, Flavio Plentz

UFMG, UFMG, UFMG
Contact e-mail:plentz@fisica.ufmg.br¿

Photoluminescence (PL) has been a powerful method for the investigation of bulk semiconductors and novel artificial low dimensional semiconductor heterostructures such as quantum wells, quantum wires and quantum dots. Recently bright PL from semiconductor, surfactant-suspended, isolated single walled carbon nanotubes (SWNT's) and from isolated SWNT's grown between silicon oxide pillars have been observed. Low temperature PL measurements in pillar suspended SWNT's have also been reported. In this latter study small blue shifts of the PL peak energies and PL excitation energies, and previously unreported PL peaks have been found. In this work we present results on the low temperature photoluminescence of surfactant-suspended SWNT's. We have found that, upon freezing of the SDS-suspended SWNT's solution, the SWNT's remains strongly luminescent. We perform PL and photoluminescence excitation (PLE) measurements in temperatures ranging from 1.5 to 250○K, for excitation energies between 0.8 and 1.75eV and compare the results with the PL and PLE maps obtained for the same suspension at 300K. The energy shifts between the low and high temperature spectra are discussed in terms of the effects of the changes in the SWNT's environment upon freezing, the temperature dependence of the energy gaps and excitonic effects for different SWNT's families.

Fluorescence and Optical Absorption of Single-Walled Carbon Nanotubes Synthesized from Alcohol

Yuhei Miyauchi, Satoshi Ogawa, Yasunori Hayashida, Shigeo Maruyama

Department of Mechanical Engineering, The University of Tokyo, 7-3-1 Hongo,
Bunkyo-ku, Tokyo 113-8656, Japan
Contact e-mail:miyauchi@photon.t.u-tokyo.ac.jp

Near-infrared fluorescence measurements [1] were performed on single-walled carbon nanotubes (SWNTs), which were catalytically synthesized from alcohol [2] under various experimental conditions. The chirality distribution was determined by measuring the fluorescence emitted from dispersed SWNTs as a function of excitation wavelength. The chiral angle distribution of small diameter tubes was distributed predominantly in the higher chiral angle region [3]. The reason for the armchair-rich chirality distribution is discussed based on the initial cap structure satisfying the 'isolated pentagon rule'. The results of fluorescence measurements were compared with the optical absorption spectra and the theoretical calculations of energy gaps. Centrifuge-based separation of small diameter SWNTs was performed to prepare samples rich in near-armchair type.

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Local photo-electronic transport in individual carbon nanotubes

Alf Mews[1], *Matteo Scolari*[1],*Kannan Balasubramanian*[2],*Tilman Assmus*[2], *Marko Burghard*[2]

[1] University of Mainz, D-55099 Mainz, Germany;
[2]Max-Planck-Institut fuer Festkoerperforschung, D-70569 Stuttgart, Germany.
Contact e-mail: alf.mews@uni-mainz.de

While the optical and charge transport properties of individual carbon nanotubes (CNTs) have been studied in detail, much less is known about their opto-electronic behavior. Here we present a method where the local electronic properties of individual CNTs are investigated under sub-micron illumination using a scanning optical microscope (SCOM). The CNTs were independently identified as metallic or semiconducting by means of electrical measurements and Raman spectroscopy on the same CNTs. Charge transport studies under illumination allowed the observation of photoconductivity in semiconducting CNTs. Furthermore, local electronic structure effects along the CNT could be monitored by determining the variations of photoresponse as a function of position [APL]. The metallic tubes exhibited reversible resistance changes upon illumination, which are likely originating from optically induced desorption of molecular species from the gas phase.

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OPTICAL PROPERTIES OF SINGLE WALLED CARBON NANOTUBES DEPOSITED ON SILICON

Vincenzo Vinciguerra, Francesco Buonocore*, Maria Fortuna Bevilacqua# and Salvo Coffa**

* STMicroelectronics, Stradale Primosole 50, 95121 Catania (Italy),
# STMicroelectronics, Via Remo De Feo 1- 80022 Arzano, Naples (Italy)
Contact e-mail:vincenzo.vinciguerra@st.com

Among the properties of Carbon Nanotubes (CNTs), the observation of luminescence in the near infrared (near IR) region from semiconducting single walled carbon nanotubes (SWNTs) along with the finding that field effect transistors (FETs) based on SWNTs can work as IR-electro-luminescent devices open new perspectives in the optoelectronic sector, determining a great interest in the optical properties of SWNTs. Nevertheless, in order to further prompt the devolpment of such new devices, a comparison with the properties of silicon, the leading material in the microelectronic industry, is of help. For this reason we have undertaken an experimental investigation of the optical properties of purified SWNTs deposited, in particular, on a (100) Si p- surface. The optical properties of SWNTs have been observed in the ultraviolet (UV)-visible and near IR regions and have been gained by measuring the absorption determined by SWNTs deposited on Si both by recurring to the transmitting mode and reflectance mode. In particular, we demonstrate as it is possible to gain information on the optical properties of SWNTs in the near IR region by determining their absorption that can be ascribed to the energy gap of semiconducting carbon nanotubes from reflectance measurements.

Ultrafast decay of excited carriers in carbon nanotubes: Time-dependent density functional approach

Yoshiyuki Miyamoto[1], *Angel Rubio*[2], *and David Tomanek*[3]

[1] Fundamental and Environmental Research Labs, NEC, Tsukuba, Japan
,[2] Dpto. Fisica de Materiales, Universidad del Pais Vasco, Spain
,[3] Physics and Astronomy Department, Michigan State University, USA
Contact e-mail:y-miyamoto@ce.jp.nec.com

We investigate the ultrafast decay of excited carriers in carbon nanotubes by combining the time-dependent density functional theory (TDDFT) [1], which describes the time evolution of electron states, with classical molecular dynamics (MD) simulations for the ionic motion using the First-Principles Simulation tool for Electron Ion Dynamics (FPSEID) [2]. This theoretical approach addresses both the electron-electron interaction (within TDDFT) and the electron-phonon coupling. We have chosen a (3,3) nanotube as a model system, since its small diameter is expected to cause a strong electron-phonon interaction [3]. If this is indeed the case, the common assumption that electron-electron interaction occurs on a shorter time scale than the electron-phonon interaction [4] should be re-examined. The formidable task to complete this calculation requires unprecedented computer resources, which have been made available on the massively parallel vector supercomputer "Earth Simulator" in Yokohama, Japan.

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Surface-modified single-walled carbon nanotubes for optical biosensors

Wei Zhao, Chulho Song

Department of Chemistry, University of Arkansas, 2801 South University Ave., Little Rock, AR 72204
Contact e-mail:wxzhao@ualr.edu

Single-walled carbon nanotubes (SWNTs) may have important applications in biosensors based on their unique electronic properties. We have found that by surface modification, the near infrared absorption of the first interband transition of semiconducting SWNTs responds to changes of several biological variables including pH and ethanol concentration. The sensing mechanism is uniquely related to the functionalizing groups on the surface of SWNTs and will be discussed in details.

Nonlinear and optical limiting properties of carbon nanostructure and polymer dispersions

Sean M. O'Flaherty, Robert Murphy, Jonathan N. Coleman and Werner J. Blau

Materials Ireland Polymer Research Centre, Department of Physics, Trinity College Dublin,
Contact e-mail:wblau@tcd.ie

Experimental measurements of nonlinear optical and optical limiting by two distinctly different polymer and carbon nanotube composite materials dispersed in solution are reported. The polymer poly(meta-phenylenevinylene-co-2,5-dioctyloxy-para-phenylenevinylene, PmPV) was used to form exclusive multiwalled carbon nanotube and polymer composites. The polymer poly(9,9-di-n-octylfluorenyl-2,7-diyl) was used to form composites consisting of multiwalled carbon nanotubes, other clearly defined carbon nanoparticles and polymer. It was found that the carbon nanostructures were stably dispersed in the polymer matrix in both cases. Both degenerate four-wave mixing and optical limiting experiments (using an open aperture Z-scan apparatus with 6 ns Gaussian pulses) were performed. In the PmPV /exclusively multiwalled carbon nanotube composite either the carbon nanotubes or the polymer dominates the nonlinear response depending on the relative mass of polymer to nanotube. In the other material saturation of the optical limiting was reached at carbon nanostructure mass percentages in excess of 3.8%, relative to the polymer mass, while the polymer exhibited no response of its own. Furthermore, the scattering of high intensity light from the materials was qualitatively probed and its angular dependence investigated. The nature of the carbon nanostructure inclusions in each material was found to significantly influence the scattering response of the composites.

Organic photovoltaic cells based on bulk heterojunctions of conjugated polymers and functionalized single walled carbon nanotubes

A. Urbina(1), *P. de la Cruz*(2), *J. L. Delgado*(2) *and F. Langa*(2)

(1) Dep. de Electronica, Universidad Politecnica de Cartagena, 30202 Cartagena, Spain.
(2) Facultad de Ciencias del Medio Ambiente, Universidad de Castilla-La Mancha, 45071 Toledo, Spain.
Contact e-mail: antonio.urbina@upct.es

Organic photovoltaic cells based in composites of conjugated polymers and soluble derivatives of fullerenes as the 1-(3-methoxycarbonyl)-propyl-1-1phenyl-(6,6)C_{61}(PCBM) have given efficiencies around 2.5%. Here we present a similar approach in which the electron acceptor molecule is a single walled carbon nanotube. Our cells have been prepared by spin coating solutions of poly-(3-octylthiophene), hereafter referred as P3OT, and single walled carbon nanotubes onto a glass substrate covered with indium tin oxide (ITO). In order to improve the solubility of the carbon nanotubes, we have functionalized them by attaching alkyl chains to the carboxylic acid groups on the open ends of commercially available single walled carbon nanotubes (NanoCyl S. A., Belgium). Aluminium back electrodes were prepared by magnetron sputtering.

We have tested with a surface force microscope the topography and adhesion of the composites and found that 1,2-dichlorobencene is the best solvent in order to avoid phase segregation of polymers and carbon nanotubes, thus providing two interpenetrating subnetworks to ensure carrier transport to the corresponding electrodes (holes to ITO and electrons to Al).

We have measured the photocurrent by illuminating the cells from the ITO side with a Xe lamp at $100 \mathrm{mW/cm}^{-2}$, the cells have been driven by a Keithley Mod.230 voltage source, and the current measured with a Keithley Mod.6514 electrometer. The obtained efficiencies are about 0.1%, with an open circuit voltage around 0.6V. This is a low value, but it is worth mentioning that it represents a two orders of magnitude increase compared with the efficiency obtained with a photovoltaic cell without carbon nanotubes (using only a

P3OT film between the electrodes).

In conclusion, single walled carbon nanotubes are a promising candidate to act as electron acceptor in bulk heterojunction organic photovoltaic cells. Their processability have been increased by a functionalization which greatly improves their solubility. Further investigation to control the nanostructuration of such composites is needed in order to increase their efficiency.

Low-Temperature Emission Spectra of Individual Single-Wall Carbon Nanotubes: Multiplicity of Subspecies within "Single-Species" Nanotube Ensembles

Han Htoon, Michael J. O'Connell, Peter J. Cox, Stephen K. Doorn and Victor I. Klimov

Chemistry Division, Los Alamos National Laboratory
Contact e-mail:skdoorn@lanl.gov

Single-wall carbon nanotubes represent a novel class of one-dimensional objects that have been considered as promising nanoscale building blocks for future electronic and optical nanodevices. The discovery of relatively bright photoluminescence (PL) from semiconducting nanotubes allowed a spectroscopic selection of "single-species" sub-ensembles that had been assigned to nanotubes of certain chiralities. Here, we report low-temperature studies of emission spectra of individual nanotubes. These studies show that "single-species" nanotube bands can be decomposed into narrow "subspecies" spectra with sub-meV line widths. The low-temperature, single-nanotube PL shows blinking and spectral wondering, behavior typical for both individual inorganic and organic chromophores. In addition to the quantitative difference in band positions, we observe a significant qualitative difference in both the line shape and the temperature dependence of the PL from individual nanotubes, which we attribute to the presence of unintentionally doped nanotubes along with undoped species.

O Contributed Session (Friday Afternoon)

Oral Poster++ *Presentation*

Tunneling junctions using internanotube spaces in multiwalled carbon nanotube

K.Tsukagoshi, E.Watanabe, I.Yagi, Y.Aoyagi

RIKEN
Contact e-mail:tsuka@riken.jp

The internanotube charge transport in a multiwalled carbon nanotube (MWNT)was investigated. We directly measured an electric transport from the outer nanotube to the inner nanotubes in a MWNT with two electrodes. The outer nanotubes between the two electrodes were disconnected remaining the innermost nanotube, so that the current flows into the innermost nanotube via the internanotube junctions. The transport properties of this device clearly showed Coulomb blockade oscillation with charging energy of 15 meV at 4.2 K. The observed Coulomb blockade oscillation was non-periodic to the gate voltage, indicating that the multiple internanotube tunnel junctions were formed underneath the electrodes.

O.1 *Transport in Complex Nanostructures; Luttinger-Liquid; Electron-Phonon Coupling*

Random telegraph signal in carbon nanotube peapods

S. H. Jhang [1], *S. W. Lee* [1], *D. S. Lee* [1], *Y. W. Park* [1], *M. S. Kabir* [2], *M. Sveningsson* [2], *E. E. B Campbell* [2], *Urszula Dettlaff-Weglikowska* [3], *Siegmar Roth* [3], *G.-H. Jeong* [4], *T. Hirata* [4] *and R. Hatakeyama* [4]

[1]School of Physics, Seoul National University, 151-747 Seoul, Korea;
[2]Department of Experimental Physics, Chalmers University of Technology SE-41296 Gothenburg, Sweden;
[3]Max-Planck Institute for Solid State Research, Heisenbergstr. 1, D-70569 , Stuttgart, Germany,
[4]Department of Electronic Engineering, Tohoku University, Sendai 980-8579, Japan
Contact e-mail:ywpark@phya.snu.ac.kr

The switching of resistance between two discrete values, known as random telegraph signal (RTS), was observed in carbon nanotube, C_{60} peapod and Cs-encapsulated peapod. The average times in high-current and low-current states, t_{high} and t_{low}, has been studied as a function of gate voltage and temperature as well as bias voltage. Since the carbon nanotube is an one dimensional system which has very narrow current path, the observed RTS could be originated from the trap state in carbon nanotubes.

Electroemission of fullerenes from a peapod

I.V. Krive, R.I. Shekhter and M. Jonson

Department of Applied Physics, Chalmers and Goteborg University
Contact e-mail:jonson@fy.chalmers.se

We have investigated whether carbon “peapods” can serve as electrically controlled nano- “peashooters”. To be able to controllable release material from a carbon nanotube working as a “nano-pipete” and deposit it molecule by molecule would be an import step forward in the area of nanotechnology. For stable peapods the encapsulation of fullerenes in a single-wall carbon nanotube (SWNT) is energetically favourable mostly due to the gain in van der Waals energy. Inside a SWNT the fullerenes are confined by a potential which is flat everywhere except near the ends of the tube, where the potential walls are high enough to make the peapod stable at room temperatures. How then can one release fullerene molecules from a peapod? A simple model calculation suggests that this can be achieved through electroemission by applying an applied electric field. We consider a finite length C-60@(10,10)SWNT peapod placed in the vicinity of a bulk metallic electrode and show that when a bias voltage is applied between peapod and electrode, there is a threshold voltage V_c for charging one of the C-60 molecules inside the tube. The charged molecule experiences a strong electrostatic force which for a certain bias voltage somewhat larger than V_c exceeds the van der Waals confining force and the singly charged C-60 will be expelled and driven towards the positively charged electrode. This result indicates that fullerenes can be released from a peapod by a purely electrostatic method.

Transition from a Luttinger liquid to a Fermi liquid in potassium intercalated single wall carbon nanotubes

H. Rauf [1], *T. Pichler* [1], *M. Knupfer* [1], *J. Fink* [1], *B. Büchner* [1], *H. Shiozawa* [2] *and H. Kataura* [2]

[1]Institut für Festkörper- und Werkstoffforschung, D-01069 Dresden, Germany
[2] Tokyo Metropolitan University, 1-1 Minami-Ohsawa, Hachioji, Tokyo, 192-0397 Japan
Contact e-mail:h.rauf@ifw-dresden.de

From an electronic point of view, individual single wall carbon nanotubes (SWCNT) can be regarded as nearly perfect one-dimensional systems. As such, the metallic part of a nanotube sample should exhibit deviations from classical three-dimensional Fermi liquid behavior in the density of states near the Fermi level. The density of states can be probed directly by means of photoemission spectroscopy and it was recently demonstrated that mats of SWCNT do not display Fermi liquid behavior but rather Luttinger liquid (LL) behavior which manifests itself as a power law renormalization of the density of states in the vicinity of the Fermi level [1]. We report on recent results of the n-type doping-induced change in the electronic structure of SWCNT in bundles investigated by high resolution photoemission spectroscopy. In detail, the LL behavior is shown to be stable at low doping levels while at higher doping levels ($C/K < 125$) a crossover to a Fermi liquid behavior is observed.

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Competition of Cooper pairs and Luttinger liquid in Nb/SWNTs-rope junctions

I. Takesue [1], *N. Kobayashi* [1], *S. Miyadai* [1] *and J. Haruyama* [1,2]

[1]Aoyama Gakuin University,
[2]JST-CREST
Contact e-mail: takesue@ee.aoyama.ac.jp

Luttinger liquid (LL), which consists of a repulsive Coulomb interaction in one-dimensional ballistic conductors, is one of the most exciting quantum phenomena observable in carbon nanotube (CNs). Recently, its existence in CNs has been reconfirmed by optical measurement without electrodes[1]. On the other hand, coexistence of LL and Cooper pair, consisting of an attractive Coulomb interaction via phonon, is attracting much attention (e.g., in terms of proximity-induced superconductivity[2][3]), because new quantum phenomena can be expected by those competition. Moreover, the solid-state nano-structured electron entangler has been theoretically proposed using LL/Cooper pair coupled systems.

Here, we investigated the transport properties of single-walled CNs (SWNTs) ropes interfaced with a niobium (Nb) electrode (SWNTs/Nb junctions), which were fabricated using ropes of SWNTs standing in nano-pores of alminum templates. We found a power-law in conductance vs temperature relationship with correlation exponents (a) well reflecting LL above the transition temperature (Tc) of proximity effect of Nb electrode, while conductance increased below Tc. This conductance decreased again at lower temperatures, showing a power-law with an increase of a. These result imply that LL and Cooper pairs compete depending on temperatures and that LL in our SWNT ropes separate most of Cooper pairs into each spins [4]. We will also report on spin entangler realizable by utilizing this system.

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Investigation and modifications of electron-electron interaction in carbon nanotubes

A.I. Romanenko [1], *O. B. Anikeeva* [1], *R.V. Gorbachev* [1], *A. V. Okotrub* [1], *A.G. Kudashov* [1], *T. V. Reshetenko* [2], *Z. R. Ismagilov* [2], *O. G. Abrosimov* [2]

[1]Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia;
[2]Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Contact e-mail:romanenk@casper.che.nsk.su

The possibility of a superconductivity in nanotubes is the one of the most important problems. The nature of a superconductivity is the electron-electron interaction. On the other hand elec-tron-electron interaction is exhibited in electronic transport properties of conductors in normal state so-called interaction effects (IE). IE are connected with the correction to density of states of conduction electrons as a result of quantum interferences of electrons at their diffuse motion in disordered conductors. It is shown that IE correction to X are dominated by quantum correc-tion to magnetic susceptibility X(T) for interaction electrons (interaction effects-IE). The effective interaction between electrons for arc-produced sample of multiwall carbon nanotubes (A-MWNTs) and graphite are repulsion and the electron-electron interaction l_c are estimated to be l_c ~ 0.26 for A-MWNTs and l_c ~ 0.1 for graphite. An additional negative contribution DR(B) to R(B) was found. It is shown that DR(B) at $B > 0.7$ T for multiwall carbon nanotubes prepared by catalyst method (C-MWNTs) and soot is connected with electron-electron interaction similarly to DR(T) for graphite. In this report we give Report-Review new results in field of superconductivity in ropes of single wall carbon nanotubes and MWNTs.

Proximity-induced superconductivity in Nb/multi-walled carbon nanotubes/Al junctions

N.Kobayashi [1], *S.Miyadai* [1], *A.Tokita* [1], *M.Nomura* [1], *I.Takesue* [1], *and J.Haruyama* [1,2]

[1]Aoyama Gakuin University
[2]JST·CREST
Contact e-mail:naoki@ee.aoyama.ac.jp

The strong spin coherence in carbon nanotubes (CNs) has been well-studied and proven to exist, leading to a variety of spin-phase interference effects and spintronics. Even at high magnetic fields, the spin phase itself is still preserved. On the other hand, the strength of the coherence of Cooper pairs have never been reported in CNs, although three groups[1] have reported the successful injection of Cooper pairs into carrier-undoped CNs from superconductor electrodes (proximity-induced superconductivity; PIS) and intrinsic superconductivity.

Here, we investigated the behaviors of magnetoresistance and upper critical fields, where Cooper pairs are broken by magnetic fields, in Nb/dirty multi-walled CN(MWNTs)/Al junctions within PIS. We report that the leaked Cooper pairs into the dirty MWNTs are primarily responsible for these behaviors and that this causes the suppression of Cooper-pair breaking against the applied high fields. Observations of the behaviors of the upper critical fields reveal the formation of quasi-multi-layered superconductors, consisting of proximity-induced superconductive shells/normal conductive shells, in the MWNTs. We find that the suppression becomes significant in the one-dimensional anisotropic dirty MWNTs. This is a manifestation that MWNTs can strongly maintain Cooper-pairs against high fields.

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(n,m) assignment and electron phonon coupling in SWNTs: theory and experiment

M. Machón (1), H. Telg (1), J. Maultzsch (1), S. Reich (2), P. Ordejón (3), C. Thomsen (1)

(1) Institut fuer Festkoerperphysik, Technische Universitaet Berlin, Hardenbergstr. 36, 10623 Berlin, Germany
(2) University of Cambridge, Department of Engineering, Trumpington Street, Cambridge CB2 1PZ, United Kingdom
(3) Institut de Ciencia de Materials de Barcelona (CSIC), Campus de la U.A.B., 08913 Bellaterra, Spain
Contact e-mail:maria@physik.tu-berlin.de

Measurements of resonance Raman profiles for the radial breathing mode (RBM) of single-walled nanotubes allowed us to assign up to forty different chiralities without arbitrary assumptions including for the first time those of metallic nanotubes. The measured Raman intensities show a strong chirality dependence, as well as a dependence on the value of (n-m)mod3 [where n and m define the (n,m) nanotube]. We calculated the electron-phonon coupling matrix elements for the RBM of several single walled carbon nanotubes using the ab initio package SIESTA. These matrix elements, which have been assumed constant throughout the literature, are essential for calculating Raman intensities. We obtained a systematic dependence of the matrix elements on the chirality and on (n-m)mod3, which explains the experimental observations. In particular, the electron-phonon coupling decreases with increasing chiral angle, which can be valuable information for an (n,m) assignment. The (n,m)mod3 dependence allows to distinguish nanotubes close in diameter and chirality comparing their resonance intensities. We discuss this dependence by means of an ab-initio zone folding model.

Electron-phonon coupling and phonon dispersions in graphite

S. Piscanec(1), M. Lazzeri(2), F. Mauri(2), A. C. Ferrari(1), J. Robertson(1)

1) Department of Engineering, University of Cambridge, Cambridge, CB2 1PZ
2) Lab de Mineralogie-Cristallographie de Paris, Universite Paris 6, France
Contact e-mail:acf26@eng.cam.ac.uk

The understanding of the physical mechanisms ruling the phonon dispersions and the electron-phonon coupling in graphite is a key step to derive the vibrational properties and the Raman intensities of carbon nanotubes. The phonon dispersions of graphite have been widely studied through the years, both theoretically and experimentally. However, only recently the complete phonon dispersions of the upper optical branches of graphite have been measured [1]. These are at odds with the previous ab-initio calculations, and the reason for this is still a matter of debate. In graphite the inter-atomic force-constant matrix elements very slowly decay with the distance [1-3]. This long-range behaviour strongly affects the phonon dispersion of the upper optical branches at the Gamma and K points. Here we use first-principles density functional calculations to compute the graphite phonon-dispersions and the matrix elements of the Electron-Phonon Hamiltonian (EPH). We demonstrate that the peculiar dispersion of the optical phonon branches is determined by the form of the EPH near the Gamma and K points. It thus is impossible to derive the phonon branches at Gamma and K by a force constant approach based on a finite number of force constants, contrary to what often done in literature. We provide a simple equation relating the shape of the phonon dispersions to the amplitude of the EPH-matrix elements. The electron-phonon coupling of the TO branch at and around K is much higher than any other branch. This clarifies the nature the D peak in the Raman spectra of graphite and explains why only the D band has an overwhelming Raman intensity between all the zone boundary peaks satisfying the double resonance conditions [3,4]. Our results have immediate implications for carbon nanotubes, since key features of their phonon dispersions cannot be properly described if the influence of the electron-phonon Hamiltonian on the phonon dispersion is neglected.

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Peierls distorted ground states of carbon nanotubes

A.C.M. Carvalho & M.C. dos Santos

Instituto de Fisica "Gleb Wataghin", Universidade Estadual de Campinas, 13083-970
Campinas SP, Brazil
Contact e-mail:cristina@ifi.unicamp.br

"Metallic" single-walled carbon nanotubes (SWNT's) are considered prototypes of one-dimensional (1-D) conductors. Recent experimental reports revealed that SWNT's aren't true metals: small energy gaps have been measured and the density of electronic states near the Fermi energy at low temperatures was observed to be strongly suppressed. The physical origin of these observations is still under debate. Several mechanisms have been proposed to explain the opening of a band gap, including the nanotube curvature, by which the gap would depend on the tube diameter, intertube and other three-dimensional interactions, and Coulomb correlations. Peierls instability, which states that 1-D systems possess a band gap as a result of the lattice distortion, was discarded based upon symmetry considerations. Here we present conformational and electronic structure analyses, based upon quantum chemical calculations, in which nanotubes are treated as molecular materials. Comparisons are made with the structure of polyacetylene, an organic conjugated polymer that conducts electricity upon chemical doping. Results are consistent with a Peierls distortion of armchair (n,n) nanotubes and the opening of a small band gap, in analogy to trans-polyacetylene, while zigzag (n,0) nanotubes do not present a distorted conformation due to an intrinsic band gap, similar to cis-polyacetylene.

Irradiation effects and ion channeling in multi-walled carbon nanotubes

A.V. Krasheninnikov, J. Pomoell, and K. Nordlund

Accelerator Laboratory, P.O. Box 43, FIN-00014 University of Helsinki, Finland
Contact e-mail:akrashen@acclab.helsinki.fi

Similar to the conventional semiconductor technology, beams of energetic particles can be used to modify the structure and properties of carbon nanotubes in a controllable manner. In particular, 50 keV Ga ion irradiation of multi-walled nanotubes (MWNTs) gave rise to the formation of highly ordered pillbox-like nanocompartments in the tube interior and to changes in the electronic structure of irradiated MWNTs [1]. Ar ion beams have been employed to enhance the field emission from MWNTs [2] and to make MWNT-based quantum dots [3] as well as single-electron inverters [4].

At the same time, despite substantial experimental progress, there is still very little understanding of irradiation-induced phenomena in carbon nanotubes. Many traditional concepts in ion-solid interaction theory do not work at the nano-scale at all or they require substantial modifications.

In our previous works [5], we addressed effects of irradiation on single-walled nanotubes which have a simpler atomic structure than MWNTs. Now, using atomistic computer simulations, we systematically study irradiation-mediated phenomena in MWNTs. By modeling impacts of energetic ions, we examine production of defects in MWNTs and estimate the ranges of ions with different characteristics.

Finally, due to the growing interest in solid-state quantum computing [6], we study how MWNTs can be used for spatially-selective ion implantation into the material. We demonstrate that MWNT can effectively channel ions with certain energies through MWNT empty cores. We put forward suggestions for making a MWNT-based nano-aperture device which can potentially be used for producing a beam just a couple of nm in cross-section, steering the beam and thus irradiating pre-selected areas of the sample.

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Collision-Induced Resistivity of Single-walled Carbon Nanotubes

Kim Bolton, Arne Rosén, Hugo E. Romero and Peter C. Eklund

Göteborg/Chalmers University and The Pennsylvania State University
Contact e-mail:kim@fy.chalmers.se

We have observed unusually strong and systematic changes in the electron transport in metallic single-walled carbon nanotubes that are undergoing collisions with inert gas atoms or small molecules. At fixed gas temperature and pressure, changes in the resistance and thermopower of thin films are observed that scale as ∼M1/3, where M is the mass of the colliding gas species (He, Ar, Ne, Kr, Xe, CH4, and N2). Results of molecular dynamics simulations are also presented that show that the maximum deformation of the tube wall upon collision and total energy transfer between the colliding atom and the nanotube also exhibit an ∼M1/3 dependence. It appears that the transient deformation (or “dent”) in the tube wall may provide a new scattering mechanism needed to explain the atom collision-induced changes in the electrical transport.

Fano Resonance and Electron Filtering in Multiply-Connected Carbon Nanotubes

Gunn Kim, Sang Bong Lee, Tae-Suk Kim, and Jisoon Ihm

School of Physics, Seoul National University, Seoul, Korea
Contact e-mail:gkim@phya.snu.ac.kr

We investigate the electron transport in multiply-connected metallic carbon nanotubes within the Landauer-Büttiker formalism. Quasibound states are coupled to the incident π^* states and give rise to energy levels of different widths depending on the coupling strength. In particular, donor-like states originated from heptagonal rings are found to give a very narrow level. Interference between broad and narrow levels produces Fano-type resonant backscattering as well as resonant tunneling. Over a significantly wide energy range, almost perfect suppression of the conduction of π^* electrons occurs, which may be regarded as filtering of particular (π^*) electrons.

Tunneling junctions using internanotube spaces in multiwalled carbon nanotube

K.Tsukagoshi, E.Watanabe, I.Yagi, Y.Aoyagi

RIKEN
Contact e-mail:tsuka@riken.jp

The internanotube charge transport in a multiwalled carbon nanotube (MWNT)was investigated. We directly measured an electric transport from the outer nanotube to the inner nanotubes in a MWNT with two electrodes. The outer nanotubes between the two electrodes were disconnected remaining the innermost nanotube, so that the current flows into the innermost nanotube via the internanotube junctions. The transport properties of this device clearly showed Coulomb blockade oscillation with charging energy of 15 meV at 4.2 K. The observed Coulomb blockade oscillation was non-periodic to the gate voltage, indicating that the multiple internanotube tunnel junctions were formed underneath the electrodes.

O.2 *Nanotube-Based Transistors*

Novel structure for carbon nanotube field-effect transistors (CNFETs) with a self-aligned doping profile

Yu-Ming Lin. Joerg Appenzeller, and Phaedon Avouris

IBM T. J. Watson Research Center, Yorktown Heights, NY 10598
Contact e-mail:yming@us.ibm.com

In this paper, we present a novel design for carbon nanotube field-effect transistors (CNFETs). This design allows us to obtain a p-i-p (or n-i-n) doping profile along the tube. Our CNFET structure is based on a back-gated geometry. An additional middle gate electrode is patterned between the source and drain contacts, so that the segments of the nanotube near the source/drain contacts can be doped in a self-aligned fashion. By using different dopants for the nanotube in the outer regions, p- or n-type CNFET devices can be fabricated. The potential of doped and undoped nanotube segments is independently controlled by the back gate and middle gate, respectively. Using the middle gate, we observed bulk switching behavior in CNFETs, rather than switching dominated by the Schottky barriers at the contacts, and achieved excellent performance close to theoretical limits.

High Performance Carbon Nanotube Field Effect Transistor with Polymer Electrolyte Gate

*Hwangyou Oh*1, *Jae-Ryoung Kim* [1], *Ju-Jin Kim* [1], *Namjung Cho* [2,3], *Yongku Kang* [2], *and Jeong-O Lee* [2]

[1] Department of Physics, Chonbuk National University, Jeonju 561-756, Korea
[2] Korea Research Institute of Chemical Technology, Daejeon 305-600, Korea.
[3] Department of Polymer Science & Engineering, Chungnam National University, Daejeon 305-764, Korea
Contact e-mail:lorentz73@mail.chonbuk.ac.kr

We have studied an electric gating effect of a carbon nanotube field effect transistor (FET) with polymer electrolyte gate. It has been shown that electrolyte gate can exhibit superior performance over conventional back-gated FETs, although the use of liquid in devices can cause problems in real electronic devices. Polymer solid electrolyte can be a model candidate to get over those problems as well as for superior device performance. Electrolyte solution containing 30% MIBK, 70 % Bisphenol aethoxylate diacrylate, 5 mMol $LiCFSO_4$ and 1 % DMPA was spun over pre-fabricated double-wall FET with PDMS mask. PDMS mask has been used for decrease the contact area with electrolyte in order to minimize the leakage current. After UV-curing for two minutes with 254 nm UV, we could observe well-defined polymer solid electrolyte in the center of the devices. Measured leakage current from the electrolyte was smaller than 10 pA at 1 V, and strong gate coupling has been observed. Detailed device performances will be presented.

n-type carbon nanotube FETs fabricated by using Ca/Al contact electrodes

Y. Nosho [1], *Y. Ohno* [1,2], *S. Kishimoto* [1], *T. Mizutani* [1]

[1] Dept. of Quantum Eng., Nagoya Univ., Japan
[2] PRESTO/JST, Japan
Contact e-mail:y_nosho@echo.nuee.nagoya-u.ac.jp

We have successfully fabricated n-type carbon nanotube FETs by using thin Ca layer as the contact electrodes. The nanotube FETs were fabricated on a SiO_2/Si substrate by utilizing position-controlled nanotube growth technique using alcohol CCVD. Ca/Al contact electrodes for the source and drain of FETs were formed by photolithography, electron-beam deposition, and lift-off process. In order to prevent oxidation of the Ca layer, the devices were passivated by using an organic film. n-type transfer characteristics were obtained in the fabricated devices with the Ca/Al contacts, whereas, in case of Ti or Pd electrodes, devices showed only p-type characteristics. The barrier height for electrons of the Schottky contact, which was formed at the interface between the nanotube channel and contact electrode, would be small because Ca has small work function. The present work demonstrates that conduction property of nanotube FETs can be controlled by changing a material for

Nanotube Transistors on $SrTiO_3$/Si Substrates

B. M. Kim [2], T. Brintlinger [1], E. Cobas [1] and M. S. Fuhrer [1]

[1] Department of Physics and Center for Superconductivity Research, University of Maryland, College Park, MD 20742-4111, USA
[2]Present address: Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA 19104, USA
Contact e-mail:mfuhrer@physics.umd.edu

Semiconducting SWNT field effect transistors (NT-FETs) have been fabricated on top of a high-dielectric-constant ($\kappa = 175$) $SrTiO_3$ gate dielectric film on silicon, with the conducting silicon acting as a back-gate electrode. The NT-FETs show transconductances normalized by channel width of 8900 S/m[1], greatly exceeding that in the best Si FETs. Interestingly, the high transconductance cannot be explained by increased gate capacitance alone; the gate capacitance is largely limited by the quantum capacitance of the nanotube in high-dielectric-constant NT-FETs. We propose that the high transverse electric field at the contact lowers or eliminates the Schottky barrier at finite gate voltage.

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Electrical and theoretical results from self-aligned side gates

L A W Robinson1, A.S. Teh3, M.H. Yang3, R.G. Lacerda3, K.B.K. Teo3, D. Gunlycke4, G.A.J. Amaratunga3, W.I.Milne3, D Willliams2, D G Hasko1

[1] Microelectronics Research Centre, Cavendish Laboratory, Cambridge University.
[2] Hitachi Cambridge Laboratory, Cambridge.
[3] Engineering Dept, Cambridge University.
[4]Dept. Materials, Oxford University
Contact e-mail:lawr2@cam.ac.uk

Electrical results from a recently discovered technique that allows self-aligned side gates to be placed within a few nanometers of a nanowire [1] will be presented. The motivation for working with self-aligned side gates will be discussed. The ability to control quantum dots with self-aligned side gates, together with interesting modelling results showing the effect the gates have on the electrical properties of single walled carbon nanotubes will be presented. A theoretical scheme that uses magnetic self-aligned side gates for single-electron spin detection and initialisation will also be shown.

[1] L A W Robinson et al. Nanotechnology 14 (2003) 290

A Novel Dual-Function CNT-Gated CNT Thin Film Transistors

Jeng-Hua Wei, Hsin-Hui Chen, Hung-Hsiang Wang, Ming-Jiunn Lai, Ming-Jer Kao, and Ming-Jinn Tsai

Electronics Research & Service Organization (ERSO), ITRI, Hsinchu, Taiwan, ROC
Contact e-mail:jhwei@itri.org.tw

In this paper, a novel dual-function CNT-gated carbon nanotube thin film transistor (CNTFET) is introduced. By using CNT as the gate electrode, a sub-50 nm CNTFET is successfully fabricated. Besides, the CNT-gated CNTFET still shows good FET characteristics after exchanging the gate and source/drain electrodes. This unique dual-function characteristic will provide new design rule in the future CNT electronics circuit.

A Tunable Conduction-Type Structure of Carbon Nanotube Field Effect Transistor

Hung-Hsiang Wang, Ming-Jiunn Lai, Jeng-Hua Wei, Po-Yuan Lo, Ming-Jer Kao, and Ming-Jinn Tsai

Electronics Research & Service Organization/ Industrial Technology Research Institute
Contact e-mail:pylo@itri.org.tw

In this paper, we report a tunable conduction-type structure of carbon nanotube field effect transistor (CNT-FET). In this study, a special designed top narrow gate is added in order to modulate the energy band within the middle region of one single CNT. Depending on the positive or negative bias of the gate voltage, the CNT-FET can be operated in either p-type or n-type conduction. We explain the physical mechanism of this tunable conduction-type device structure by the energy band diagram and also demonstrate the conversion of electrical characteristics from the n-type CNTEFT to p-type like behavior.

Electrostatic Mechanisms for Conductance Modulation on Metallic SWNTs

Salvador Barraza-Lopez, Slava V. Rotkin, Yan Li and Karl Hess

Beckman Institute and Department of Physics, University of Illinois at Urbana-Champaign
Contact e-mail:barrazal@uiuc.edu

Carbon nanotubes exhibit high mobilities, approaching the ballistic limit. Transverse electrostatic fields with a large gradient can be used to locally open a band gap in metallic single-wall carbon nanotubes (SWNTs). This effect modulates ballistic conductance and may have device applications. We use the Green's function formalism to obtain the electronic transmittance as a function of energy for a [5,5] SWNT of finite size. An explicit calculation of the Green's function for the open system of the finite SWNT is performed within the first-neighbor tight binding approach using an analytical expression for the electron self-energy (due to the coupling to the lead). Our analytical expression assumes semi-infinite SWNT leads.

The local opening of a band gap by inhomogeneous fields lowers the conductance. We discuss possible experimental manifestations of this effect for realistic device geometries.

Local Electric Field Effects on Double Walled Carbon Nanotube Field Effect Transistors

Jae-Ryoung Kim [1], *Hwangyou Oh* [1], *Ju-Jin Kim* [1], *Jinhee Kim* [2], *C. J. Lee* [3]

[1] Department of Physics, Chonbuk National University, Jeonju 561-756, Korea
[2] Korea Research Institute of Standards and Science, Daejeon 305-600, Korea
[3] Department of Nanotechnology, Hanyang University, Seoul133-791, Korea
Contact e-mail:jrkim@chonbuk.ac.kr

We have fabricated field effect transistors (FET) with the individual double walled carbon nanotube (DWCNT) with the local top gates. DWCNTs were synthesized by using arc discharge method and have an outer diameter of 2∼4 nm. DWNT-FET devices showed both the p-type semiconducting behavior with high on/off ratio and ambi-polar characteristics originate from the relatively large diameter of outer shell at room temperature. In order to investigate the local gating effects on the CNT channel and contacts, we fabricated the top gate electrodes with very thin gate oxides, which are located locally on top of nanotube channel and contact, respectively. By applying a voltage to each local gate independently, we have studied the channel and Shottky contact effects on the FET performance. We will also report the transport characteristics due to a transverse electric field applied perpendicular to the axis of tube.

Carbon Nanotube p-n Junction Diode

Ji Ung Lee

GE Global Research Center
Contact e-mail:leeji@research.ge.com

We demonstrate a single walled carbon nanotube p-n junction diode device. The p-n junction is formed along a single nanotube. The diode current-voltage characteristics show forward conduction and reverse blocking characteristics, i.e. rectification. The diode has a well-defined electron-hole recombination region and the characteristics show near ideal diode characteristics at low bias conditions.

O.3 *Magneto-Transport and Magnetism*

Magnetic behaviour of metallic particles encapsulated into carbon nanotubes

CS Cojocaru, C. Meny, A. Derory, S. Colis and F. Le Normand

IPCMS, UMR 7504 CNRS, Po Box 43, Bat 69, 23, rue du Loess, 67 034
STRASBOURG Cedex, France
Contact e-mail:francois.le-normand@ipcms.u-strasbg.fr

The next generation of materials for magnetic recording media will require i) the design of regular arrays of ferromagnetic nanoparticles with well controlled morphology and behaviour and ii) to physically separate these particles, either by vacuum or by a nonmagnetic material to fully discriminate the bits of information. Other requirements are the chemical stability, the obtention of a definite direction for magnetization, the mecanical stiffness. . . The growth of carbon nanotubes by a catalytic CVD process requires the presence of nanoscaled transition metals particles (Fe, Co, Ni), which are ferromagnetic. These particles are encapsulated after growth on the top of the nanotubes. Moreover in appropriate deposition conditions they took a very anisotropic shape, and the particle fullfills the nanotube which is a nonmagnetic material. Various other carbon nanostructures can be grown (nanocones, carbon nanofibers, . . .) depending on the experimental CVD and the metallic dispersion parameters. The magnetic properties of these arrays of Co nanoparticles encapsulated into carbon were investigated by SQUID and MFM. Different magnetic behaviour were evidenced - Superparamagnetic behaviour for small particles (5 - 8 nm) encapsulated into non oriented nanotubes - Strong magnetic anisotropy in the plan of the substrate for nanoparticles ($\sim$30 nm) encapsulated at the top of nanocones, due to an exchange coupling between a metallic core and a thin antiferromagnetic CoO external layer. - Strong magnetic anisotropy perpendicular to the plan of the substrate of metallic nanowires (diameter$\sim$25 nm and aspect ratio from 1/4 to 1/10), induced by the cork-like shape of the nanoparticles. In this case the coercitive field (750 Oe), the magnetic anisotropy combined with high density (1010particles/cm2) and the weak dipolar interactions evidenced by MFM are very attractive for dense storage media.

Magnetic properties of hydrogen and helium on graphene and carbon nanotubes

P. O. Lehtinen [1], Yuchen Ma [1], A. S. Foster [1], A. Krasheninnikov [2] and R. M. Nieminen [1].

[1] Laboratory of Physics, Helsinki University of Technology, P.O.Box 1100, Helsinki 02015, Finland;
[2] Accelerator Laboratory, University of Helsinki, P.O.Box 43, Helsinki 00014, Finland
Contact e-mail:pol@fyslab.hut.fi

It is well know that irradiation of graphite and carbon nanostructures results in the production of defects, especially vacancies and adatoms on the surface. Theoretical calculations show that these defects are magnetic [1], but the high adatom mobility suggests that recombinationand clustering is likely to significantly reduce the effect at room temperature. Recent experimental results [2] indicate that proton bombardment of graphite results in a strong residual magnetic signal, but He ion bombardment has a much smaller effect. To attempt to understand this, we have performed spin-polarized density functional theory calculations of the properties of H and He adsorbed on an ideal and defected graphene sheet.

We find that helium is very weakly interacting with surface, and although magnetic when adsorbed at a vacancy, this is a very energetically unfavourable site. For hydrogen, we find that it will adsorb strongly at the vacancy site, resulting in a magnetic moment double that of the naked vacancy - combined with its high mobility and recombination energy on graphite, hydrogen at a vacancy represents a strong candidate for explaining the experimental results. Further, we consider the properties of H adsorbed at vacancy sites on single-walled carbon nanotubes, and discuss how the magnetic properties depend on the tube physical and electronic structure.

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Contact-induced spin polarization in carbon nanotubes

M. S. Ferreira and S. Sanvito

Physics Department, Trintiy College Dublin, Ireland
Contact e-mail:ferreirm@tcd.ie

Motivated by the possibility of combining spintronics with molecular structures, we investigate the conditions for the appearence of spin polarization in low-dimensional tubular systems by contacting them to a magnetic substrate. We derive a set of general expressions describing the charge transfer between the tube and the substrate and the relative energy costs. Using a tight-binding model for the electronic structure we are able to estimate the magnitude and stability of the induced moment. This indicates that sizeable magnetic moments can be induced in carbon nanotubes.

Magneto-transport in small diameter carbon nanotubes : Novel features under 60T.

B. Raquet [1], *B. Lassagne* [1], *G. Fedorov* [1], *M. Sagnes* [1], *J-M Broto* [1], *F. Triozon* [2], *S. Roche* [2]

[1]Laboratoire National des Champs Magnetiques Pulsés, UMR 5147, 143 av. de rangueil, 31342 Toulouse, France
[2]Commissariat a l'Energie Atomique, DSM/DRFMC/SPSMS and DRT/LETI/DIHS/LMNO, 17 rue des Martyrs, 38054 Grenoble, Cedex 9 France.
Contact e-mail:raquet@insa-tlse.fr

Theoretical studies on electronic transport properties of carbon nanotube (CN) demonstrate that small diameter CN behave like unconventional mesoscopic system [1,2]. For instance, in the quasi-ballistic regime, weak localization (WL) due to backscattering along the circumference of the tube, flux-dependent density of states (DOS) oscillations and Fermi level location interplay the magneto-transport in a very unusual manner [1].
Here, we present transport and magneto-transport experiments on double wall carbone nanotubes (DWNT), using the 62T pulsed magnetic field LNCMP facilities. Resistivity versus temperature and differential conductivity experiments give evidences for electronic transport through an interacting disorder metal. Our high magnetic field measurements are mainly focused on the high kinetic energy regime, eV>kT, involving massive and massless subbands. In the high temperature regime, large positive magneto-conductance which reaches saturation around 60T gives evidence for quasi-2D WL in DWNT. At low temperature, both geometrical field configuration and gate voltages drastically change the magnitude and the sign of magneto-resistance. This unconventional magneto-resistance behavior is ascribed to the magnetic field effect on the CN band structure, which is probed by tuning the location of the Fermi level. We bring experimental evidence of van Hove singularities displacement under the high magnetic field regime and its interplay with the magneto-transport.

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Magneto transport of diluted magnetic semiconductor GaMnN nano wire

K.I.Lee1,3, J.Y. Chang1, H.J. Choi2, H.K. Seong2, W.Y. Lee3*

1.Nano Device Research Center, Future Technology Research Divisions, Korea
Institute of Science and Technology, Seoul 136-791
Contact e-mail:presto@kist.re.kr

In recent years, ferromagnetic semiconductors have been of great interests due to potential applications in spintronics, in which simultaneously manipulating both charge and spin in a semiconductor leads to fundamentally novel functionality with respect to semiconductor device physics. Both theoretical and experimental studies indicate that Mn doped GaN shows high Curie temperature exceeding room temperature, which would be advantageous for device applications. Nanotubes and nanowires are currently being extensively studied as a possible miniaturization for electronic devices of sub 100 nm or smaller. The fundamental understanding of magneto transport in low dimensional ferromagnetic semiconductor is crucial to the development of nano wire based spintronic devices. We have studied ferromagnetism and magneto transport features of GaMnN nano wire found Curie temperature above room temperature amn negative magnetoresistacne (MR) of 1.3% and 0.3% at 4K and 300K respectively in 9T.

Production and Characterization of Ferromagnetic Alloyed-Nanowires inside Carbon Nanotubes

A. L. Elías, J. A. Rodríguez Manzo, A. Zamudio, S. Baltazar-Rojas, F. López-Urías, E. Muñoz-Sandoval, H. Terrones, M. Terrones, M. McCartney, D. J. Smith, D. Golberg, C. H. Tang, Y. Bando

Advanced Materials Department, IPICyT;
Department of Physics and Astronomy and Center for Solid State Science, ASU;
International Center for Young Scientists, National Institute for Materials Science.
Contact e-mail: alaura@ipicyt.edu.mx

We describe the production of aligned multi-walled carbon nanotubes filled with Fe-Co alloys. The method involves the aerosol thermolysis of toluene-ferrocene-cobaltocene solutions at temperatures ranging from 650 to 800°C in an inert atmosphere. The materials have been carefully characterized using state-of-the-art high-resolution transmission electron microscopy (HRTEM), energy electron loss spectroscopy (EELS), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), electron diffraction, HREELS-STM elemental mapping, X-ray powder diffraction and SQUID magnetometry. The results indicate that different stoichiometries of $\mathrm{Fe}_x\mathrm{Co}_z$ alloys could be produced at different temperatures. We noted that the formation of FeCo alloys only occurs at relatively low pyrolytic temperatures (e.g. 650 - 750 °C). Above this temperature, segregation of Co and Fe domains start to occur. The alloy nanowires (5-30 nm OD; 1 micron long) are monocrystalline and always exhibit the FeCo (110) parallel to the carbon nanotube axis. The $\mathrm{Fe}_x\mathrm{Co}_z$ nanomaterial has shown unusual ferromagnetism and large coercive fields at room temperature (e.g. 1500 Oe). We envisage that these aligned ferromagnetic nanowires could be used in the fabrication of high-density magnetic storage devices.

The role of magnetic fields on the electronic and transport properties of metallic carbon nanotube quantum dots

C. G. Rocha [1], *A. Latgé* [1], *P. Venezuela* [1], *and L. Chico* [2]

[1]Instituto de Fisica, Universidade Federal Fluminense, Av. Litoranea sn, 24210-340
Niteroi- Rio de Janeiro Brazil
[2]Departamento de Fisica Aplicada, Faculdad de Ciencias del Medio Ambiente,
Universidad de Castillo-La Mancha, 45071 Toledo Spain.
Contact e-mail:latge@if.uff.br

Based carbon-tube quantum dots are shown to exhibit discrete and interface states[1] that may be modulated by changing the dot size. Moreover, metallic quantum dots studied recently [2] and composed of achiral carbon nanotubes, provided conductance gaps and localized electronic states. Interesting physical phenomena such as metal-insulator transition, may also be manipulated by just switching external fields. Here we study the particular metallic dots reported in reference [2] named as (12,0)/(6,6)N/(12,0), N being the number of rings forming the central nanometric dot. The modeled junctions present intercalated pairs of pentagon and heptagon, disposed along the circumferential tube direction and allows the connection of the dot with the metallic contacts (leads). A detailed investigation of the mechanical stability of the dot formation is addressed by using a Monte Carlo simulation and considering an interatomic potential propose by Tersof. The temperature dependence of the total atomic energy and the formation energy of the carbon structure is calculated. The results show unambiguously that the studied dots are stable structures, composed solely by metallic tubes. Local density of states are obtained via a single-band tight binding Hamiltonian and a superposition of discrete and continuum states are found in the region of the Fermi level. The conductance is calculated within the Landauer formalism The effects of an external magnetic field, applied along the axial direction of the dot, are studied. The vector potential associated with the magnetic field is described within the Peierls approximation. By investigating the local density of states and the system conductance behavior, one finds that metal-insulating-like transitions are induced by turning on the magnetic field. The dependence of the energy spectra on the size of the quantum dot and on the intensity of the magnetic field is reported illustrating new possibilities to induce physical properties of the studied metallic dots. The shifting of the single-electron levels and the electronic transitions are also analyzed taking into account the spin-magnetic field interaction. An important result is the fact that the associated Aharanov-Bohm oscillation periods of the new dot-carbon-tube structures strongly change when including Zeeman effects in the theoretical description.

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Dynamics of Chiral Carbon Nanotubes in Magnetic Fields: Magnetochirodynamic Effects

V. Krstic [1], *G. Wagnière* [2], *G.L.J.A. Rikken* [3]

[1]Grenoble High Magnetic Field Laboratory, Max-Planck-Institut für Festkörperforschung/CNRS, 25, Ave. des Martyrs, F-38042 Grenoble, France.
[2]Institute of Physical Chemistry, University of Zürich, Zürich, Switzerland.
[3] Laboratoire Nationale des Champs Magnétiques Pulsés, CNRS/INSA/UPS, B.P. 4245, F-31432 Toulouse, France.
Contact e-mail:krstic@grenoble.cnrs.fr

Depending on their helicity carbon nanotubes can be classed in three forms named zigzag, armchair and chiral. The first two forms are achiral, whereas the so-called chiral nanotubes are real chiral molecular structures. Due to their chiral character, the mechanical dynamics of chiral nanotubes in a magnetic field are not equivalent to the behaviour of zigzag and armchair nanotubes under the same conditions. By fundamental symmetry considerations it can be shown that the movement of the chiral nanotubes depends on both, the relative orientation and magnitude, of the nanotube's linear momentum and the externally applied magnetic field. The magnitude of these effects is estimated by the application of the model of a free electron on a helix which is quantum-mechanically solved. An analytical solution of this model is possible and the results will be quantitatively evaluated for chiral carbon nanotubes. The experimental conditions for an observation of these effects will be discussed based on the theoretical predictions.

Exchange coupling between magnetic impurities in carbon nanotubes

A. T. Costa Jr. and M. S. Ferreira

Departamento de Ciencias Exatas, Universidade Federal de Lavras, MG, Brazil and
Physics Department, Trinity College Dublin, Ireland
Contact e-mail:ferreirm@tcd.ie

We calculate the coupling between two magnetic impurities adsorbed to non-chiral nanotubes. We show that the exchange coupling mediated by metallic nanotubes is oscillatory and long-ranged, decaying as 1/r, where r is the distance between impurities. For semiconducting tubes the coupling decays exponentially with r at zero temperature. When impurities are close enough to each other, such that a direct hopping between them is possible, the system presents bi-stability, meaning that both ferro and antiferro alignment of the impurities' spins are locally stable, separated by a large energy barerier. We comment briefly on consequences of our findings for spin-dependent electronic transport through nanotubes, and potential applications of bi-stability.

Electronic Propagating Waves in Carbon Nanotubes for the Electrodes of the Spin Wave Device

Toshihito UMEGAKI, Matsuto OGAWA, Yasuyuki MAKINO, and Tanroku MIYOSHI

Graduate School of Science and Technology, Kobe University
Contact e-mail:umegaki@lerl.eedept.kobe-u.ac.jp

We have proposed a novel ferrite device which will work as a high-frequency filter in THz domain [1]. In this device, the high-frequency current flowing on the carbon nanotubes (CNTs) may excite and receive directly spin waves in the ferrite film beneath them. The wavelength is as small as a few tens nanometers, since the diameter of the CNT matches it to excite the spin waves. One of the main issues of applying CNTs to this device is improving the conductivity. We have analyzed the electronic propagating waves in the CNTs to study the current density distributions around the circumference of the CNTs and the current-voltage characteristics based upon the transfer matrix (TM) method. The conductivity of the CNTs in this device may be improved since the numbers of the multi-modes which contribute to the conductivity can be controlled by the position of the Fermi level in the CNTs. The conductivity may be also improved by excitation schemes of the electronic waves.

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Magnetic Properties of Carbon Nanostructures: The role of negative and positive curvature

Rodríguez-Manzo, J.A., López-Urías, F., Terrones, M., Terrones, H.

Advanced Materials Department, IPICYT, Camino a la Presa San José 2055, Lomas 4a, 78216 San Luis Potosí, México
Contact e-mail: hterrones@ipicyt.edu.mx

A Pi-orbital nearest-neighbor tight-binding Hamiltonian in conjunction with the London approximation is used to study uniform external magnetic field effects on different graphitic nanostructures with negative and positive Gaussian curvature. Ring currents and the induced magnetic moment are calculated on coalesced C60 structures (peapod-like corrugated nanotubes) and Haeckelite-tubules (structures containing heptagons, hexagons and pentagons of carbon). It is found that coalesced C60 fullerenes connected along the five-fold symmetry axes and Haeckelites tubes are metallic and exhibit large magnetic moments. These results have important implications in the magnetic properties of corrugated carbon nanotubes (coalesced peapods). The magnetism observed experimentally in rombohedral C60 is also discussed in the context of ring currents generated by the sp2 polymerization of C60. Finally, the possiblity of witnessing magnetism in interconnected graphene layers is also studied.

Ferromagnetism in the graphitic fragment

Noejung Park

Samsung Advanced Institute of Technology
Contact e-mail:noejung.park@samsung.com

We carried out the first-principles density functional calculations to investigate electronic and magnetic structures of the graphitic fragments. Ferromagnetically ordered ground state is found to be stable in the isolated graphenes with zigzag edge terminated with hydrogens or dangling bonds. However, the spins localized in the hydrogen-terminated edge do not survive in the stacked graphite fragments. Interlayer and inter-edge interactions are investigated in detainl,and we find that the spins originated from the dangling bonds favor the ferromagnetic ordering over the stacked graphitic fragments.Revealed results in this work is thought to explain the recently observed magnetism in the proton-irradiated graphite.

P Invited Session (Saturday Morning)

Controlling Electronic Structure of Nanotubes

Electronic Structure Control of Single Walled Carbon Nanotube Functionalization

Michael S. Strano

University of Illinois at Urbana/Champaign
Contact e-mail:strano@uiuc.edu

The ability to selectively attach chemical groups to nanotubes based on their electronic structure has wide ranging applications: from controlling FET properties to fabricating novel optical biosensors. We review successful covalent and non-covalent approaches. Diazonium reagents functionalize single-walled carbon nanotubes suspended in aqueous solution with high selectivity and enable manipulation according to electronic structure. For example, metallic species are shown to react to the near exclusion of semiconducting nanotubes under controlled conditions. Selectivity is dictated by the availability of electrons near the Fermi level to stabilize a charge-transfer transition state preceding bond formation. The chemistry can be reversed by using a thermal treatment that restores the pristine electronic structure of the nanotube. Applications are discussed, including recent results from our lab using this chemistry to control semiconductor properties and separate nanotube by electronic type. We also use these chemical methods to fabricate a new class of tissue implantable, near infrared optical biosensors based upon single walled carbon nanotubes.

Quantum Conductance of Nanojunctions under Finite Bias and Field Emission of Double-Wall Carbon Nanotubes

Jisoon Ihm

School of Physics, Seoul National University, Seoul 151-747, Korea
Contact e-mail:nsjisoon@phya.snu.ac.kr

We have developed a first-principles pseudopotential method to calculate the quantum conductance of nanostructures under finite bias. The present method allows us to calculate the self-consistent potential nad wavefunctions across a nano-sized junction for a given chemical potential difference. To test the present algorithm, the conductance of a few nanostructures with various contact geometries has been calculated. We have also performed first-principles pseudopotential calculations for the field emission from carbon nanotubes by solving the time-dependent Schroedinger equations under high applied voltage. Both capped and open-ended geometries are considered. Carbon atoms bridging two walls are assumed to exist in the open-ended double-wall tubes. The outer wall screens the external field very effectively in general. Double-wall nanotubes with at least one metallic wall are shown to produce more stable emission current than single-wall nanotubes. Implications to the performance of the actual field emission display developed in the industry are discussed.

Carbon nanotube transistors and electroluminescence in 1D

R. Martel, J. Misewich$^{\#}$, J.C. Tsang and Ph. Avouris*

IBM T. J. Watson Research Center, Kitchewan Road, Yorktown Heights, NY 10598
Materials Science Department, Brookhaven National Lab, Upton NY 11973
Université de Montréal, C.P. 6128 Succursale Centre-Ville, Montréal, H3C-3J7 Canada
IBM T. J. Watson Research Center, Kitchewan Road, Yorktown Heights, NY 10598
Contact e-mail:r.martel@umontreal.ca

We will present a short review of the recent advances in nanotube electronics and focus the discussion on the general properties of the metal-nanotube contacts. In particular, we will describe the operation of ambipolar nanotube transistors, in which the current originates from either electrons or holes depending on the gate field. The metal-nanotube Schottky contact enables efficient charge injection, and this is true even in the presence of a significant contact barrier. For specific operating voltages, bipolar conduction and weak electroluminescence is observed. The optical emission originates for a band gap recombination process of carriers in the nanotube. The emitted light is in the near IR and is linearly polarized along the nanotube axis. The emission wavelength depends on the nanotube diameter and its intensity peaks at Vd=2 Vg. To our knowledge, this nanotube device represents the smallest electrically pumped optical emission source. This work opens up new possibilities for studying fundamental carrier interaction in 1D.

Q Contributed Session (Saturday Morning)

Oral **Poster++ *Presentation***

Single atom C-chain formation in SWCNT breaking experiments

R.Caudillo (1), M.A.L. Marques(2), H.E.Troiani(3), M.Miki Yoshida(4), A. Rubio (5), and M. José Yacamán(6)

(1)Texas Materials Institute, UT-Austin;
(2)Institut fur Theoretische Physik, Freie Universitat Berlin;
(3)Centro Atómico Bariloche, Argentina;
(4) Centro de Investigacion en Materiales Avanzados, Chihuahua, México;
(5)Dpto. de Física de Materiales, Universidad del Pais Vasco, San Sebastain, Spain;
Contact e-mail:yacaman@che.utexas.edu

We previously reported a method for forming SWCNTs in situ in the TEM by strongly condensing the beam on an amorphous carbon film and creating two through-holes. A thin graphitic fiber forms in between the two holes and is subsequently narrowed until forming a SWCNT by the application of a tensile stress. The fracture mechanism involves a size reduction in gradual steps from graphitic fiber to MWCNT until the SWCNT is formed with a diameter of ∼1nm. This SWCNT continues to thin until the minimum achievable size of ∼0.35 nm. In many cases, we observe a further size reduction corresponding to the formation of a single chain of carbon atoms. We previously reported experimentally observed carbon chain lifetimes of up to 20 seconds and confirmed our observations with molecular dynamics simulations indicating cumulene-type bonding in the carbon chain. In this work, we report a method to control and increase chain lifetimes up to 5-10 minutes by adjusting current density in the microscope. This provides a unique opportunity to experimentally study the structure and behaviour of chains of carbon atoms. It also opens up the possibility of performing quantized conductivity experiments on the carbon chain. We also report that after the breaking of the nanotube/C-chain, a number of disturbances in the structure of the graphite grow and eventually lead to a full reconstruction of the amorphous carbon film. This effect will be described in this work and might be used in future applications, such as self-repairing membranes.

chafa

Author Index

Aditional Information

ACCOMPANYING PERSONS SPECIAL PROGRAM

SUNDAY 18	MONDAY 19	TUESDAY 20	WEDNESDAY 21	THURSDAY 22	FRIDAY 23	SATURDAY 24
	REAL DE CATORCE	**SANTA MARIA DEL RIO**		**GUANAJUATO**	**TAMASOPO**	
	An old mining ghost town.	**Trip to two Haciendas and a famous town for Silk scarfs**		**Trip to the most beautiful Colonial City in Mexico**	**Trip to the fascinating Water Falls**	
	$35 USD**	**$25 USD****		**$35 USD****	**$35 USD****	
	INCLUDES	**INCLUDES**		**INCLUDES**	**INCLUDES**	
	* Round trip in a first class bus	* Round trip in a first class bus		* Round trip in a first class bus	* Round trip in a first class bus	
	* English speaking guide	* English speaking guide		* English speaking guide	* English speaking guide	
	* Traveler Insurance	* Traveler Insurance		* Traveler Insurance	* Traveler Insurance	
	* Refreshments	* Refreshments		* Refreshments	* Refreshments	
	* Breakfast in Matehuala	* Entrance to Haciendas Jesus Maria and La Ventilla		* Entrance to two museums	* Entrance to Tamasopo Water Falls and Puente de Dios	
					* Breakfast in Rio Verde	
						

* PLEASE NOTE THAT THESE COSTS ARE NOT INCLUDED IN THE ACCOMPANYING PERSON'S FEE.

* EACH TOUR HAS A LIMITED NUMBER OF PEOPLE.

* DEPENDING ON NUMBER OF PEOPLE, THE TRIP WILL BE IN A VAN

VENUE AND HOTELS

REAL DE MINAS

VENUE HOTEL
Carr. Central (México) km.426.6, Zona Hotelera
San Luis Potosí, S.L.P. 78090, México

Phone: 52 444 **818 2676**

SANDS HOTEL

NEXT TO VENUE HOTEL
Carr. Central (México) Zona Hotelera
San Luis Potosí, S.L.P. 78090, México

Phone: 52 444 **818 2413**

COUNTRY INN

5 km TO THE VENUE HOTEL
Carr Central, San Luis Potosi , Mexico 78399

Phone: 52 444 **826 99 00**

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EMERGENCIES
Phone: 066

STATE POLICE
Phone: 812 1037

FEDERAL HIGHWAY POLICE
Phone: 824 0891

RED CROSS
Phone: 815 3635
820 3902

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ABC EMERGENCIES
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Phone: 815 3583

ANGELES VERDES HIGHWAY ASSISTANCE
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International Conference on the
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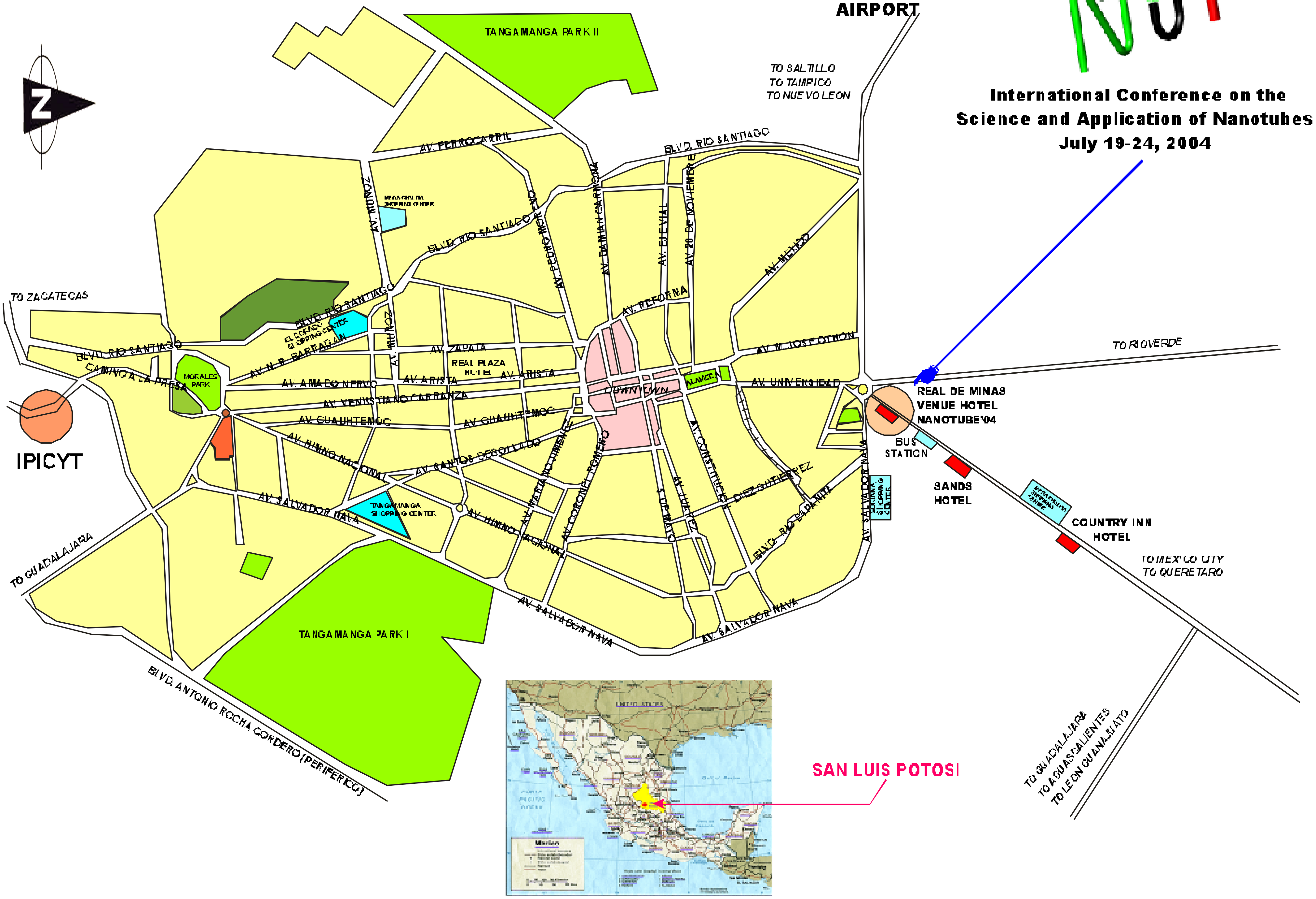
July 19-24, 2004



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