## XXIst International Winterschool



# MOLECULAR NANOSTRUCTURES

10.3.-17.3.2007

Hotel Sonnalp | Kirchberg | Tirol | Austria

IWEPNM 2007

## PROGRAM



## **20 YEARS**

## IWEPNM @ HOTEL SONNALP

Thank you for 20 years hosting the molecular nanostructures community

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The financial assistance from the sponsors and from the supporters is greatly acknowledged.

Prof. Dr. H. Kuzmany FAKULTÄT FÜR PHYSIK DER UNIVERSITÄT WIEN A-1090 Wien, Strudlhofgasse 4

Tel. ++43-1-4277-51306

Kirchberg, 10. 3. 2007

Ref.: International Winterschool on:

"Electronic Properties of Novel Materials: molecular nanostructures" IWEPNM 2007, Kirchberg/Tirol, Austria

Dear Friend:

Welcome to the 21st International Winteschool on:

Electronic Properties of Novel Materials: "Molecular nanostructures"

This Winterschool is a sequel of twenty previous meetings held in Kirchberg in the last years on problems related to the electronic structure of novel materials. The idea of the meeting is to bring together experienced scientists from universities and industry with advanced students working in the selected field and thus create a fruitful and prosperous community for the exchange of scientific information and personal experience. It is a tradition of the Winterschools in Kirchberg that this exchange is not restricted to the lectures and poster sessions but occurs throughout the whole week.

The Winterschool is dedicated to molecular nanostructures as a new class of materials. Like the previous winterschools it is supposed to run on an informal level.

This years IWEPNM is again an anniversary as for the 20<sup>th</sup> time the event takes place in the Hotel Sonnalp. On occasion of this anniversary there will be a small celebration on Tuesday night with a Welcome presented by the owner of the Hotel, Dr. Taus, and a guest ski race on Thursday afternoon. All participants including accompanying persons are invited to participate at these two events.

If you have any questions concerning the organization and the program, come and see one of us or one of the colleagues involved in the preparation of the meeting. These persons are:

Wolfgang Plank (general assistance, program Viktor Siegle (video side room) receipts, poster)

Rudolf Pfeiffer, (technical assistance, Hagen Telg (presentations, Matthias Müller video transfer, poster) microphone)

Christoph Schaman (commercials, computer, poster) Björn Corzilius (presentations, microphone)

We want, at this point, acknowledge their help for the organization of the IWEPNM 2007. Also, the manager of the Hotel, Frau Mayer, and her staff promised to help us wherever they can.

Thus, we wish you an interesting, successful, and pleasant week in Kirchberg. We are also very much looking forward to your contributions at the event.

Sincerely yours,

Hans, Peter, Siegmar, Christian

PS: If you want to buy a ticket for the ski lifts in the Kirchberg/Kitzbühel area, ask at the Hotel reception on Saturday evening.

PPS: Internet connection through WLAN is available for all participants, even if they are not accommondated at the Hotel Sonnalp. Please check at the front desk.

# INTERNATIONAL WINTERSCHOOL on ELECTRONIC PROPERTIES of NOVEL MATERIALS

#### MOLECULAR NANOSTRUCTURES

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C. Thomsen (D)
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#### SCOPE

This winterschool will provide a platform for reviewing and discussing new developments in the field of electronic properties of molecular nanostructures and their applications. Subjects included are: • Carbon nanotubes growth and selection • Carbon nanotube optics and electronics • Carbon nanotube spectroscopy • Material science of graphene • Molecular nanostructure transport and spintronics • Theory of molecular nanostructures

- Applications of molecular nanostructures Molecular machines and molecular motors
- Template grown molecular nanomaterials Single molecule experiments

#### INFORMATION FOR PARTICIPANTS

#### Time and location

The IWEPNM 2007 starts on Saturday, March 10, evening at the HOTEL SONNALP in Kirchberg / Tirol, Austria and extends to Saturday, March 17, breakfast. There will be a reception party on March 10, after dinner and a farewell party including dinner on Friday, March 16.

#### Transport

The hotel Sonnalp can be reached by privat car from downtown Kirchberg by driving about one kilometer towards Aschau. Participiants arriving at the railway station in Kirchberg or Kitzbühel should hire a taxi to get to the hotel.

#### Addresses

The address of the winterschool is:

IWEPNM 2007, Hotel Sonnalp, A-6365 Kirchberg/Tirol, Austria

Tel: ++43 5357 27410, Fax: ++43 5357 2741 200

e-mail: info@hotelsonnalp.info, Web: www.tiscover.at/sonnalp.parkhotel However, all questions concerning the the IWEPNM 2007 should be directed to:

Prof. H. Kuzmany, Fakultät für Physik, Universität Wien

Strudlhofgasse 4 A-1090 Wien, Austria

Tel: ++43 1 4277 51306, Fax: ++43 1 4277 51375

email: hans.kuzmany@univie.ac.at

WWW: http://www.univie.ac.at/spectroscopy/iwep.htm

#### Participation

Participation at the IWEPNM 2007 is possible for students and scientists working in the field covered by the scope of the meeting. Because of the limited space the participation requires prearranged acceptance by the organizers.

#### Contributions

All oral contributions will be presented in the big seminar room of the Hotel Sonnalp. Participants are invited to contribute comments to research and tutorial lectures where 10 minutes for discussion are reserved at each lecture. Overhead projections and presentations using data video projection will be possible. Presentation of video films needs prearranged confirmation. Posters will be presented in the hall of the seminar room.

#### **Proceedings**

The contributions to the IWEPNM 2007 will be published by physica status solidi. The expected date for the appearance of the proceedings is September 2007.

Guidelines for the preparation of the manuscripts can be picked from the web site of the IWEP. A hardcopy is attached to this program booklet. Manuscripts must be submitted by e-mail to Sigmar Roth at iwep@fkf.mpg.de.

They can only be published if they arrive before April 30, 2007. The manuscripts will be reviewed within the following weeks. Acceptance of a contribution for presentation at the winterschool does not automatically include acceptance for publication in the proceedings.

#### IWEPNM 2007 CHAIRPERSONS FOR THE ORAL SESSIONS

The following participants are asked to support the program of the winterschool by serving as chairperson.

Sun., 11.03.	morning morning, after coffee break evening	QISR QISR O&S	Briggs Forró Kataura
Mon., 12.03.	morning morning, after coffee break evening	FCNT FCNT RAS	Kalbac Kavan Krause
Tue., 13.03.	morning morning, after coffee break evening	NAWI NAWI APL	Bakkers W. Weber Kuznetsov
Wed., 14.03.	morning morning, after coffee break evening	G&G1 G&G1 G&G2	Ferrari Kürti Mauri.
Thu., 15.03.	morning morning, after coffee break evening	NTG NTG NCN	Galiotis Obraztsova Monthioux
Fri., 16.03.	morning morning, after coffee break evening	TRP TRP MNM	Bockrath Chen Klingeler

Chairpersons are asked to start the sessions in time and to terminate the lectures according to schedule. The discussions may be extended up to 5 minutes beyond the schedule.

Chairpersons please remember: YOU HAVE TO ASK FOR QUESTIONS FROM THE SIDEROOM (BAR)!

Chairpersons please remember: FOR QUESTIONS FROM THE MAIN ROOM PLEASE ASK THE SPEAKER TO REPEAT THE QUESTION. THE CHAIR-PERSON'S MICROPHON SHOULD ONLY BE PASSED ON TO QUESTIONS FROM THE FIRST ROW.

If there are any objections to the suggested list of chairpersons, please let us know at the beginning of the winterschool.

We acknowledge your support.

The Organizers

IWEPNM2007 - Final program

			IWEPNM2007	- Final	program			
Final program schedule: morning								
Sess. Day	08:30	09:00	09:30	Break	10:30	11:00	11:30	
Sat. 10.3.								
Sun. 11.3 QISR	Principles of quantum computing		Manipulation of quantum information in N@C60	×	Progress in N@C60 quantum computing	Magnetic resonance in carbon nanotubes	Probing the EP of bulk samples SWNT by resonant and non- resonant microwave abs.	
	MEHRING, DE		ARDAVAN, UK	< <	HARNEIT, DE	SIMON, HU	CORZILIUS, DE	
Mon 12.3.	Tailoring electronic structures of carbon	Electrochemically functionalized carbon	Carbon nanotubes in liquid crystals as		Chemical doping effect on double walled carbon	Thermal and electromechanical studies	Separation techniques for single-walled carbon	
FCNT	nanotubes	nanotubes	versatile, functional materials	Ш	nanotubes	of nanotubes	nanotubes	
	LEE, KR	BURGHARD, DE	SCALIA, DE	Œ	ENDO, JP	ZETTL, US	HENNRICH, DE	
Tue 13.3. NAWI	Growth, properties and applications of semiconductor nanowires		Silicon nanowire transistorswith axially intruded nickel silicide contacts	В	Molecularly and atomically thin semiconductor and carbon nanoshells	VLS nanowire growth dynamics	Role of materials in emerging nanoelectronic devices	
	SAMUELSON, SE		W. WEBER, DE		PRINZ, RU	BAKKERS, NL	PATTERSON, IR	
Wed 14.3. G&G1	QED in a pencil trace		Asymmetry gap in the electronic band structure of bilayer graphene	ш	The spectral function of monolayer graphene films	Transport Measurements in Graphene	Bipolar Supercurrent in Graphene	
	NOVOSELOV, UK		McCANN, UK	Ш	ROTENBERG, US	JARILLO-HERRERO, US	MODBURGO NI	
Thu	In-situ observations of	Title to be announced	In situ time-resolved	ш	Growth mechanisms of	Filling up metallic valley	Structural and electronic	
15.3. NTG	catalyst dynamics during surface-bound carbon nanotube nucleation		measurements of carbon nanotube and nanohorn growth	ш	innershell tubes in double- walled carbon nanotubes	on photoluminescence map by organic Molecules encapsulated in SWNT	properties of vacancies in nanotubes	
	HOFMANN, US	IIJIMA, JP	GEOHEGAN, US		PFEIFFER, AT	KATAURA, JP	CALAME, NL	
Fri 16.3. TRP	Carbon nanotube field- effect transistors as tunneling devices	Graphene ribbon electronics	Aharonov-Bohm conductance modulation in ballistic carbon nanotubes	о О	Changes in electronic transport in CNT networks with thickness and chemical treatment	Coupling electronic transport to vibrational modes in suspended nanotube resonators	Carbon nanotube superconducting quantum interference device	
	APPENZELLER, US	CHEN, US	RAQUET, FR		KAISER, NS	VD ZANT, NL	CLEUZIOU, FR	
Sat. 17.3.	Departure							

12:00	17:00	18:30		19:00	19:30	20:00	20:30	Sess. Day
	'						Reception Party 21:00	Sat 10.3.
S	Œ	Optical spectroscopy of Individual single-walle carbon nanotubes		Excitons in carbon nanotubes: insights from model calculations	Growth and optical properties of small-bundled vertically aligned single- walled carbon nanotubes	Electron-phonon interaction in low-dimensional solids probed with time-resolved spectroscopy		Sun. 11.3. O&
Δ.	ш			CAPAZ, BR	MARUYAMA, JP	WOLF, DE		
О Т		Fano lineshape in the h energy modes of metall carbon nanotubes		Theoretical Raman intensi of the RBM of SWCNTs	Raman spectroscopy of well-identified single- walled carbon nanotubes	Raman studies of exciton- phonon coupling in SWNT: quantitation of bundled vs. isolated behavior	The importance of excitons for the intensity of the RBM and the disorder induced band in SWNT	Mon 12.3. RA
S		MAULTZSCH, US		POPOV, BG	SAUVAJOL, FR	DOORN, US	JORIO, BR	
О Д Ж	Z	Carbon for printed electronics		From Electrical to Fuel Powered Artificial Muscle	Industrial production of multiwalled carbon nanotubes	Welcome Hotel Sonnalp Taus, A	Poster reading Special Poster (SP)	Tue 13.3. AP
> - z z	z	GRUNER, US  Raman spectroscopy of pristine and doped graphene		BAUGHMAN, US	VOETZ, DE			
				Non-adiabatic Kohn- anomaly in a doped graphene monolayer	Low energy electronic structure of graphite by angle resolved photoemission spectroscopy	resolved Poster	r I (PTU)	Wed 14.3. G&G
_	-	FERRARI. UK		LAZZERI. FR	GRUENEIS. DE			
Σ	۵	LOISEAU. FR		Optical properties of graphite, h-BN and nanotubes: coherent excitations	Equilibrium and non- equilibrium optical properties of MoSI nanowires	Poster II (PTH)		Thu 15.3. NCN
				RUBIO-SECADES, ES	GADERMAIER, SI			
	Charge transport across single-molecule junctions			tubes by bio-directed	DNA-carbon nanotube interactions and nanostructuring based on DNA	Summary	Bauernbuffet, fare well	Fri 16.3. MN
	H. WI	H. WEBER, DE FIL		ORAMO	RICHERT	PICHLER		
		,			-	-		Sat 17.3

## **PROGRAM**

## AND

ABSTRACTS



NANOCYL S.A. IS A LEADER IN DEVELOPING AND MANUFACTURING CARBON NANOTUBES AND THEIR APPLICATIONS

## NANOCYL

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- > Cooperative Development of products

#### Quantum Information, Spin Resonance

8:30 – 9:30 M. MEHRING, DE

Principles of quantum computing

9:30 - 10:00 A. ARDAVAN, UK

Manipulation of quantum information in  $N@C_{60}$ 

10:00-10:30 Coffee break

10:30 - 11:00 W. HARNEIT, DE

Progress in  $N@C_{60}$  quantum computing

11:00 - 11:30 F. SIMON, HU

Magnetic resonance in carbon nanotubes

11:30 – 12:00 B. CORZILIUS, DE

Probing the electronic properties of bulk samples SWNT by resonant and non-resonant microwave absorption

12:00 – 17:00 Mini Workshops

17:00 - 18:30 Dinner

#### Optics & Spectroscopy

18:30 - 19:00 T.F. HEINZ, US

Optical spectroscopy of individual single-walled carbon nanotubes

19:00 – 19:30 R. CAPAZ, BR

Excitons in Carbon Nanotubes: Insights from Model Calculations

19:30 - 20:00 S. MARUYAMA, JP

Growth and optical properties of small-bundled vertically aligned single-walled carbon nanotubes

20:00 - 20:30 M. WOLF, DE

Electron-phonon interaction in low-dimensional solids probed with time-resolved spectroscopy

#### 8:30 Principles of Quantum Computing

Michael Mehring

2. Physikalisches Institut, Univ. Stuttgart, Germany

Quantum bits (qubits) are two-level quantum systems which are abundant in nature. Inspired by this it has become a custom to mention quantum computers as soon as one encounters qubits. However, performing a quantum algorithm is much more involved than just having access to qubits. In this lecture I will introduce the concepts of qubits, entanglement and quantum algorithms. We will embark on a tour through Hilbert and eventually Liouville space. Having introduced the principles of quantum computing I will review some of the experimental implementations their difficulties and limits.

#### 9:30 Manipulation of quantum information in $N@C_{60}$

QISR

QISR

1

Arzhang Ardavan<sup>1</sup>, John Morton<sup>1</sup>, Alexei Tyryshkin<sup>2</sup>, Simon Benjamin<sup>3</sup>, Kyriakos Porfyrakis<sup>3</sup>, Stephen Lyon<sup>2</sup>, G. Briggs<sup>3</sup>

<sup>1</sup>Department of Physics, University of Oxford <sup>2</sup>Department of Electrical Engineering, Princeton University <sup>3</sup>Department of Materials, University of Oxford

Atomic nitrogen incarcerated in a  $C_{60}$  cage (N@C<sub>60</sub>) exhibits the longest electron spin lifetimes observed in any molecular species with a phase coherence time  $T_2=240\mu s$  in solution in CS<sub>2</sub> at 170 K, and this has led to speculation that it may be a useful component in an electron-spin-based quantum computer. Such a device would employ pulsed electron spin resonance (ESR) to implement single-qubit rotations; we have studied the various classes of errors that occur in such manipulations. We have demonstrated the implementation in ESR of one class of error-correcting composite pulse sequence, known as BB1, that corrects the dominant errors independently of the starting state and is therefore suitable for use as a quantum gate.

In addition to the electron moment, the nitrogen atom hosts a nuclear moment which is also, in principle, capable of storing quantum information. We have shown that it is possible to generate an extremely rapid arbitrary phase gate on the nuclear qubit by exciting an electronic transition, and we have used it to implement a "bang-bang" protocol to decouple the nuclear qubit from and external decohering perturbation.

#### Progress in N@C<sub>60</sub> quantum computing

Wolfgang Harneit

Freie Universitaet Berlin, Institut fuer Experimentalphysik, Arnimallee 14, 14195 Berlin, Germany

10:30 QISR 3

11:00

We report recent progress in N@C<sub>60</sub> quantum computing, including conceptual, materials, and experimental aspects. Nitrogen in fullerenes behaves as a free atom having an electron spin with exceptionally long coherence times. The fullerene provides a shielding and handling environment for this spin, which might thus make a good electron spin qubit. On solid-state samples of the companion system P@C<sub>60</sub>, we determined a  $T_2$  time in the millisecond range at low temperatures. Entanglement between nuclear and electron spin was engineered in fullerenes encapsulated in a matrix, allowing full access to the eight quantum levels (electron spin  $4 \times 2$  nuclear spin). We also present first results on spin-state read-out techniques suitable for small ensembles or even single spins. Finally, we discuss routes towards scalable solid-state devices containing many fullerene qubits.

#### Magnetic resonance in carbon nanotubes

 $\underline{\text{Ferenc Simon}}^1, \text{Hans Kuzmany}^2, \text{András Jánossy}^3, \text{Bálint Náfrádi}^4, \text{László Forró}^4, \text{Henri Alloul}^5, \text{Andreas } \mathbf{QISR}$ Hirsch<sup>6</sup>

<sup>1</sup>Technical University of Budapest, University of Vienna <sup>2</sup>University of Vienna <sup>3</sup>Technical University of Budapest <sup>4</sup>Ecole Polytechnique Federal de Lausanne <sup>5</sup>Laboratoire de Physique des Solides <sup>6</sup>University of Erlangen

Magnetic resonance (ESR, NMR) methods are powerful to study low energy excitations i.e. the vicinity of the Fermi surface. This potentially enables to study strongly correlated phenomena in SWCNTs such as the Tomonaga-Luttinger phase, the Peierls transition, or superconducting correlations. Much as these studies are desired, they are hampered by the absence of well defined and understood ESR active electron spins on them and the uniform distribution of the NMR active <sup>13</sup>C nuclei in all species of carbons present. Our solution is to encapsulate magnetic fullerenes (N@C<sub>60</sub> and C<sub>59</sub>N) inside SWCNTs to enable ESR and to grow <sup>13</sup>C enriched inner tubes from <sup>13</sup>C enriched encapsulated fullerenes to enable NMR. The earlier material contains SWCNTs filled with linear spin chains. ESR relaxation time measurements on the encapsulated  $C_{59}N$  reveal a uniform metallic-like DOS for the SWCNTs in bundles and the opening of a spin-gap at 20 K. Temperature and field dependent  $^{13}$ C NMR  $T_1$  studies on the  $^{13}$ C enriched inner tubes detects a low energy  $\sim 3 \text{ meV}$  gap that is assigned to a correlation induced transition in the small diameter SWCNTs.

#### Probing the electronic properties of bulk samples SWNT by resonant and non-resonant 11:30 microwave absorption

Björn Corzilius<sup>1</sup>, Klaus-Peter Dinse<sup>1</sup>, Joris van Slageren<sup>2</sup>, Kenji Hata<sup>3</sup>

<sup>1</sup>Chem. Dept., Darmstadt University of Technology, Petersenstr. 20, 64287 Darmstadt, Germany <sup>2</sup>Physical Institute, University of Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Germany <sup>3</sup>AIST, Tsukuba Central 5, Tsukuba 303-8565, Japan

Earlier investigations of the electronic properties of bulk samples of single wall carbon nanotubes (SWNT) were complicated by the presence of remaining catalysts. With the recent introduction of a CVD synthesis method which yields ultra-pure, catalyst-free SWNT it was possible to examine the electronic and magnetic properties in detail. By the use of electron paramagnetic resonance (EPR) it was possible to identify two different temperature regimes: at high temperatures the spectrum shows clear evidence for the presence of itinerant spins with a freezing temperature of about 100 K; below this temperature the spectrum is dominated by localized spins not detectable at higher temperatures. At very low temperatures (T < 12 K) the samples show strong non-resonant and non-linear mw absorption. This behaviour could be interpreted by the formation of a superconducting phase of a part of the sample. In addition, a part of the sample shows a magnetic ordering transition at a somewhat higher temperature, which can be suppressed by the application of a small magnetic field.

**QISR** 

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#### 18:30 Optical Spectroscopy of Individual Single-Walled Carbon Nanotubes

O&S Tony Heinz

1 Columbia University

In this talk, we describe recent experimental investigations of optical spectroscopy at the level of an individual nanotube. The principal experimental method has been Rayleigh scattering (elastic scattering) spectroscopy, an approach suitable for probing both semiconducting and metallic nanotubes. Recent measurements include a direct determination of the correlation between optical spectra and nanotube chiral index, as achieved through a combination of Rayleigh scattering measurements and electron diffraction on individual nanotubes; investigation of the influence of the local environment on nanotube electronic spectra, notably the effect of the formation of small nanotube bundles; a determination of the shifts in the electronic transitions induced by controlled axial strain applied to individual nanotubes; investigations of the mechanical properties of individual nanotubes of defined chiral index; and the identification and electrical characterization of nanotubes with spontaneous changes in structure along their length. (These investigations were carried out in collaboration with the groups of Profs. Louis Brus, James Hone, and Stephen O'Brien at Columbia University and the group of Dr. Yimei Zhu at Brookhaven National Lab.)

#### 19:00 Excitons in Carbon Nanotubes: Insights from Model Calculations

O&S Rodrigo Capaz

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Instituto de Fisica, Universidade Federal do Rio de Janeiro

We review our recent work on excitons in carbon nanotubes. In particular, we address the usefullness and limitations of model calculations of exciton properties. A We review our recent work on excitons in carbon nanotubes. In particular, we address the usefulness and limitations of model calculations of exciton properties. When parametrized by ab initio calculations and constrained to reproduce the proper exciton symmetries, variational tight-binding schemes can be extremely useful to obtain the diameter and chirality dependences of excitonic properties. Binding energies and spatial extents show a leading dependence on diameter as 1/d and d, respectively, with chirality corrections exhibiting strong family behavior. Bright-dark exciton splittings show a  $1/d^2$  leading dependence. Such dependences can be described by simple analytical formulas that should be useful to guide future experiments. We also address the limitations of model 1D potentials in describing the ground and excited states of excitons in carbon nanotubes.

## 19:30 Growth and Optical Properties of Small-Bundled Vertically Aligned Single-Walled Carbon Nanotubes

Shigeo Maruyama

Department of Mechanical Engineering, The University of Tokyo

A new insight is gained on the structure of the vertically aligned single-wall carbon nanotubes (VA-SWNTs) generated by ACCVD technique [1]. Our recent finding of the simple removal method using hot-water enabled us to transfer this film to various flat substrates [2]. Transferring this film on TEM grid made it possible to directly observe the morphology of nanotubes from the top. To our surprise, the average number of nanotubes of a bundle is less than about 10. Electronic properties measured by EELS revealed that nanotubes are virtually electronically isolated. Then, the characteristic resonant Raman features are reconsidered. The high resolution Raman measurements show the sharp features for the RBM peak which have been assigned to cross-polarized resonance [3]. The isolated and cross-polarized absorption resonance in Raman will be discussed based on the recent identification of the excitonic cross-polarized absorption through photoluminescence spectroscopy [4].

- [1] S. Maruyama, E. Einarsson, Y. Murakami, T. Edamura, Chem. Phys. Lett. 403 (2005) 320.
- [2] Y. Murakami, S. Maruyama, Chem. Phys. Lett. 422 (2006) 575.
- [3] Y. Murakami, S. Chiashi, E. Einarsson, S. Maruyama, Phys. Rev. B 71 (2005).
- [4] Y. Miyauchi, M. Oba, S. Maruyama, Phys. Rev. B 74 (2006).

#### Electron-phonon interaction in low-dimensional solids probed with time-resolved spec- 20:00 troscopy

0&S

4

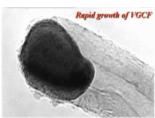
Tobias Kampfrath, Luca Perfetti, Christian Frischkorn, Uwe Bovensiepen, Martin Wolf Department of Physics, Freie Universität Berlin

The electronic properties of low-dimensional materials (e.g. quasi 1D or 2D systems) are often governed by strong electron correlation and electron-phonon coupling. We use time-resolved photoemission (TR-PES) and THz spectroscopy to study the dynamics of carriers in various low-dimensional systems after excitation with an ultrashort laser pulse. TR-PES provides a direct probe of the ultrafast insulator to metal transition in the quasi 2D Mott insulator TaS2 and discriminates between the collapse of the electronic gap and the excitation of coherent phonon modes. In the high  $T_c$  cuprate Bi2212 we observe an ultrafast (<50 fs) electron thermalization followed by rapid cooling, which allows to determine the electron-phonon interaction strength. On the other hand, broadband THz spectroscopy (1-40 THz) provides complementary information about low-energy excitations of free versus localized carriers, e.g., in graphite and carbon nanotubes.

# MEFS Co., Ltd.

Choei-Nagano Higashiguchi Building 2F, 1000-1 Gentakubo Kurita, Nagano-city 380-0921, Japan Phone.+81-26-225-7891, Fax...+81-26-225-789, ichinose@mefs.co.jp

In these days, the foundation of a "university-based venture" which aims to transfer intellectual and technical accomplishments to the community to create a new industry is prosperous all over the world. This new type of enterprise formation is just an element indispensable to innovation of an industrial structure. As first step to realize my desire of contribution to the community based on its requirements, I founded MEFS [mef-es] Co., Ltd. in October, 2003 to be CTO, with Showa Denko K.K., a joint investor, which I have had a cooperative relationship with in research and development of carbon nanotube. Core business of MEFS is, firstly to implement a research and development program of a new application for carbon nanotube, and secondly to provide a client company with technical consultation. "M and E" in "MEFS" are initials of my name, and "S" for "Showa Denko". "F" is loaded with the expectation of business success in the near "Future".





MEFS will emerge as a global leader to develop intellectual properties in the carbon nanotube technology

#### Rapid growth of VGCF



..... VGCF

**Exposed SWNT during the growth of crossing** the tubes

- J. Cryst. Growth, 32(1976) 335-349
- A. Oberlin, M. Endo and T. Koyama

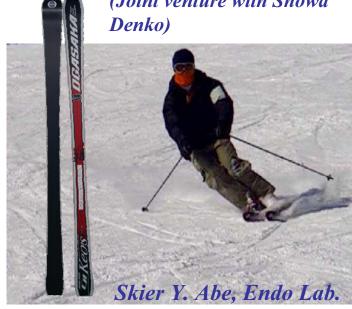
I have recognized contribution to the community is essentially important for a university-based venture. I would extend a sphere of our activities to the community, eventually to the world, and step into uncharted territories of carbon nanotube, while opening a window of such a venture originated from an academic university which had a tendency to close it to the community. I would also like to proceed with anticipated cooperation between industry and university with a company having higher technical potential, and contribute to development of the community full of vitality. A dream in my boyhood is closely connected to my present dream, and begins to grow up steadily towards its realization today to have my heart leaping up.

Never, never, never and never give up! magic words to make a dream come true. would say "don't give up by any means."

Development of The high speed ski board New feeling of **NanoTechnology** 

University venture of Prof. M.Endo

(Joint venture with Showa



Monday, March 12

#### Functionalization of carbon nanotubes

8:30 – 9:00 Y.H. LEE, KR

Tailoring electronic structures of carbon nanotubes

9:00-9:30 M. BURGHARD, DE

Electrochemically functionalized carbon nanotubes

9:30 - 10:00 G. SCALIA, DE

Carbon nanotubes in liquid crystals as versatile, functional materials

10:00-10:30 Coffee break

10:30 – 11:00 M. ENDO, JP

Chemical Doping Effect on Double Walled Carbon Nanotubes

#### COMMERCIALS

11:00 - 11:30 A. ZETTL, US

Thermal and Electromechanical Studies of Nanotubes

11:30 - 12:00 F. HENNRICH, DE

Separation Techniques for Single-Walled Carbon Nanotubes

12:00 – 17:00 Mini Workshops

17:00 - 18:30 Dinner

#### Raman scattering

18:30 – 19:00 J. MAULTZSCH, US

Fano lineshape in the high-energy modes of metallic carbon nanotubes

19:00 – 19:30 V.N. POPOV, BG

Theoretical Raman intensity of the RBM of SWCNTs

19:30 – 20:00 J.-L. SAUVAJOL, US

 $Raman\ spectroscopy\ of\ well-identified\ single-walled\ carbon\ nan-otubes$ 

20:00 - 20:30 S. DOORN, US

Raman Studies of Exciton-Phonon Coupling in Single Walled Carbon Nanotubes: Quantitation of Bundled vs. Isolated Behavior

20:30 – 21:00 A. JORIO, BR

The Importance of Excitons for the Intensity of the Radial Breathing Mode and the Disorder Induced Band in Single Wall Carbon Nanotubes

22 Monday, March 12

#### 8:30 Tailoring electronic structures of carbon nanotubes

FCNT Young Hee Lee

1

Sungkyunkwan University

One important feature of carbon nanotubes is its peculiar electronic structure that can be metallic and semiconducting depending on the chirality and diameter of nanotubes. Up to now, it has not been possible to control the chirality of nanotubes systematically by the conventional synthesis approaches. Both metallic and semiconducting nanotubes coexist in the grown sample, which often hinders device applications with high performance. Therefore, tailoring the metallicity of nanotubes is highly desired. One approach is to transform the electronic structures by functionalization using gas adsorbates. Simple gases such as fluorine and hydrogen gases are intriduced to transform electronic structures from metallic to semiconducting.

Another approach is to select either metallic or semiconducting nanotubes from their mixtures. Several methods of selectiing semiconducting nanotubes from metallic ones or vice versa using dielectrophoresis, octadecylamine (ODA), bromination, and DNA have been reported. We found a method for a selective removal of metallic single-walled carbon nanotubes from semiconducting ones by stirring SWNT powder in tetramethylene sulfone (TMS)/chloroform solution with nitronium hexafluoro-antimonate (NO2SbF6:NHFA. Positively charged nitronium ions (NO2+) were intercalated into nanotube bundles, where the intercalation was promoted also by the counter ions. Nitronium ions selectively attacked the sidewall of the metallic SWNTs due to the abundant presence of electron density at the Fermi level, thus yielding stronger binding energy compared to the counterpart semiconducting SWNTs.

#### 9:00 Electrochemically functionalized carbon nanotubes

FCNT

 $\underline{\text{Marko Burghard}^1}$ , Kannan Balasubramanian<sup>1</sup>, Tilman Assmus<sup>1</sup>, Eduardo Lee<sup>1</sup>, Matteo Scolari<sup>2</sup>, Nan Fu<sup>2</sup>, Alf Mews<sup>2</sup>

<sup>1</sup>Max Planck Institut fuer Festkoerperforschung <sup>2</sup>Department of Chemistry, University of Siegen

A major advantage of electrochemical methods for chemical functionalization of individual carbon nanotubes is the possibility to evaluate the effect of chemical modification on defined tubes and to precisely control the tubes' functionalization degree. Here we present studies on two different types of electrochemically modified SWCNTs to which a functional organic layer and discrete noble metal particles, respectively, were attached.

First, a novel approach to nanoscale chemical sensors, based upon metallic rather than semiconducting SWCNTs, will be demonstrated. It involves the gentle modification of individual metallic tubes via covalent attachment of amino-substituted phenyl groups, whereby the tubes are rendered sensitive towards the pH of an aqueous solution.

Secondly, individual SWCNTs were partially decorated by gold nanoparticles with sizes of a few tens of nanometers and investigated by confocal Raman spectroscopy. It was found that isolated metal particles lead to a local increase in Raman intensity. Moreover, polarization dependent Raman experiments revealed no disturbance in the single particle case, whereas for tubes decorated by nanoparticle aggregates significant distortions of the polarization characteristic occur.

#### 9:30 FCNT

3

#### Carbon nanotubes in liquid crystals as versatile, functional materials

Giusy Scalia<sup>1</sup>, Giusy Scalia<sup>2</sup>, Jan Lagerwall<sup>3</sup>, Stefan Schymura<sup>4</sup>, Miroslav Haluška<sup>5</sup>, Siegmar Roth<sup>6</sup>

<sup>1</sup>Max Planck Institute for Solid State Research, 70569 Stuttgart, Germany <sup>2</sup>ENEA, C. R. Portici, 80055 Portici, Napoli, Italy <sup>3</sup>University of Stuttgart, Institute of Physical Chemistry, 70569 Stuttgart, Germany <sup>4</sup>1; 3 <sup>5</sup>3) <sup>6</sup>1) Max Planck Institute for Solid State Research, 70569 Stuttgart, Germany

Carbon nanotubes (CNTs) dispersed in a liquid crystal (LC) spontaneously align in the same direction as the molecules of the host. This finding is particularly interesting as it on the one hand gives the possibility to obtain macroscopic directional control of the nanotubes—static as well as dynamic—with various superstructures being possible, all the complex geometries that the soft liquid crystal phase can adopt being available for transferring to the CNT guests. On the other hand the nanotubes can act as a functional dopant of LCs, the dominating active material in modern display technology, modifying the switching behavior of the LC without destroying its orientational order. In the quest for further improvement of display performance in terms of switching speed and low driving voltage, CNT doping is one of the most recently proposed approaches. The reported positive effects are however far from understood and many practical issues remain to be addressed before CNTs will find their way into LC displays. We will here present the recent progress in our studies of CNT-LC composites, where we deal with both issues: CNT control with LCs as well as LC improvement using CNTs.

#### Chemical Doping Effect on Double Walled Carbon Nanotubes

Morinobu Endo

Shinshu University

10:30 FCNT 4

The small but interesting one-dimensional carbon nanotubes consisting of rolled graphene layer built from sp2 units have attracted the imagination of scientists as one-dimensional macromolecules. Their unusual physical and chemical properties make them useful in the fabrication of nanocomposite, nano-electronic device and sensor etc. Through judicious selection of transient metal, support materials and synthetic conditions (temperature, duration), we are able to synthesize 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 talk, I will describe the catalytic synthesis of highly pure and crystalline DWNTs. The second part of my talk deals with Raman studies on the chemically doped DWNTs (e.g., Li+ and bromine) in related with charge transfer. Then, fluorination of DWNTs will be described because fluorine atoms were selectively attached to the outer shell of the DWNT. Finally, their high potential toward nanocomposites as multi-functional filler (e.g., hybrid nanocomposite) and their bio-medical applications (e.g., micro-catheter)will be discussed in detail from the point of industrial concerns. It is envisaged that carbon nanotubes will play an important role in the development of nano-technology in the near-future.

#### Thermal and Electromechanical Studies of Nanotubes

Alex Zettl

University of California at Berkeley

11:00 FCNT 5

Previous experiments and theoretical studies suggest extraordinary electronic, thermal, and mechanical properties of nanotubes. In this presentation recent experiments designed to explore such properties in detail will be described. We have constructed thermal test platforms capable of measuring the thermal transport of geometrically tailored nanotube-based systems. Tunable thermal links (i.e. thermal rheostats) and thermal rectifiers are demonstrated. We also measure the transport properties of individual nanotubes to 4,000K. Nanotube-based electromechanical oscillators have been designed which operate in air and at room temperature, with operational frequencies in the microwave range. Exceptional mass sensitivity and low friction is inherent in these devices. Some of the structures can be exploited for biological applications.

#### Separation Techniques for Single-Walled Carbon Nanotubes

<u>Frank Hennrich</u><sup>1</sup>, Ralph Krupke<sup>1</sup>, Manfred Kappes<sup>2</sup>

<sup>1</sup>Forschungszentrum Karlsruhe, Institut für Nanotechnologie, D-76021 Karlsruhe, Germany <sup>2</sup>Institut für Physikalische Chemie, Universität Karlsruhe, D-76128 Karlsruhe, Germany

11:30 FCNT

A successful separation depends on the intrinsic capability of the chosen technique, but also on many other parameters. For example the separation efficiency strongly depends on the degree of individualization and up to date no technique exists which individualizes SWCNT samples by 100%. Besides that no integral measurement is available today to quantitatively determine the bundle content in a nanotube dispersion.

Individualizing SWCNTs often needs several processing steps (purification, sonication, acid treating, functionalizing) and during every step the properties of the tubes might be altered which often influences the results of the chosen separation techniques or even inhibits separation. Also because different researchers use tubes from different source made by a different synthesis method the SWCNTs require a different treatment.

In any dispersing step sonication is always required to overcome van der Waals forces between the walls of neighbouring tubes. Unfortunately sonication introduces defects and causes rupture of the tubes.

My talk aims at giving an overview over separation techniques we are currently using for SWNTs and the characteristics of separated nanotube material. I will discuss (i) how one can achieve separation due to different electronic properties (metallic, semiconducting), length, diameter and chirality via size exclusion chromatography, electrophoresis, dielectrophoresis and density gradient centrifugation, (ii) how those separation methods work for different SWNT materials (HiPco, Laser ablation, CoMoCat) and (iii) how different pre-treatments and surfactants influence the separation efficiency.

#### 18:30 Fano lineshape in the high-energy modes of metallic carbon nanotubes

J. Maultzsch<sup>1</sup>, Y. Wu<sup>1</sup>, E. Knoesel<sup>2</sup>, B. Chandra<sup>1</sup>, J. Hone<sup>1</sup>, T. Heinz<sup>1</sup>

<sup>1</sup>Nanoscale Science and Engineering Center, Columbia University, New York <sup>2</sup>Dept. of Physics, Rowan University

We present Raman measurements of individual metallic carbon nanotubes suspended in air. The nanotubes were identified as metallic by Rayleigh scattering combined with the radial breathing mode frequency. We find that even individual metallic nanotubes show a broadened and slightly asymmetric high-energy mode (HEM). The width, however, varies strongly with the chiral index of the tube. In particular, in armchair and close-to-armchair nanotubes the Raman spectra resemble those of semiconducting tubes. The HEM broadening reflects the coupling between the phonon and the electron-hole excitations near the Fermi level. By applying a gate voltage, we shift the Fermi level, making low-energy electron-hole-pair excitations unavailable. The electron-phonon coupling is reduced and the Raman modes become narrow, in agreement with theoretical predictions.

#### 19:00 Theoretical Raman intensity of the RBM of SWCNTs

RAS

 $\mathbf{2}$ 

RAS

1

Valentin N. Popov<sup>1</sup>, Philippe Lambin<sup>2</sup>

<sup>1</sup>Faculty of Physics, University of Sofia, Sofia, Bulgaria <sup>2</sup>Laboratoire de Physique du Solide, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium

The atomistic calculations of the physical properties of perfect single-walled carbon nanotubes can be performed successfully by use of the helical symmetry of the nanotubes. We demonstrate this approach by carrying out calculations of the electronic band structure[1], lattice dynamics[2], and the resonant Raman intensity[3] of all nanotubes in the diameter range from 0.6 nm to 2.4 nm within a symmetry-adapted non-orthogonal tight-binding model.

In particular, we show that the Raman intensity of the radial-breathing mode depends strongly on tube diameter, chiral angle, and laser excitation energy. The obtained intensity can be used for characterization of the nanotube samples by Raman scattering spectroscopy[4].

- 1. New J. Phys. 6 (2004) 17; Phys. Rev. B 70 (2004) 115407.
- 2. Phys. Rev. B 73 (2006) 085407.
- 3. Nano Letters 4 (2004) 1795; Phys. Rev. B 72 (2005) 035436; Phys. Rev. B 73 (2006) 165425.
- 4. Phys. Rev. Lett. 96 (2006) 257401.

#### Raman spectroscopy of well-identified single-walled carbon nanotubes

19:30 RAS 3

Jean-Louis Sauvajol

LCVN

By combining, on the same freestanding single-walled carbon nanotubes, electron diffraction and Raman experiments, we have been able to obtain unambiguously some information on (n,m)-identified single-walled carbon nanotubes. A relation between diameter (d) and the radial breathing mode (RBM) frequency was determined. The comparison with previous RBM frequency vs d relations obtained on SWNTs wrapped in a surfactant allows to discuss the role of the environmental conditions on the Raman response of SWNT.

The comparison between the incident excitation energies and the calculated transition energies (in a nonhortogonal tight-binding approach) allows us to determine the values of the optical transition energies EM11, ES33 and ES44 for SWNTs in the 1.2-2.4 nm diameter range. These latter results question the origin of the differences between the experimental and calculated transition energies. Our experimental findings suggest the processes involved in ES33 and ES44 to be different of those involved in the lower order transitions, ES11 and ES22

#### Raman Studies of Exciton-Phonon Coupling in Single Walled Carbon Nanotubes: Quanti- 20:00 tation of Bundled vs. Isolated Behavior

Stephen Doorn<sup>1</sup>, Andrew Shreve<sup>1</sup>, Sergei Tretiak<sup>1</sup>, Zhengtang Luo<sup>2</sup>, Fotios Papadimitrakopoulos<sup>2</sup> <sup>1</sup>Los Alamos National Laboratory <sup>2</sup>Dept. of Chemistry, Univ. of Connecticut

Exciton-phonon and electron-phonon coupling are important for a number of carbon nanotube optical and transport behaviors and have recently drawn attention for their role in chirality-dependent intensities observed in radial breathing mode (RBM) Raman spectra. 1,2 Given the importance of these effects, there is a need to quantitate the magnitude of the exciton-phonon coupling. We present a Raman transform analysis of RBM fundamental and overtone intensities that yield the magnitude of coupling for five specific nanotube chiralities.3 These results agree with values predicted through quantum chemical calculations and indicate that non-Condon effects may be important in describing nanotube transitions. We extend the analysis of the coupling to bundled nanotube samples and find it decreases significantly in these sample types. We also discuss the coupling behavior of a new class of intermediate frequency modes (IFMs) that display step-wise dispersive behavior. These IFMs are associated with coupling between the E11 and E22 transitions. Bundling is found to increase the coupling observed for these modes.

- 1 Goupalov, S.V.; Chikkannanavar, S.B.; Doorn, S.K.; Phys. Rev. B, 73, 115401 (2006).
- 2 Satishkumar, B.C.; Goupalov, S.V.; Haroz, E.H.; Doorn, S.K.; Phys. Rev. B, 74, 155409 (2006).
- 3 Shreve, A.P.; Haroz, E.H.; Tretiak, S.; Bachilo, S.; Weisman, R.B.; Doorn, S.K.; Phys. Rev. Lett., in press.

#### The Importance of Excitons for the Intensity of the Radial Breathing Mode and the Disorder 20:30 Induced Band in Single Wall Carbon Nanotubes

Ado Jorio<sup>1</sup>, Paulo Araujo<sup>1</sup>, Indhira Maciel<sup>1</sup>, Leandro Moreira<sup>1</sup>, Marcos Pimenta<sup>1</sup>, Grace Chou<sup>2</sup>, Mildred 5 S. Dresselhaus<sup>2</sup>, Jie Jiang<sup>3</sup>, Riichiro Saito<sup>3</sup>, Sergei Tretiak<sup>4</sup>, Stephen Doorn<sup>4</sup> <sup>1</sup>UFMG <sup>2</sup>MIT <sup>3</sup>Tohoku University <sup>4</sup>Los Alamos National Laboratory

We present resonance Raman spectroscopy of the radial breathing modes (RBM) on single wall carbon nanotubes (SWNT) up to 4nm in diameter. The experiment sheds light into the nature of the optically active levels. The results have not been predicted by solid state approaches, but are understood on the basis of quantum chemical calculations. Consideration of the excitonic effects are important to account for the strong diameter dependence of the RBM intensities, and for using the resonance Raman technique with metrology purposes. Despite the strong development related to the first-order spectra, intensity issues related to disorder induced bands are still poorly explored. We will address intensity issues for the D band in SWNTs and nano-graphite.

RAS

4

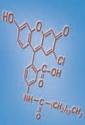
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Tuesday, March 13

#### **Nanowires**

8:30-9:30 L. SAMUELSON, SE

Growth, properties and applications of semiconductor nanowires

9:30 - 10:00 W. WEBER, DE

Silicon Nanowire Transistors with Axially Intruded Nickel Silicide Contacts

10:00-10:30 Coffee break

10:30 - 11:00 V. PRINZ, RU

 $Molecularly \quad and \quad atomically \quad thin \quad semiconductor \quad and \quad carbon \\ nanoshells$ 

#### **COMMERCIALS**

11:00 – 11:30 E. BAKKERS, NL

VLS Nanowire Growth Dynamics

11:30 – 12:00 J. PATTERSON, IR

Role of Materials in Emerging Nanoelectronic Devices

12:00 – 17:00 Mini Workshops

17:00 - 18:30 Dinner

#### **Applications**

18:30 - 19:00 G. GRUNER, US

Carbon for printed electronics

19:00 - 19:30 R. BAUGHMAN, US

From Electrical to Fuel Powered Artificial Muscles

19:30 – 20:00 M. VOETZ, DE

Industrial Production of Multiwalled Carbon Nanotubes

#### Welcome address of Hotel, J. Taus

Poster reading

Special Poster (SP)

#### 8:30 NAWI

1

#### Growth, properties and applications of semiconductor nanowires

Lars Samuelson

Lund University, Solid State Physics / the Nanometer Structure Consortium Box 118, S-221 00 Lund, Sweden

In this talk I will survey the state of the art in controlled growth of semiconductor nanowires using a combination of top-down definition of seeding or growth together with the self-assembly of nanowire growth, by which ideal arrays of nanowires can be formed with the wires epitaxially nucleated on a single-crystalline semiconductor wafer. I will also describe how multiple-seeding of nanowire growth can lead to the formation of complex tree-like structures. I will then turn to describe the formation of controlled tunnel-barriers using either heterostructure-induced or gate-induced tunnel-barriers and I will give examples of transport studies made possible in this way. Besides the interest in using one-dimensional nanowires for physics studies they are attracting much interest for their possible use as building blocks in electronic and photonic device applications. I will give a few examples of what has been achieved in applying the nanowire technology for wrap-gate field-effect transistors, for memory applications and for formation of heterostructure defined light-emitting structures.

#### 9:30 NAWI 2

#### Silicon Nanowire Transistors with Axially Intruded Nickel Silicide Contacts

Walter Weber<sup>1</sup>, Lutz Geelhaar<sup>1</sup>, Caroline Cheze<sup>1</sup>, Franz Kreupl<sup>2</sup>, Paolo Lugli<sup>3</sup>, Henning Riechert<sup>2</sup>
<sup>1</sup>Qimonda Dresden GmbH & Co. <sup>2</sup>Qimonda AG <sup>3</sup>Technische Universitaet Muenchen, Institute for Nanoelectronics

Silicon nanowire (NW) Schottky contact field effect transistors (FET) with axially intruded nickel-silicide source-drain (S/D) contacts have been fabricated and extensively characterized. Intrinsic silicon NWs with diameters between 7 and 30nm have been grown by catalytic chemical vapor deposition to constitute the transistors active-region. The NWs were contacted with Ni reservoirs so that uppon annealing Ni diffused axially into the the NWs creating a single-crystalline nickel-silicide NW segment as proven by high-resolution transmission electron microscopy images. (1) The sharp Si to Ni-silicide interfaces form the Schottky S/D-contacts to the active region. Due to the needle-like silicide regions, there is an enhanced electrostatic coupling between the common back-gate and the S/D-contacts as shown by electrostatic calculations. Back-gated FETs exhibit a p-type behaviour, have current densities in the on state of up to  $0.5 \mathrm{MA/cm^2}$  and the drain current can be modulated over 7 orders of magnitude. Further on, Si-NW-FETs with different gate configurations and gate dielectics are analyzed and compared. A gate length (Lg) dependent study of the SiNW-FETs shows, that for a given NW diameter the on-current is practically constant for Lg ilum, since the transport is primarily controlled by the Schottky contacts. For Lg>1um the Si-NWs resistance becomes dominant and I-on decays exponentially with increasing Lg. In principle stress variations or defects along the active region could account for this effect. (1) Weber, W. M. et al. Nano Lett.; vol.6 pp2660-2666(2006).

## Molecularly and atomically thin semiconductor and carbon nanoshells $\operatorname{Victor}\operatorname{Prinz}$

10:30 NAWI 3

Institute of Semiconductor Physics, Russian Academy of Sciences, Siberian Branch

A brief overview of the existing approaches to the formation of molecularly and atomically thin solid shells is given. Original data concerning the fabrication of functional two- and three-dimensional highly-ordered systems of interacting nanoobjects are reported. Also presented are first data on the formation of suspended graphene. A comparative analysis of electrical, mechanical, transport, and quantum properties of semiconductor, hybrid, and graphene nanoshells is given. Based on this analysis, future trends in the application of such nanoshells are outlined.

#### **VLS Nanowire Growth Dynamics**

11:00 NAWI

<u>Erik Bakkers, Magnus Borgstrom, George Immink, Marcel Verheijen VLS Nanowire Growth Dynamics</u>

Semiconducting nanowires are one of the most promising materials for the monolithic integration of high-performance semiconductors with silicon technology. For the fabrication of optical or electrical devices, local variations in the electronic structure of the wire, such as hetero junctions, are required. Ultimate control over the growth rates of segmented nanowires is desired since the opto-electronic properties of the sections critically depend on their dimensions in the nanometer regime. We have studied the Vapor-Liquid-Solid (VLS) growth dynamics of GaP and GaAs in heterostructured GaP-GaAs nanowires. The wires containing multiple GaP-GaAs junctions were grown by the use of metal-organic vapor-phase-epitaxy (MOVPE) and the lengths of the individual sections were obtained from transmission electron microscopy (TEM). In addition p-n junctions have been incorporated in these wires during growth. Single wires were contacted by the use of e-beam lithography to study the electronic properties. Finally, electroluminescence from homogeneous InP wires and nanowires, containing a quantum dot will discussed.

#### Role of Materials in Emerging Nanoelectronic Devices

11:30

<u>Jennifer Patterson,</u> Matthew Shaw, Richard Farrell, Peter Gleeson, Christopher Murray, Bernard Capraro, **NAWI** Paolo Rapposelli, Leonard Hobbs

5
Intel Ireland Ltd.

The semiconductor industry will continue to need new materials for future technologies, and future generations of nanoelectronic devices will increasingly rely on innovations in materials science and technology. It is accepted that a number of challenges now exist to continue increasing density and performance while reducing power at the pace dictated by Moore's Law. As the semiconductor industry continues to reduce dimensions, many of the existing materials used in manufacturing will limit future improvements in density and will need to be replaced with new materials with unique properties and nanometer control. To identify such materials research is needed to understand synthetic processes that can control material structure and composition at the nanometer scale and how this structure controls the properties of the materials. Large scale integration of these new materials with current CMOS processing and design is also a major consideration. Critical nano-materials for the ICT and semiconductor industry include, nanometer size lithography templates, nanostructured device materials (such as carbon nanotubes and magnetic materials for spintronic applications), low resistance nanometer scale electrical interconnects, ultra-low capacitance dielectrics to separate metal interconnects, ultrahigh capacitance materials for fast delivery of power, and nano-material composite polymer materials to enable low stress packaging of silicon.

This talk will focus on the industry needs, research challenges, and research progress to achieve material requirements for charge-based and non-charge-based nanoelectronic devices beyond the 22 nm technology node.

#### 18:30 Carbon for printed electronics

## $\begin{array}{ccc} \mathbf{APL} & & \frac{\text{George Gruner}}{\text{University of California}} \\ \mathbf{1} & & \end{array}$

While the integration of carbon nanotube or graphene based electronic devices with CMOS architectures is decades away, significant progress has been made in integrating nanoscale carbon structures into printed electronics applications. This talk will examine the roadmap of carbon based printed electronics, with carbon nanotube networks as the prime examples. Such networks can be regarded as a novel "electronic material" with tunable electrical properties, mimicking both metals and semiconductors. In addition, the films are transparent, flexible, and can be produced by room temperature fab processes. Several product lines based on these attributes are being developed, from touch screens, through displays, OLEDs and solar cells. I will also discuss the five (not so easy) pieces of a science-to-product roadmap: Proof-of-concepts, Patents, Prototypes, Pilot and Product lines.

#### 19:00 From Electrical to Fuel Powered Artificial Muscles

APL Von Ebron<sup>1</sup>, Zhiwei Yang<sup>1</sup>, Daniel J. Seyer<sup>1</sup>, Mikhail Kozlov<sup>1</sup>, Jiyoung Oh<sup>2</sup>, Hui Xie<sup>1</sup>, Joselito Razal<sup>1</sup>, John P. Ferraris<sup>1</sup>, Alan G. MacDiarmid<sup>1</sup>, Ray H. Baughman<sup>1</sup>

<sup>1</sup>Department of Chemistry and NanoTech Institute, University of Texas at Dallas, Richardson, TX 75083-0688, USA <sup>2</sup>Research Center of Dielectric & Advanced Matter Physics and Dept. of Physics, Pusan National University, Busan 609-735, Korea

We here experimentally demonstrate artificial muscles that convert the energy of a high-energy-density fuel to mechanical energy. These muscles are fuel cells that in some embodiments store electrical charge and use changes in stored charge for mechanical actuation. The highest demonstrated actuator generated strains and mechanical output power densities are comparable to natural skeletal muscle, and the actuator generated stresses are over a hundred times higher than for natural skeletal muscle. Since the energy density of fuels like methanol is  $\approx 30$  times higher than for advanced Li batteries, this advance seems quite important for such applications as autonomous robots or prosthetic limbs, where long operation without recharging or refueling is needed.

#### Industrial Production of Multiwalled Carbon Nanotubes

M. Bierdel, S. Buchholz, V. Michele, L. Mleczko, R. Rudolf, <u>M. Voetz</u>, A. Wolf Bayer Technology Services GmbH, 51368 Leverkusen

Carbon Nanotubes are currently synthesized by different methods. The methods differ largely by the achievable Space-Time-Yield, amorphous carbon content and carbon purity.

High space-time-yields can only be achieved by CVD processes. Though usually low contents of amorphous carbon are observed in CVD processes, C-purity is generally decreased due to catalyst residues. Bayer Technology Services has developed a high-yield process for MWNT (Baytubes®) based on a CCVD process starting from light hydrocarbons. The produced Baytubes® are characterized by a very high graphite content and an excellent purity (carbon content > 98 wt.%). Due to their high purity and quality, Baytubes® can be employed directly in further processing. The Baytubes® were incorporated into different polymers and also into liquids. The primary feature for good mechanical and electrical properties of the polymer composites is a full dispersion of the CNT in the polymer matrix.

TEM analysis is an important method to investigate the CNT dispersion on the nanometer scale. But it is also necessary to combine different methods to ensure a good and constant dispersion quality. Thus, different analysis methods were developed by BTS during product development.

Process scale-up is under way and a short-term production capacity of several tons will be realized.

19:30

 $rac{ ext{APL}}{3}$ 

#### Chemical Vapor Deposition of Functionalized Single Wall Carbon Nantubes with Defined SP Boron and Nitrogen Doping

Paola Ayala<sup>1</sup>, Fernando Freire Jr.<sup>2</sup>, Iván Solórzano<sup>3</sup>, Bernd Büchner<sup>4</sup>, Daniel Grimm<sup>5</sup>, Mark Rümmeli<sup>4</sup>, Alexander Grüneis<sup>6</sup>, Thomas Gemming<sup>6</sup>, Thomas Pichler<sup>6</sup>

<sup>1</sup>IFW-Dresden, Germany and Departamento de Fisica PUC-Rio, Rio de Janeiro, Brazil <sup>2</sup>Departamento de Fisica PUC-Rio, Rio de Janeiro, Brazil <sup>3</sup>DCMM PUC-Rio, Rio de Janeiro, Brazil <sup>4</sup>IFW-Dresden, Germany <sup>5</sup>IFW-Dresden, Germany and Universidade Federal do Rio de Janeiro, Brazil <sup>6</sup>IFW-Dresden

Defined n- and p-doping of carbon nanotubes can find potential applications in nanoelectronics and as sensors. An efficient doping can be achieved by substituting Carbon by heteroatoms such as Boron and Nitrogen.

We explored the formation process of B and N doped tubes within hot wall chemical vapor deposition (CVD) employing different C/N and C/B feedstocks such as Benzylamine, Acetonitrile, Triisopropyl Borate and Triethyl Borate, combined with the use of supported powder catalysts and multilayered sputtered films. The CVD process was optimized regarding the formation of substitutionally doped single (SWCNT) and double (DWCNT) walled carbon nanotubes. The samples were analyzed using, transmission and scanning electron microscopy, photoemission, electron-energy-loss spectroscopy and optical probes (Raman, optical absorption). We find a growth window for doped SWCNT and DWCNT with diameters ranging between 1 and 3 diameters between 770 and 1000 C. The optimal temperature depends according to the employed feedstock. The maximum N doping for SWCNT was below 0.2%, the B doping never exceeds 4%. For supported powder catalysts the maximum yield of SWCNT was observed, whereas for the multilayered films we find a high relative content of MWCNT associated to the formation of vertically aligned CNTs. We find that the different bonding environment leads to a strongly reduced internal charge transfer and novel electronic properties of the substitutionally doped CNx and CBx nanotubes in comparison to pristine and intercalated nanotubes.

#### Wigner crystallization of electrons in carbon nanotubes and nanotube self-assembly

Marc Bockrath, Vikram Deshpande, Hareem Maune, Si-Ping Han, Erik Winfree, William Goddard, Paul 2 Rothemund

Caltech

We report transport spectroscopy experiments on free-standing small-bandgap carbon nanotubes that are nearly disorder free. By studying the spin- and band index of added electrons near the gap we find strong evidence that these electrons form a one-dimensional Wigner crystal. By varying the charge density with a gate electrode, we can tune interelectronic exchange interaction. In an axial magnetic field, exchange drives electrons into three regimes: spin and orbital polarized ordering at low densities, orbital polarized, spin anti-ferromagnetic ordering for intermediate densities, and four-fold ordering, alternating in spin and orbital quantum numbers for large density. Finally, in non-linear transport at high magnetic fields, we find anomalous spin-dependent tunnel rates which cannot be explained from a constant interaction picture. We will discuss our latest experimental results and interpretations.

We also address a major challenge in carbon nanotube science: the rational assembly of individual nanotubes into integrated devices. Our approach is to use deoxyribonucleic-acid origami recently developed by Paul Rothemund in Erik Winfree's group at Caltech as templates for self-assembling nanotubes according to a pre-set plan. The initial results from our collaboration will be presented, showing small arrays of parallel nanotubes and self-assembled nanotube crossbars.

#### The effects of a pyrrolidine functional group on the magnetic properties of N@C<sub>60</sub> Jinying Zhang, John J. L. Morton, Mark R. Sambrook, Kyriakos Porfyrakis, Arzhang Ardavan, Andrew Briggs

University of Oxford

A stable pyrrolidine functionalized fullerene derivative, C<sub>69</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>, has been synthesized, purified by high performance liquid chromatography, and characterized by MALDI mass spectrometry, ultravioletvisible spectroscopy, Fourier transform infrared, <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance. The magnetic properties of the analogous endohedral species have been studied by both continuous wave (CW) and pulsed EPR. CW-EPR spectra indicated an anisotropic hyperfine interaction and a permanent zero-fieldsplitting (ZFS). Both CW and pulsed EPR showed the ZFS parameter  $D_{eff}$  to be around 17 MHz. Pulsed EPR revealed a biexponential decay in both  $T_1$  and  $T_2$ , yielding a molecular tumbling correlation time  $\tau_c$  of  $31.4 \pm 2.5$  ps.

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### SP Charge and Spin Transport in Graphene Nanostructures 4 Sung Jae Cho, Yung-Fu Chen, Michael Fuhrer

Sung Jae Cho, Yung-Fu Chen, Michael Fuhrer University of Maryland

We report our efforts toward graphene electronic and spintronic devices. We have prepared single-and few-layer graphene samples by mechanical exfoliation of Kish graphite on SiO2. We occasionally find narrow (25-50 nm) strips of graphene upon exfoliation. At low temperature (300 mK) electron and hole transport in narrow strips remains delocalized over the entire range of gate voltages studied. The resistivity on-off ratio may exceed 100. Thermal activation suggests bandgaps much smaller than predicted for an armchair-edge strip. We have also studied spin injection from ferromagnetic (permalloy) electrodes into single- and few-layer graphene devices using both two-probe and non-local four-probe geometries. In both geometries we have observed resistance changes correlated with the parallel vs. anti-parallel alignment of the electrode magnetizations. In the non-local four-probe geometry we observe sign reversal of the non-local resistance upon switching of the magnetization direction of the electrodes, clearly indicating injection and detection of a spin current. The two-probe tunneling magnetoresistance ratio (TMR) may be positive or negative, and we have observed TMRs of up to +20% and -10%. We have also observed a reversal of the sign of the four-probe non-local spin valve signal at particular gate voltages (carrier densities).

### SP Utilising de-novo peptides to enhance the uptake of carbon nanotubes by living cells Shook-Fong Chin<sup>1</sup>, Ray Baughman<sup>1</sup>, <u>Alan Dalton</u><sup>2</sup>, Eric Brunner<sup>2</sup>, Gregg Dieckmann<sup>1</sup>, Rockford Drap

Shook-Fong Chin<sup>1</sup>, Ray Baughman<sup>1</sup>, <u>Alan Dalton</u><sup>2</sup>, Eric Brunner<sup>2</sup>, Gregg Dieckmann<sup>1</sup>, Rockford Draper<sup>1</sup>, Carole Mikoryak<sup>1</sup>, Inga Musselman,<sup>1</sup>, Vasiliki Zorbas-Poenitzsch,<sup>1</sup>, Peter Goldfarb<sup>2</sup>, Paul Pantano<sup>1</sup>

<sup>1</sup>UT Dallas <sup>2</sup>University of Surrey

The success of many projected applications of carbon nanotubes (CNTs) to living cells, such as intracellular sensors and nanovectors, will depend on how many CNTs are taken up by cells. In this work, we report the enhanced uptake by a variety of cell types of single-walled and multi-walled CNTs coated with designed amphiphilic peptides. We find that that our peptide-wrapped CNT dispersions are taken up by HeLa and Chinese hamster ovarian cells in a time- and temperature-dependent fashion, and that they do not affect the growth rate of cells, evidence that the CNTs inside cells are not toxic during the observed time period. We also find that that up to  $\approx$ 8-fold more CNTs are taken up by cells in the presence of peptide compared to medium containing a serum but no peptide. We also show that the uptake of CNTs is dependent on the degree of aggregation of CNTs in the dispersion. The fact that coating CNTs with a peptide enhances uptake offers a strategy for improving the performance of applications that require CNTs to be inside cells.

### PTUe Electronic Dynamics in a linear chain of metallic quantum dots and implementation of ternary logic gates

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We studied the electronic dynamics in a linear chain of quantum dots in order to implement ternary logic, for which the variable can take one of three values: -1, 0, +1. For the description of the many-electron electronic structure and dynamics, we use the semi-empirical Hubbard Hamiltonian in the unitary group approach formalism. Then, we give the description of the formalism implemented to numerically integrate with sufficient accuracy the time dependent Schrödinger equation when we apply a time dependent perturbation in the nanosecond time scale. For finally, with the formalism described above, we implement a set of five ternary logic gates by putting in resonance and/or resonance the levels of the quantum dots, using the time dependent perturbation.

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#### New principle of hydrogen adsorption inside nanotubes

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New principle of hydrogen (or other gases) adsorption inside single wall nanotubes is proposed. This principle is based on using of mixing of hydrogen with small quantity of special additive molecules. The diameter of these molecules is chosen to be on 2.5-4A smaller than the nanotube diameter. So these molecules can be moved along the tube axis. Due to interaction of the molecule and the nanotube walls this molecule movement has potential barriers which should be of  $\approx 0.5$ -1 eV value for the best effect. At that the mobility of these molecules would be very low at usual temperatures.

At high pressures and temperatures (600K-900K) the additive molecules have high mobility, so they can penetrate throw open ends into nanotube quite easily together with molecular hydrogen.

These additive molecules divide whole volume of nanotube on separate pieces in which molecular hydrogen is locked. After temperature decreasing the mobility of additive molecules is strongly decreased and hydrogen become accumulated inside all pieces of the nanotube.

As an example- it was investigated the hydrogen adsorption inside CNT (7,7). The chosen impurity was 1,1,3,3,7,7-sextometylbicyclo[2,2,2]octan ?14H26. It was shown that the hydrogen could be very effectively locked inside CNT at usual temperatures and can be freely released at temperature  $T\approx750$ K.

### Single-walled carbon nanotubes/photosynthetic reaction center protein composite: a possible candidate for photovoltaics 8

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Carbon nanotubes are a major focus of bionanotechnology since they offer the possibility of integrating them with biomatter, e.g. proteins, to create protein-based nanodevices with formidable capabilities. Among the proteins the photoreceptors are very promising because they can be activated by light in the visible and/or in the near infrared range. We report the study of the photosynthetic reaction center (RC) pigment protein complex attached to single walled carbon nanotubes (SWNT). The protein, the well known redox-active enzyme in which light energy initiates a chain of intraprotein electron transport reactions, was purified from purple bacterium Rhodobacter sphaeroides R-26. The change in the kinetics of light absorption, Electron Spin Resonance and electrical conductivity measurements induced by illumination indicates a charge dynamics between the RC and the SWNT. In our experiment, the photochemical activity of the RC/SWNT complex remained stable for several weeks. The stabilization of light induced charges by the carbon nanotube environment opens the possibility to new applications, the most promising one being in energy conversion in photovoltaic devices

#### Investigation of the shift of Raman modes on graphene flakes

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In the present work samples of graphene were prepared by rubbing graphite on substrates patterned with markers for position identification. Unambiguous identification of mono- and bi-layers was achieved by analyzing the shape of the Raman D\* mode according (1). Raman spectroscopy can additionally provide information such as the presence of defects or doping. We observed shifts in the position of the Raman modes in various as-prepared graphene flakes, suggesting presence of non-intentional doping or stress, as also confirmed by electrical conductance measurements. The shift of D\* position could reach a value as large as 20cm-1. In order to identify the origin of the shift, we checked the effect of various source materials for the preparation of graphene (natural single crystal of graphite and HOPG), different substrates (Si/SiO2, Al2O3) and the effect of annealing. A systematic shift was found only when measuring the Raman modes on flakes before and after deposition of Cr/Au electrodes. We also investigated the dependence of the Raman shift on temperature by heating the graphene from 35 to 300°C in argon. We found a temperature coefficient of -0.03cm-1/K for the shift of D\* mode in this temperature range.

(1) Ferrari AC, Meyer JC, et al., Phys. Rev. Lett. 97, (2006), 187401

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#### SP Electron - phonon coupling in suspended carbon nanotube quantum dots

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We study the vibrational modes of single suspended carbon nanotubes (CNT's) in low temperature transport measurements. The single electron tunneling excitation spectrum of the CNT-embedded quantum dots displays regular excited states at an energy scale compatible to the longitudinal (stretching) mode. A good agreement with Franck-Condon theory has been observed. At low bias, current is suppressed by phonon blockade-like effects up to an excitation number of serveral vibrational quanta. However, the mechanism for such a strong electron-phonon coupling of this mode is still unclear, as an extremely high coupling is mainly expected for the lateral (bending) modes of the nanotube. Our work targets this interplay of effects, also aiming towards resolving the bending mode in transport.

#### SP Nanostructured thin films for gas sensing applications

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A number of important characteristics for preparation of nanostructured thin films with foci on Laser Ablation (LA), Laser-assisted Chemical Vapour Decomposition (LCVD) and Advanced Gas Deposition (AGD) are presented. The preparation techniques allow a wide variety of materials to be prepared. Size-related features and structures of the deposited layers are compared and associated with process parameters. Materials characterizations include TEM, SEM, XRD, XPS, elastic recoil detection analysis, neutron diffraction and IR spectroscopy methods. Metal-oxide (primarily WO<sub>3</sub>) nanoporous films are deposited for simple electronic gas sensor applications detecting hazardous gases such as H<sub>2</sub>S, NO<sub>2</sub>, ethanol and CO. Different methods are presented for improving sensitivity and most importantly, chemical selectivity of the devices. Finally, a novel technique is presented and discussed for chemical sensing. It uses resistance fluctuation spectroscopy for determining the power density spectra of the fluctuations of the sensor response. It is shown that nanoparticle sensor films can exhibit excellent sensitivity and improved chemical selectivity when using the temperature modulation and resistance fluctuation spectroscopy techniques.

#### SP Torsional Electromechanics of Carbon Nanotubes

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Carbon nanotubes are known to be distinctly metallic or semiconducting depending on their diameter and chirality. Here we show that continuously varying the chirality by mechanical torsion can induce conductance oscillations, which can be attributed to metal-semiconductor periodic transitions. The phenomenon is observed in multi-walled carbon nanotubes, where both the torque and the current are shown to be carried predominantly by the outermost wall. The oscillation period with torsion is consistent with the theoretical shifting of the corners of the first Brillouin zone of graphene across different subbands allowed in the nanotube. Beyond a critical torsion, the conductance irreversibly drops due to torsional failure, allowing us to determine the torsional strength of carbon nanotubes. Our experiments indicate that carbon nanotubes could be used as self-sensing torsional springs for nanoelectromechanical systems (NEMS).

- [1] T. Cohen-Karni, L. Segev, O. Srur-Lavi, S. R. Cohen, E. Joselevich, Torsional electromechanical quantum oscillations in carbon nanotubes, *Nature Nanotechnology* **2006**, *1*, 36.
- [2] E. Joselevich, Twisting nanotubes: From torsion to chirality, ChemPhysChem 2006, 7, 1405.

#### Infrared and Raman spectra of cubane-fullrene systems

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Fullerene-cubane systems combine two platonic forms of extreme high symmetry: the cube and the icosahedron. Symmetry lowering in these solids, caused by any external effect, can be probed with high sensitivity by vibrational spectroscopy. We present infrared and Raman spectra of fullerene-cubane systems based on  $C_{60}$  and  $C_{70}$  both in the rotor-stator (monomer) and polymer phases.

In the monomer phases, the spectra reflect the symmetry of the environment caused by the rotor-stator nature: they are superpositions of the spectra of the constituents, almost identical to those expected for isolated molecules. It is worth noting that the cubane spectra show higher symmetry than that in solid cubane.

Polymerization can occur on heating or by a photochemical reaction. Vibrational spectra before and after polymerization reveal that this reaction results in a copolymer with the fullerene balls remaining closed and the cubane cube opening up. We will present a detailed study based on symmetry considerations and propose a model for the connection pattern in the polymers.

#### Filled carbon nanotubes for biomedical applications

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Leibniz Institute for Solid State and Materials Research IFW Dresden

There is a fastly increasing interest in applying carbon nanotubes (CNT) in biomedicine since they can be filled with tailored material, thereby acting as chemically and mechanically stable nano-containers. The carbon shells provide wear resistance and oxidation protection, can stabilize novel magnetic molecules and enhance the possibilities for exohedral (e.g. bio-) functionalisation of the nanoparticles. We report on a systematic approach to exploit the potential of filled CNT to act as magnetic nano-heaters, drugcarrier systems and sensors which allow a diagnostic and therapeutic usage on a cellular level. We have studied the magnetic properties of individual, iron-filled multi-walled CNT which imply their potential for magnetic nano-heaters. Indeed, there is a substantial temperature increase of Fe-CNT treated muscle tissue under applied AC magnetic fields. Moreover, we successfully inserted ferromagnetic CNT into cancer cells which shows their applicability for local in-situ-heating (hyperthermia). Filled CNT can also be used for diagnostic purposes since the nanocontainers can be filled with appropriate sensor materials. One example is their filling with CuI, which exhibits a strongly temperature dependent NMR signal so that nanoscaled contactless temperature sensors are realised. The potential for drug-delivery by CNT is demonstrated by inserting cytostatics into CNT.

#### Towards applications of lyotropic liquid crystal-aligned carbon nanotubes

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Jan Lagerwall<sup>1</sup>, Giusy Scalia<sup>2</sup>, Clemens von Bühler<sup>1</sup>, Siegmar Roth<sup>2</sup>, Frank Giesselmann<sup>1</sup>

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We recently demonstrated [1] that carbon nanotubes (CNTs) can be aligned and at the same time well dispersed in lyotropic liquid crystals based on the standard surfactant SDS. Since then we have taken the study to a more applied level, addressing a number of practical issues. Here we present the results of our recent research efforts, currently focusing on two main issues:

- by combining an- and cationic surfactants, the former counteracting CNT aggregation and the latter forming the liquid crystal phase, we aim to weaken the depletion attraction, thus allowing substantially higher CNT loading,
- by adding polymerizable and crosslinkable components we wish to fixate the liquid crystal-templated structure, yielding a soft solid with well dispersed and uniaxially aligned CNTs.
- [1] J. Lagerwall et al., Adv. Mater. in press; J. Lagerwall et al. Phys. Status Solidi B, 243, p. 3046 (2006)

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#### SP Graphite under the magnetic force microscope

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Recently, the first direct evidence of the ferromagnetic spin polarization in damaged graphite was obtained in an element-specific manner (H.Ohldag et al., cond-mat/0609478). In an attempt to find the defect structures responsible for the triggering of magnetic ordering, we have undertaken the magnetic force microscopy study of intrinsic defects at the surface of highly oriented pyrolytic graphite. We demonstrate an experimental fact that two types of sharp step edges exist on the surface: magnetically dead and magnetically active ones. The latter provide the magnetic gradient response exactly at the position of the step. Having analyzed and excluded all possible contributions to the measured magnetic images, such as electrostatic, electrochemical and capillary forces, workfunction differences and dissipative effects, we conclude that two type of effects cannot be explained without invoking inconvential magnetic properties of graphite: (i) Magnetic force gradient signals on the edges which are sensitive to the polarity of the tip magnetization and (ii) Strong repulsive signals from the single-layer graphene stripes.

#### SP Linear and nonlinear transport across carbon nanotube quantum dots

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We present a low energy-theory for non-linear transport in finite-size interacting single-wall carbon nanotubes. It is based on a microscopic model for the interacting  $p_z$  electrons and successive bosonization. We consider weak coupling to the leads and derive equations of motion for the reduced density matrix. We focus on the case of large-diameter nanotubes where exchange effects can be neglected. In this situation the energy spectrum is highly degenerate. Due to the multiple degeneracy, diagonal as well as off-diagonal (coherences) elements of the density matrix contribute to the nonlinear transport. At low bias, a four-electron periodicity with a characteristic ratio between adjacent peaks is predicted. Our results are in quantitative agreement with recent experiments.

#### SP Thermal transfer in SWNTs and peapods under UV-irradiation

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C<sub>60</sub> encapsulated in SWNTs (peapods) have been shown able to coalesce into contained distorted capsules or SWNT upon electron irradiation and/or thermal treatment, thereby eventually forming DWNTs. Similar coalescence effects have been observed using Infra-Red and Ultra-Violet (UV) photon irradiation, as followed by Raman spectroscopy. However, related coalescence mechanisms are unclear. We report here the results of UV irradiation experiments in vacuum on SWNTs and peapods, as followed by in-situ Raman spectroscopy and transmission electron microscopy. By increasing the laser power up to 500mW, photon absorption was found to generate local temperature increase up to 1000°C. Ultraviolet micro-Raman measurements were used to record spectra free of black body radiation. The changes in line width differ considerably for the SWNT-related G+ and G- bands respectively. This gives evidence that the phonon decay process in the nanotubes differs in axial with respect to radial directions. Meanwhile, a specific sensitivity to oxidation of the nanotubes from peapods was revealed, due the fullerene-catalysed dissociation of molecular oxygen traces into active species. In addition, both silica and diamond substrates were used. The different thermal conductivity of the substrates has the effect of changing the laser power levels needed to induce structural transformations.

Inkjet printing of single-walled carbon nanotubes and SWCNT/PEDOT-PSS composites SF Tero Mustonen<sup>1</sup>, Géza Tóth<sup>1</sup>, Krisztián Kordás<sup>1</sup>, Jari Penttilä<sup>2</sup>, Panu Helistö<sup>2</sup>, Heikki Seppä<sup>2</sup>, Heli Jantunen<sup>1</sup>

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Transparent and conductive patterns of carboxyl functionalized single-walled carbon nanotubes (SWCNT-COOHs) and the composites of those with poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) were deposited on various substrates by the inkjet printing technique. For low print repetitions, the SWCNT-COOH/PEDOT-PSS composite patterns show enhanced conductance as compared to the corresponding PEDOT-PSS conductors. The results suggest a decreased percolation threshold for the printed composite since the nanotubes establish electrical interconnections between the separate PEDOT-PSS (conductive phase) islands being dispersed in the insulating PSS-phase. However, the interaction between PEDOT-PSS and SWCNTs becomes insignificant and the conductivity is not enhanced by the nanotubes, when the amount of PEDOT-PSS is sufficient to form a continuous conducting phase. Up to now, patterns having sheet resistivities as low as  $\approx 1 \text{ kO/square}$  could be achieved. Though there is a trade-off between transparency and conductivity - we achieved highly transparent patterns  $T\approx 0.9$  with a reasonably low resistivity of  $\approx 10 \text{ kO/square}$ . The ink and printing method proposed here offer new alternatives of conventional transparent conductive materials based on either polymers or indium oxides; and pose scaleable production of cost-effective transparent electronics.

### Conduction Electron Spin Resonance study of doped Single-Walled Carbon Nanotubes and SP Related Structures 20

<u>Balint Náfrádi</u><sup>1</sup>, Norbert Nemes<sup>2</sup>, Ferenc Simon<sup>3</sup>, Laszlo Forró<sup>1</sup>, Hans Kuzmany<sup>4</sup>

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Conduction electron spin resonance (CESR) can probe the doping dependence of the electronic structure. The temperature-independent Pauli paramagnetism of conduction electrons is a signature of metallicity, and  $\chi_P$  is a direct measure of the density of states at the Fermi energy. Also, comparison of the temperature and doping dependences of the CESR-linewidth with the momentum relaxation rate can reveal non-Fermi-liquid and/or reduced dimensionality effects. A small ESR line already present in well purified undoped samples and its temperature dependence reveals a striking 'super-Curie' paramagnetic rise as we reported earlier [1]. Here we report new results on the electron spin resonance of alkali-doped single-walled carbon naotubes, peapods and double walled carbon nanotubes.

[1] Nafradi B, Nemes NM, Feher T, et al. PHYSICA STATUS SOLIDI B-BASIC SOLID STATE PHYSICS 243 (13): 3106-3110 NOV 2006

#### Decoherence and Spin Relaxation in P@C<sub>60</sub>

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 $P@C_{60}$  and other group V endohedral fullerenes have recently been proposed as quantum bits for a scalable quantum computer architecture due to their long spin relaxation times.

In this study we investigate the mechanisms of spin relaxation in polycrystalline  $P@C_{60}$ . We find that the spin-lattice is influenced mainly by the fluctuations of the hyperfine constant, caused by the oscillations of the endohedral atom inside the fullerene carbon cage. The spin-spin relaxation measurements of samples with low spin concentration reveal no contribution of instantaneous diffusion to the decoherence and that the latter is determined by spectral diffusion. We managed to increase the decoherence time  $T_2$  up to  $416.6 \,\mu s$  using the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence.

#### SP GENERATION of SUB-PICOSECOND PULSES in SOLID STATE LASERS WITH SAT-22 URABLE ABSORBERS BASED ON CELLULOSE DERIVATIVES INCORPORATING

<u>Elena Obraztsova</u><sup>1</sup>, Anton Tausenev<sup>2</sup>, Anatolii Lobach<sup>3</sup>, Sergey Garnov<sup>1</sup>, Alexander Chernov<sup>4</sup>, Vitaly Konov<sup>1</sup>, Petr Kryukov<sup>2</sup>, Eugeny Dianov<sup>2</sup>

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Non-linear optical properties of single-wall carbon nanotubes (SWNTs) is a basis for new optical media for ultrafast modulation of laser beams. Earlier we have developed three types of such media: aqueous suspensions [1]; polymer films with homogeneously distributed nanotubes; nanotube films, grown directly onto quartz substrates. Working as saturable absorbers, such media are efficient for ultrafast (sub-picosecond) modulation of output beams in different solid-state lasers (1.06-1.56 mkm). In this work we demonstrate a new type of saturable absorbers based on cellulose derivatives incorporating SWNTs. They have been used both in lasers with bulk elements (YAP:Nd, 1.34 mkm) and in Er3+-fiber lasers (1.5 mkm) with liner and circular resonators [2]. The spectra and autocorrelation functions for output pulses have been measured. The minimal pulse duration achieved was 470 fs. The cellulose provided a high concentration of nanotube phase [3], a small film thickness (8-10 mkm) and a low pump threshold (25-30 mW) in regime of ultrashort pulse generation.

The work is supported by RFBR 06-02-08151 and by RAS Presidium programs.

- 1. N.N. Il'ichev, E.D. Obraztsova, et al., Quantum Electronics 34(2004)572.
- 2. A.V. Tausenev, E.D. Obraztsova et al., Quantum electronics (2007) (in press).
- 3. N. Minami et al., Appl. Phys. Lett. 88(2006)093123.

#### SP Functionalised carbon nanotubes for integrated nano-electronic sensors

Yann Pouillon, Angel Rubio

23

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Despite an exponentially increasing interest for the use of carbon nanotubes (CNTs) as sensors in industrial or medical environments, most of the efforts carried out so far still have to address the issue of reducing the number of sensing elements. The unreliable contacts between the CNTs and the electrical circuit are also greatly hindering progresses in this field, and call for a better theoretical understanding. The SANES (Self-Adjusting Nano-Electronic Sensors) project aims at designing, building, and characterising multifunctional nanotube-based sensor micromodules, able to monitor simultaneously temperature, pressure, gas concentration, etc., in various conditions. These modules will be integrated into a matchbox-sized electronic device which will hopefully be produced industrially afterwards. The sensing unit itself is made of a small number of functionalised CNTs.

In order to provide the experimentalists with a valuable insight into the electronic properties of these CNTs, and to speed-up the process of selection of the functional molecules, we focus on the transport properties of single functionalised metallic and semi-conducting CNTs. We study the contact between a CNT and different metallic pads, compare the influence of a large number of interesting functional groups for gas detection, and investigate the effects of the presence of water.

### SP Low Temperature Spin-Transport and Structural Characterisation of Single Wall Carbon Nanotubes

<u>D. Preusche</u><sup>1</sup>, E. Pallecchi<sup>1</sup>, S. Schmiedmeier<sup>1</sup>, S. Jhang<sup>1</sup>, B. Witkamp<sup>2</sup>, H. van der Zant<sup>2</sup>, C. Strunk<sup>1</sup> Universität Regensburg <sup>2</sup>TU Delft

We investigate spin-dependent transport in and characterise the structure of individual carbon nanotubes. Low temperature magnetoconductance was found to be also gate-dependent and showed spin-valve effect, Coulomb blockade and spin-1/2 Kondo effect. Furthermore, the chiral indices of suspended nanotubes can be identified by means of selected area electron diffraction with a TEM. The micromagnetic properties of the ferromagnetic PdFe contacts as well as their hysteretic magnetic switching have been studied by means of Lorentz microscopy and SQUID measurements. When performed on the same nanotube, structural characterisation will facilitate the interpretation of the magnetoconductance measurements and allow more direct comparison with theoretical simulations.

#### Will spin-relaxation times in molecular magnets permit quantum information

SP

Arzhang Ardavan<sup>1</sup>, <u>Olivier Rival</u><sup>1</sup>, John Morton<sup>1</sup>, Stephen Blundell<sup>1</sup>, Alexei Tyryshkin<sup>2</sup>, Grigore Timco<sup>3</sup>, **25** Richard Winpenny<sup>3</sup>

<sup>1</sup>Clarendon Laboratory, Department of Physics, University of Oxford, United Kingdom <sup>2</sup>Department of Electrical Engineering, Princeton University, United States <sup>3</sup>Department of Chemistry, University of Manchester, United Kingdom

Certain computational tasks can be efficiently implemented using quantum logic, in which the information-carrying elements are permitted to exist in quantum superpositions. But a physical system suitable for embodying quantum bits (qubits) must be identified first. Some scenarios employ electron spins in the solid state, for example phosphorous donors in silicon, quantum dots, heterostructures and endohedral fullerenes, motivated by the long relaxation times in these systems. An alternative electron-spin based proposal exploits the large number of states and the non-degenerate transitions available in high-spin molecular magnets. Although these advantages have stimulated vigorous research in molecular magnets, the key question of whether the intrinsic spin relaxation times are long enough has hitherto remained unaddressed.

Using X-band pulsed electron spin resonance, we measure the intrinsic spin-lattice  $(T_1)$  and phase coherence  $(T_2)$  relaxation times in molecular nanomagnets for the first time. In  $\operatorname{Cr}_7 M$  heterometallic wheels, with  $M=\operatorname{Ni}$  and  $\operatorname{Mn}$ , phase coherence relaxation is dominated by the coupling of the electron spin to protons within the molecule. In deuterated samples  $T_2$  reaches  $3\approx \mu s$  at low temperatures, which is several orders of magnitude longer than the duration of spin manipulations, satisfying a prerequisite for the deployment of molecular nanomagnets in quantum information applications.

#### Molecular Scale Memory Elements

SP 26

<u>Marina Zavodchikova</u><sup>1</sup>, Andreas Johansson<sup>2</sup>, Marcus Rinkiö<sup>1</sup>, Päivi Törmä<sup>3</sup>, Esko Kauppinen<sup>4</sup>

<sup>1</sup>Researcher <sup>2</sup>Post-doctoral researcher <sup>3</sup>Professor at the University of Jyväskylä <sup>4</sup>Professor at Helsinki University of Technology

We investigate the potential solutions for the fabrication of future molecular scale memory elements. The studied devices are carbon nanotube field-effect transistors (CNT-FETs) based on single-walled carbon nanotubes (SWCNTs) as conduction channels. SWCNTs, with a diameter of 0,6-2 nm, have been produced by a novel aerosol method (floating catalyst)1. The gate insulator film has a crucial influence on the operation of proposed device structure. For a strong capacitive coupling and enabling gate voltages, a thin dielectrically strong film is required. On the other hand, in order to achieve the desired hysteretic behavior for non-volatile memory, the gate-nanotube coupling has to include mobile charge(s) within the gate-insulator or at some interface in the system. Measurement results in various conditions exhibiting possible charge trapping as well as the device fabrication technique will be demonstrated.

- 1. A.G. Nasibulin, A. Moisala, D.P. Brown, H. Jiang, and E.I. Kauppinen, Chem. Phys. Lett. 402 (2005) 227
- 2. J.B. Cui, R.Sordan, M.Burghard, and K.Kern, Appl. Phys. Lett. 81 (2002) 3260
- 3. H. Lin, S. Tiwari, Appl. Phys. Lett. 89 (2006) 073507

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#### Graphene & Graphite 1

8:30 – 9:30 K. NOVOSELOV, UK

QED in a Pencil Trace

9:30 - 10:00 E. McCANN, UK

Asymmetry gap in the electronic band structure of bilayer graphene

10:00-10:30 Coffee break

10:30 - 11:00 E. ROTENBERG, US

The spectral function of monolayer graphene films

#### COMMERCIALS

11:00 - 11:30 P. JARILLO-HERRERO, US

Transport Measurements in Graphene

11:30 – 12:00 A. MORPURGO, NL

Bipolar Supercurrent in Graphene

12:00 – 17:00 Mini Workshops

17:00 - 18:30 Dinner

#### Graphene & Graphite 2

18:30 – 19:00 A.C. FERRARI, UK

Raman Spectroscopy of Graphene and Doped Graphene

19:00 – 19:30 M. LAZZERI, FR

Breakdown of the adiabatic Born-Oppenheimer approximation in graphene

19:30 – 20:00 A. GRÜNEIS, DE

Low energy electronic structure of graphite by angle resolved photoemission spectroscopy

#### Poster I (PTU)

G&G1

1

#### 8:30 QED in a Pencil Trace

Kostya Novoselov, Andre Geim

School of Physics & Astronomy, University of Manchester, Manchester, M13 9PL, UK

When one writes by a pencil, thin flakes of graphite are left on a surface. Some of them are only one angstrom thick and can be viewed as individual atomic planes cleaved away from the bulk. This strictly two dimensional material called graphene was presumed not to exist in the free state and remained undiscovered until the last year. In fact, there exists a whole class of such two-dimensional crystals. The most amazing things about graphene probably is that its electrons move with little scattering over huge (submicron) distances as if they were completely insensitive to the environment only a couple of angstroms away. Moreover, whereas electronic properties of other materials are commonly described by quasiparticles that obey the Schrödinger equation, electron transport in graphene is different: It is governed by the Dirac equation so that charge carriers in graphene mimic relativistic particles with zero rest mass

#### 9:30 Asymmetry gap in the electronic band structure of bilayer graphene

#### G&G1 Edward McCann

2 University of Lancaster

Recently there has been a huge amount of theoretical interest in the low energy electronic properties of ultrathin graphite films, including graphene monolayers and bilayers. This activity followed the successful fabrication of ultrathin graphite films and subsequent measurements of an unusual sequencing of quantum Hall effect plateaus. While the Hamiltonian for low energy electrons in a monolayer describes Diraclike chiral quasiparticles with Berry phase  $\pi$ , the low energy Hamiltonian for a bilayer describes chiral quasiparticles with a parabolic dispersion and Berry phase  $2\pi$  [1].

A tight binding model is used to calculate the band structure of bilayer graphene in the presence of a potential difference between the layers that opens a gap between the conduction and valence bands [2]. We describe imperfect screening of an external gate, employed primarily to control the density of electrons on the bilayer, resulting in a potential difference between the layers and a density dependent gap, and we discuss the influence of a finite asymmetry gap at zero density on observations of the quantum Hall effect.

- [1] E. McCann and V.I. Fal'ko, Phys. Rev. Lett. 96, 086805 (2006).
- [2] E. McCann, Phys. Rev. B 74, 161403(R) (2006).

#### The spectral function of monolayer graphene films

10:30 G&G1

Aaron Bostwick<sup>1</sup>, Taisuke Ohta<sup>1</sup>, Jessica McChesney<sup>1</sup>, Thomas Seyller<sup>2</sup>, Karsten Horn<sup>3</sup>, <u>Eli Rotenberg</u><sup>1</sup> Carlamente Berkeley National Laboratory <sup>2</sup>Univ. Erlangen-Nürnberg <sup>3</sup>Fritz Haber Institute der MPG, Berlin

Graphene, a 2D honeycomb lattice of carbon atoms, is the building block of graphite, fullerenes, and nanotubes and has fascinating electronic properties deriving from the effectively massless, relativistic behaviour of its charge carriers. The study of many-body interactions amongst its carriers is of interest owing to their contribution to superconductivity and other phenomena.

We describe the synthesis of graphene thin films (1-4 layers) grown on insulating silicon carbide wafers and the evolution of their electronic band structure using angle-resolved photoemission spectroscopy (ARPES) [1,2]. For monolayer graphene, we can determine the electronic spectral function, which encodes the many-body interactions amongst the quasiparticles in the system—namely the charge and vibrational excitations. Our measurements show that the bands around the Dirac crossing point are heavily renormalized by electron-electron, electron-plasmon, and electron-phonon coupling, showing that these interactions must be considered on an equal footing in attempts to understand the quasiparticle dynamics in graphene and related systems.

- [1] Bostwick, A., Ohta, T., Seyller, T., Horn, K. & Rotenberg, E. Quasiparticle Dynamics in Graphene. Nature Physics, 3, 36 (2006).
- [2] Ohta, T., Bostwick, A., Seyller, T., Horn, K. & Rotenberg, E. Controlling the Electronic Structure of Bilayer Graphene. Science **313**, 951-954 (2006).

### Transport Measurements in Graphene P. Jarillo-Herrero

11:00 G&G1

In this talk I will review recent experiments at Columbia on electronic transport in graphene nanostructures. We define the nanostructures by e-beam lithography followed by oxigen plasma etch. In this way we can pattern nanoribbons, rings, etc. I will comment on the band gap engineering of graphene nanoribbons and phase coherent transport in graphene devices.

#### Bipolar Supercurrent in Graphene

Alberto Morpurgo Delft University 11:30 G&G1 5

Measurements of phase coherent transport in graphene have so far given unexpected results. For instance, the magnitude of weak localization appears to be sample dependent and it is often suppressed or even absent. Another phenomena, that like weak-localization depends on the presence of phase coherence and of time reversal symmetry, is Josephson supercurrent. Here, I report the observation of supercurrent in graphene Josephson junctions. We have observed supercurrent in all the devices that we have fabricated approximately 15-, four of which could be unambiguously proven from quantum Hall measurements to consist of single-layer graphene. Using a gate electrode, we have measured the dependence of the supercurrent on carrier density. Supercurrent is present irrespective of gate voltage, both when the Fermi level is located in the conduction or in the valence band of graphene, and it remains finite even when the Fermi level is swept across the Dirac point. I will conclude by emphasizing the conceptual difference between the microscopic interference processes responsible for the presence of supercurrent and of weak-localization.

This work has been done in collaboration with H. Heersche, P. Jarillo-Herrero, J. Oostinga, and L. Vandersypen.

#### 18:30 Raman Spectroscopy of Graphene and Doped Graphene

A.C. Ferrari<sup>1</sup>, S. Pisana<sup>1</sup>, M. Lazzeri<sup>2</sup>, C. Casiraghi<sup>1</sup>, J.C. Meyer<sup>3</sup>, V Scardaci<sup>1</sup>, S Piscanec<sup>1</sup>, K. Novoselov<sup>4</sup>, G&G2A. Geim<sup>4</sup>, F. Mauri<sup>2</sup>

<sup>1</sup>Cambridge University, Engineering Department, Cambridge CB3 0FA, UK <sup>2</sup>Institut de Mineralogie et de Physique des Milieux Condenses, Paris cedex 05, France <sup>3</sup>Max Planck Institute for Solid State Research, Stuttgart 70569, Germany <sup>4</sup>Department of Physics and Astronomy, University of Manchester, Manchester, M13 9PL, UK

We present the Raman spectra of graphene and graphene layers [1]. The G and 2D Raman peaks change in shape, position and relative intensity with number of layers. This reflects the evolution of the electronic structure and electron-phonon interactions [1,2]. We give a set of simple empirical correlations between Raman fit parameters and number of layers. Transmission electron microscopy and electron diffraction validate the Raman layer count. We also report a detailed I(D)/I(G) mapping of graphene edges oriented at different relative angles and compare the temperature dependence of the Raman spectra of graphene, graphite and nanotubes. We then consider the effects of doping on the Raman spectra of graphene [3]. The Fermi energy is tuned by applying a gate-voltage. We show that this induces a stiffening of the Raman G peak for both holes and electrons doping [3]. Thus Raman spectroscopy can also be used to monitor the doping level. Finally we discuss the implications for the interpretation of the Raman spectra of nanotubes [4].

- 1. A. C. Ferrari et al. Phys. Rev. Lett. 97, 187401 (2006)
- 2. S. Piscanec et al. Phys. Rev. Lett. 93, 185503 (2004)
- 3. S. Pisana et al. Nature Materials (in press), Cond-Mat 0611714 (2006)
- 4. S. Piscanec et al. Phys. Rev. B 75, 1 (2007)

#### 19:00 Breakdown of the adiabatic Born-Oppenheimer approximation in graphene

M. Lazzeri<sup>1</sup>, F. Mauri<sup>1</sup>, K.S. Novoselov<sup>2</sup>, A. Geim<sup>2</sup>, S. Pisana<sup>3</sup>, C. Casiraghi<sup>3</sup>, A.C. Ferrari<sup>3</sup>
IMPMC, Universites Paris 6-7, CNRS, IPGP, Paris, France <sup>2</sup>Department of Physics and Astronomy, University of Manchester, Manchester, M13 9PL, UK <sup>3</sup>Cambridge University, Engineering Department, Cambridge CB3 0FA, UK

The evolution of the Raman G peak (the zone-center E2g phonon) of graphene with doping provides a remarkable failure of the adiabatic Born-Oppenheimer (ABO) approximation [1,2]. In particular, a stiffening of the Raman G peak frequency as a function of the doping has been recently measured for both hole and electron doping [2,3]. I will present a study of the frequency of the graphene E2g phonon using i) the ABO approximation and ii) time-dependent perturbation-theory to explore dynamic effects beyond ABO. The two approaches provide different results. While, the adiabatic phonon-frequency weakly depends on the doping, the dynamic one rapidly varies, in agreement with measurements. Graphene pibands have a two-dimensional massless dispersion, described by Dirac cones. The E2g vibrations cause rigid oscillations of the Dirac-cones. If the electrons followed adiabatically these oscillations, no change in the phonon frequency would be observed. Instead, since the electron-momentum relaxation near the Fermi level is much slower than the phonon motion, the electrons do not follow the Dirac-cone displacements. This invalidates the adiabatic approximation and results in the observed phonon stiffening.

- [1] M.Lazzeri, F.Mauri, Phys. Rev. Lett. 97, 266407 (2006)
- [2] S.Pisana et al. Nature Materials (in press), cond-mat/0611714
- [3] J.Yan et al. cond-mat/0612634

#### 19:30 Low energy electronic structure of graphite by angle resolved photoemission spectroscopy <u>Alexander Grüneis</u><sup>1</sup>, Thomas Pichler<sup>1</sup>, Claudio Attaccalite<sup>2</sup>, Ludger Wirtz<sup>2</sup>, Angel Rubio<sup>3</sup> G&G2

<sup>1</sup>IFW Dresden <sup>2</sup>Institute for Electronics, Microelectronics, Dept. ISEN B.P. 60069 59652 Villeneuve d'Ascqm, France <sup>3</sup>Dept. Fisica de Materiales, Donostia International Physics Center and European Theoretical Spectroscopy Facility, Spain

The low energy electronic structure of semi-metallic graphite is investigated with high resolution angle resolved photoemission in the whole three dimensional Brillouin zone. The experimental band structure is compared quantitatively to calculations at the tight-binding and ab-initio level. We find that the electron band structure of graphite is strongly renormalized due to correlations. The local density approximation underestimates the band dispersion and the Fermi velocities. In the GW approximation, correlation effects are treated properly, yielding a good agreement to the experiment. In-situ electron doping by alkali metals allows one to measure the conduction band dispersion near the Fermi level and to map the tiny electron and hole pockets of graphite. A new set of tight-binding parameters that reproduce the experimental dispersion is given.

G&G22

3

1

### Morphology and bonding structure of fullerene-like nanocomposite C:Ni ( $\approx 30$ at%.) thin PTU films grown by ion beam sputtering

<u>Gintautas Abrasonis</u><sup>1</sup>, Arndt Mücklich<sup>1</sup>, Karsten Kuepper<sup>1</sup>, Matthias Krause<sup>1</sup>, Ulrich Kreissig<sup>1</sup>, Andreas Kolitsch<sup>1</sup>, Wolfhard Möller<sup>1</sup>, Katarina Sedlácková<sup>2</sup>, György Radnóczi<sup>2</sup>, Ricardo Torres<sup>3</sup>, Ignacio Jiménez<sup>3</sup>, Raul Gago<sup>4</sup>

<sup>1</sup>Forschungszentrum Dresden-Rossendorf, Dresden, Germany <sup>2</sup>Research Institute for Technical Physics and Materials Science, Budapest, Hungary <sup>3</sup>Instituto de Ciencia de Materiales de Madrid, Madrid, Spain <sup>4</sup>Centro de Micro-Análisis de Materiales, Universidad Autónoma de Madrid, Spain

The morphology and bonding structure of nanocomposite C:Ni ( $\approx 30$  at.%) thin films grown by ion beam sputtering at different temperatures (RT-500°C) is investigated by means of X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray absorption near edge structure (XANES). XRD and XANES of the LII-LIII absorption edges of Ni reveal that at lower temperatures nickel is in the carbidic state whose signatures become more pronounced when the growth temperature increases up to  $\approx 300^{\circ}$ C. Further increase in the growth temperature results in XRD and XANES features resembling to those of metallic nickel. According to the TEM observations, nickel or nickel carbide nanoparticles embedded in a carbon matrix have a columnar structure with the diameter of  $\approx 2-5$  nm, which is typical for the films grown under surface diffusion dominated conditions for the structuring processes. At lower temperatures carbon is mainly in an amorphous state, while the transition into a fullerene-like structure, which consists of nickel nanoparticles wrapped in curved graphite sheets, can be clearly identified at  $\approx 200^{\circ}$ C. The present results show that the nickel nanoparticles act as nucleation centres for the formation of the fullerene-like structures in both carbidic and metallic states, provided that the temperature for surface diffusion during the deposition process is sufficiently high.

### FULLERENE CLUSTERS IN THE SYSTEM $C_{60}/\text{NMP}/\text{WATER}$ BY SMALL-ANGLE PTU NEUTRON SCATTERING $\mathbf{2}$

<u>V. Aksenov</u><sup>1</sup>, M. Avdeev<sup>2</sup>, T. Tropin<sup>2</sup>, O. Kyzyma<sup>3</sup>, M. Korobov<sup>4</sup>, L. Rosta<sup>5</sup>

<sup>1</sup>1 Russian Research Center "Kurchatov Institute", 2 Joint Institute for Nuclear Research <sup>2</sup>2 <sup>3</sup>2, 3 Physical Faculty, Kyiv Taras Shevchenko National University, Kyiv, Ukraine <sup>4</sup>4 Department of Chemistry, Moscow State University, Russia <sup>5</sup>5 Research Institute for Solid State Physics and Optics, Budapest, Hungary

Solutions of fullerenes in nitrogen-containing solvents constitute a specific class characterized by formation of fullerene clusters. We report the effect of cluster rearrangement in the system  $C_{60}/N$ -methylpyrrolidone (NMP) after addition of water (miscible with NMP) as observed by small-angle neutron scattering (SANS). In contrast to large (size more than 100 nm) clusters in pure NMP, the appearance of clusters with characteristic size within 10-100 nm in the NMP/water mixture is detected. The effect has a critical character and takes place only for the water relative content more than 40 %. Despite the small scattering, estimates of the mean scattering length density of the clusters by the SANS contrast variation can be done. The density is close to that corresponding to the packed structure of fullerene molecules. The effect depends on the time between preparation of the solution  $C_{60}/NMP$  and addition of water, the more the age of the initial solution the larger clusters are observed in the final solution. We connect this observation with the idea that fullerene cauterization in NMP has several stages. The added water influences the last structural level of clusters and destroys it. However, the mechanism of the interaction responsible for this effect is unclear.

#### PTU Caracterization of CVD Grown Single Wall Carbon Nanotube Films on Quartz Glass

Alberto Ansaldo<sup>1</sup>, Viera Skákalová<sup>2</sup>, Davide Ricci<sup>1</sup>, Ermanno Di Zitti<sup>1</sup>, Silvano Cincotti<sup>1</sup>, Siegmar Roth<sup>2</sup>
<sup>1</sup>Dipartimento di Ingegneria Biofisica ed Elettronica, Università di Genova, via Opera Pia 11a, I-16145

– Genova, Italy <sup>2</sup>Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 – Stuttgart, Germany

Transparent electronic materials are one of the most challenging applications of present technology. Transparent conductors and transistors are embedded in a large number of common use devices, in particular LCD and OLED screens. The rather low availability of indium tin oxide (ITO) forces industry to search for long term alternatives.

Sprayed carbon nanotubes networks have already proved that CNTs could be one of the most promising candidates both as transparent films [1] and for transparent and flexible electronics [2], but, due to the tendency of CNTs dispersed in solution to form bundles, the conductance is still far from that of ITO thin films.

One way to improve CNT transparent film performance could be to directly use a CVD grown CNT network. In this way, it should be possible to virtually eliminate bundling, mechanically induced defects, and presence of insulating molecules such as surfactants.

In this work we present our results concerning the properties and electrical performance of our as grown SWCNT transparent networks on quartz glass in comparison to a variety of differently prepared CNT films and ITO glass.

- [1] M.Kaempgen, G.S.Duesberg and S.Roth, "Transparent carbon nanotube coatings" Applied Surface Science, 2005, 252(2), pp425-429
- [2] E.Artukovic, M.Kaempgen, D.S.Hecht, S.Roth, and G. Grüner "Transparent and Flexible Carbon Nanotube Transistors", Nano Letters, 2005, 5(4), pp757–760

### PTU On the disparities from different feedstocks in the synthesis of carbon nanotubes in chemical vapour deposition

Alicja Bachmatiuk<sup>1</sup>, Ryszard Kalenczuk<sup>1</sup>, Mark Rümmeli<sup>2</sup>, Christian Kramberger<sup>2</sup>, Thomas Pichler<sup>2</sup>, Thomas Gemming<sup>2</sup>, Ewa Borowiak-Palen<sup>1</sup>

<sup>1</sup>1) Centre of Knowledge Based Nanomaterials and Technologies, Institute of Chemical Engineering and Chemical Technology, Szczecin <sup>2</sup>2) Leibniz Institute for Solid State and Materials Research Dresden, Germany

Of the many means for carbon nanotube (CNT) synthesis, chemical vapour deposition (CVD shows the most promise for industrial scale production. Further, there are additional advantages to the CVD synthesis of nanotubes. Unlike the arc-discharge and laser evaporation routes for the synthesis of CNT, CVD is capable of growing nanotubes directly on a desired substrate, whereas the nanotubes must be collected in the other growth techniques. The growth sites are controllable by careful deposition of the catalyst. Also, no other growth methods have been developed for the production of vertically aligned nanotubes. It is for these reasons that CVD is the most popular CNT synthesis technique. The flexibility of CVD allows a great variety of gases and vapours to be used as the carbon feedstock. However, few if any studies on the different feedstock's have been conducted and in these study we look at some of the disparities for a variety of feedstock's in terms of the obtained nanotubes and the causes behind these differences.

### PTU Raman and Absorption Spectroscopy of the Doping of Carbon Nanotubes in Water Based Suspensions

Priya Baskar Rao, Hugh Byrne

Focas Institute, Dublin Institute of Technology

Here we report on concentration dependent studies of HiPco Single Wall Nanotubes (SWNTs) in aqueous surfactant, Sodium Dodecyl Benzene Sulphonate (SDBS) and Triton X solutions, the solubility limits, the effects of sonication and solution pH, using Raman and UV/vis/NIR absorption spectroscopies. Curve fitting was performed for the Radial Breathing Modes of the Raman spectra, for all the concentrations to analyse the debundling of the nanotubes. Clear regions of debundling are indicated and the results correlate well with analysis by Atomic force microscopy.

The pH of the solution also plays a major role showing a significant change in the intensities of both the absorption spectra and Raman spectra giving fine details about protonation and deprotontaion of the electronic states by decreasing and increasing the concentration of H+ ions respectively. Both the RBMs and the G-line were analysed to study the system under investigation using curve fitting. We have investigated the value of the rate constant using a simple regression for different tubes diameters and the relationship between the rate constant and the diameter of the tubes.

#### Extreme Thermal Stability of Carbon Nanotubes

PTU

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Gavi Begtrup<sup>1</sup>, Keith Ray<sup>2</sup>, Brian Kessler<sup>3</sup>, Thomas Yuzvinsky<sup>4</sup>, Henry Garcia<sup>5</sup>, Alex Zettl<sup>4</sup>

<sup>1</sup>University of California, Berkeley; Lawrence Berkeley National Laboratory <sup>2</sup>University of California, Berkeley; Center of Integrated Nanomechanical Systems <sup>3</sup>University of California, Berkeley <sup>4</sup>University of California, Berkeley; Lawrence Berkeley National Laboratory; Center of Integrated Nanomechanical Systems <sup>5</sup>University of California, Berkeley; Center of Integrated Nanomechanical Systems

The versatility of carbon-carbon bonding creates a wealth of extraordinary physical properties. Of the two common allotropes of carbon, diamond (sp-3 bonded) exhibits record thermal conductivity but is metastable and transitions to graphite at elevated temperatures. Graphite (sp-2) is electrically conducting but sublimes at temperatures as low as 2400K. Carbon nanotubes (also sp-2) capitalize on the extraordinary strength of the sp-2 hybridized carbon-carbon bond and exhibit high electrical and thermal conductivities as well as tremendous mechanical strength. Here we report a new technique to measure the thermal properties of nanosystems. We apply this technique to determine the extreme high temperature stability and thermal conductivity of multiwalled carbon nanotubes.

#### Investigation of alkali-metal doped phthalocyanines

PTU

<u>Matteo Belli,</u> Mauro Riccò, Daniele Pontiroli, Massimo Pagliari, Toni Shiroka CNISM and Dipartimento di Fisica, Università di Parma

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Metal-phthalocyanines (MPc-s) are metal-organic compounds with rather attracting features, widely exploited in industrial processes. Despite this fact, they have recently received a renewed attention, thanks to their intriguing red-ox properties upon intercalation with alkali metals. Relatively recent experiments demonstrated the possibility to tune their electronic properties by doping phthalocyanine thin films with alkali metals (a property which is observed only in a limited number of other compounds, like fullerenes).

One of the most intriguing questions is whether the same achievements can be obtained in the bulk compounds. The most studied MPc-s are characterized by the presence of an inner divalent metal, like Cu, Mg, etc. Once doped in the solid state, these materials show a pronounced tendency to substitute the divalent metal atom with the intercalated species, despite the fact that the metal is linked to the macrocycle by both covalent and coordination bonds. Thus alkali-metal phthalocyanines become the best candidates for this study, being intrinsically immune to the substitution effect.

The present contribution will deal with the synthesis of doped and undoped LiPc and KPc, along with the structural characterization (by XRD), and magnetic characterization (by SQUID magnetometry, Nuclear Magnetic Resonance and  $\mu$ SR).

#### Probing dielectrophoretic force fields with metallic carbon nanotubes

PTU

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Dielectrophoretic assembly of nanoscale objects has attracted much attention recently. Understanding the influence of substrate and electrode geometry on the dielectrophoretic force fields near the substrate surface allows for specific device fabrication. We show that single walled carbon nanotubes can be used as probes for the dielectrophoretic force fields, which are visualized by the deposition pattern of the nanotubes. [1]

Short, dispersed single walled carbon nanotubes were exposed to different DEP force fields, generated by electrodes on insulating oxide with or without conducting substrate underneath. We characterized the deposition patterns by scanning electron microscopy and performed finite element simulations to validate their correlation to the dielectric force fields. For certain geometries a sign change in the normal component of the dielectrophoretic force near the substrate surface leads to a repulsion of the metallic carbon nanotubes. By observing certain geometrical constraints such a sign change can be avoided.

[1] Marquardt et al., Appl. Phys. Lett. 89, 183117 (2006)

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#### PTU Hydrogen Storage in Carbon Nanofoam

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Hydrogen based fuel cells are considered to be an important future alternative to fossile based energy sources such as oil, natural gas and coal. For many aplications such as hydrogen driven cars, the limiting factor is the weight of the hydrogen fuel storage device which seems to be excesive for hydrogen stored in metals. This is the reason for the search for ultralight hydrogen storage materials such as carbon nanotubes or graphite layers. Here we report on the investigation of the possibility of hydrogen storage in carbon nanofoam. This system has an ultra-low density of 2-10 mg/cm2 and a large surface area 300 - 400 m2/g. Electron diffraction showed the presence of hyperbolic "schwarzite" layers making the system suitable for hydrogen storage. Preliminary proton NMR experiments showed that hydrogen can indeed be stored in carbon nanofoam at room temperature and that the corresponding proton spin lattice relaxation time T1 of the stored hydrogen is 400 ms. Deuteron and proton absorption/desorption and diffusion data will be presented.

#### PTU RAMAN and OPTICAL ABSORPTION STUDY of "METALLIC WINDOW" for DIF-10 FERENT TYPES of SINGLE-WALL CARBON NANOTUBES

Sofya Bokova<sup>1</sup>, Elena Obraztsova<sup>1</sup>, Akos Kukovecz<sup>2</sup>, Hans Kuzmany<sup>3</sup>

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Since single-wall carbon nanotubes (SWNTs) can be metallic or semiconducting it is important to have an instrument to determine their conductivity type. The most convenient approach is measuring of UV-VIS-NIR optical absorption spectra. An absorption of metallic nanotubes demonstrates a separate band (E11m) situating in the spectrum between two absorption bands of semiconductor nanotubes (E22s and E33s). However, preparation of samples (suspensions or films) for UV-NIR-VIS optical absorption measurements a substantial amount of material is needed. Moreover, in case of materials with a wide nanotube distribution over diameter different absorption bands are overlapped and it is difficult to separate the "metallic window". Alternative approach to solve this problem is measurement of Raman spectra with different excitation wavelengths. For excitation energies being resonant for metallic nanotubes the tangential Raman mode is asymmetrically broadened due to electron-phonon Fano-resonance. This works perfectly even for a tiny material amount. In this work Raman spectra have been registered at different excitation energies (14 laser lines) for arc-produced and HipCO SWNTs. UV-VIS-NIR optical absorption spectra has been measured for aqueous suspensions of these materials. The energy range for "metallic window" measured by both techniques have coincided very well. The work is supported by RAS Presidium programs.

#### PTU Single-walled carbon nanotube as a nano-reactor for a replacement reaction

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In our study we use a wet chemistry route to perform a simple chemical replacement reaction in the interior of a singlewalled carbon nanotube (SWCNT). We show high resolution TEM evidence for the formation of very long ( $\approx$  100-200 nm) silver nitrate quantum wires within SWCNT, and their optical properties are probed using optical absorption spectroscopy (OAS). In a subsequent step NO3- is replaced by Cl- resulting in long AgCl nanowires. Further, OAS studies confirmed that these carbon nanotubes, which serve as nanoreactors, could be fully purged through an additional treatment thus enabling them to be re-used. This highlights the potential for SWCNT as nano test tubes.

#### A nanoscale probe for fluidic and ionic transport

PTU 12

<u>Bertrand Bourlon</u><sup>1</sup>, Joyce Wong<sup>2</sup>, Csilla Mikó<sup>3</sup>, László Forró<sup>3</sup>, Marc Bockrath<sup>1</sup>

California Institute of Technology <sup>2</sup>Schlumberger, California Institute of Technology <sup>3</sup>EPFL

Fluid dynamic properties are expected to differ when governed by nanoscale geometries, with strong implications in different fields of science and technology. With advances in nanofabrication techniques, the study of fluid flow around a nano-object or in a nano-channel is now more accessible experimentally. Nevertheless, developing nanoscale probes for fluid dynamic properties that can be easily integrated remains challenging. Carbon nanotubes have shown great potential to act as nanoscale sensors. However, while carbon nanotube based flow sensors have been reported at the macroscopic scale using bulk nanotubes, such sensors are not readily integrated into micro- or nano- scale fluidic channels. We will discuss our recent work investigating the use of individual carbon nanotubes to sense fluid properties at very small length scales. We have demonstrated that electrolytically-gated  $\approx 2$ nm diameter SWNT transistors incorporated into microfluidic channels can locally sense the change in charge environment or electrostatic potential induced by a flow of ionic solution (electrokinetic phenomena). More precisely, the streaming potential generated by the flow of ionic solutions in the channels shifts the transistor threshold of our devices. Finally, by operating at a fixed gate voltage, the nanotube conductance changes in response to the flow rate functioning as nanoscale flow sensor.

### X-ray spectroscopy probing of the electronic structure of nitrogen-doped carbon nanotubes PTU Lyubov Bulusheva<sup>1</sup>, Alexander Okotrub<sup>1</sup>, Yuliya Lavskaya<sup>1</sup>, Egor Pazhetnov<sup>2</sup> 13

<sup>1</sup>Nikolaev Institute of Inorganic Chemistry SB RAS <sup>2</sup>Boreskov Institute of Catalysis SB RAS

Nitrogen-doped carbon (CNx) nanotubes have been synthesized by chemical vapor deposition (CVD) method using acetonitrile as a source for nanotube growth. Random CNx nanotubes were produced over catalytic particles formed in the result of thermolysis of bimaleates of the transition metals. Aligned CNx nanotubes were grown vertically on the silicon support when ferrocene was used as a catalyst source. X-ray photoelectron spectroscopy revealed a presence of pyridinic and three-coordinated nitrogen in the random CNx nanotubes. The aligned CNx nanotubes were found to contain molecular nitrogen additionally. This result was confirmed by X-ray absorption spectroscopy near the NK-edge. The broadening of the features of NK-edge spectrum of the aligned CNx nanotubes relative to those of the gaseous nitrogen molecules spectrum suggests interaction of N2 with graphitic layers. The sample of this type of CNx nanotubes was irradiated by primary photon beam during  $\approx 10$  minutes. The N K-edge spectrum of the irradiated sample showed slight decrease in intensity that could be due to removing of nitrogen molecules from the nanotubes.

#### The Resonant G'-band Dependence on Environment

PTU 14

Juan Cardenas

Universitetet i Oslo

The resonant G'-band Raman spectra of single wall carbon nanotubes are known to depend on excitation energy and the diameter. Recently, it was shown that the G'-band features of SWNTs in solution may reveal a bimodal distribution depending on environmental conditions. We have further shown that the linewidth decreases gradually with the degree of solubilisation, which explains why the bimodal distribution is not readily observable in bundles. Hence the environment strongly modifies the features of the G'-band. Here, it is shown how the G'-band depends on the pH of the solution, which is discussed with the double resonant process.

#### PTU Theoretical insight into the oxidation of nanoporous carbon materials

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Oxygen can be used to modify the properties of graphene based carbon materials such as graphite, nanotubes and nanoporous carbon(NPC). STM indicates that  $O_2$  etches edges and vacancies in graphitic materials. TPD shows desorption of CO and CO<sub>2</sub> indicating the presence of C-O-groups on the surface. However, the characterization of the atomic surface structure and the reaction steps during oxidation is still unsatisfactory. We have therefore carried out an extensive study of oxidation of NPC using ab-initio thermodynamics. NPC may be visualized as crumpled graphene sheets with a significant amount voids in the structure. Our density-functional theory (DFT) calculations show that the origin of the voids may be vacancies that transform into combinations of non-hexagonal rings, which we call the "motifs of NPC". The motifs are very reactive towards oxygen such that the dissociation of  $O_2$  is exothermal. The O-atoms attach to the undercoordinated C-atoms at the motifs forming C-O-groups. C-O-C (Ether) groups dominate and C=O (Carbonyl) groups may also appear. The C=O groups are precursors for CO-desorption, but our thermodynamic treatment shows that CO only desorbs above 700 K from these sites in agreement with TPD experiments. Based on these results we propose that the oxidative etching of NPC materials proceeds via a sequence of dissociative O2 adsorption and CO desorption.

### PTU Electrical properties of Titania/Multi-walled carbon nanotube nanocomposites irradiated with $CO_2$ laser

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Conductive coatings made from very thin functionalized (-NH2) multi-walled carbon nanotubes (Nanocyl S. A.) dispersed in a titanium-based sol were irradiated with  $CO_2$  laser using different intensities. It was observed that the electrical and optical properties of the film have changed after irradiation. Regions of the film irradiated with high intensity laser power present lower sheet resistance than the original coating or regions irradiated with less intensity of  $CO_2$  laser. This behaviour was probably due to a better densification of the nanotubes with the assist of the laser. For a better understanding of the effect, the structural morphology of the diverse regions which had their optical properties preserved were investigated and correlated with their respective electrical properties.

#### PTU SOLUBILISATION OF SWNT USING ORGANIC DYES

17 Qiaohuan Cheng, <u>Sourabhi Debnath</u>, Theresa Hedderman, Hugh Byrne Focas Institute from Dublin Institute of Technology

Single walled carbon nanotubes (SWNT) have unique mechanical and optical properties which point to potential applications. But the as prepared SWNT are obtained in bundled form and are impure which is a major problem in the field of carbon nanotube research. Organic dyes have been shown to interact with and solubilise SWNT [1].

Here we report the solubilization of SWNT in toluene in the presence of the two oligomic series naphthalene, anthracene, 2, 3-benzanthracene and bi-phenyl, p-terphenyl, p-quarterphenyl. UV/VIS/NIR and Luminescence spectroscopies were employed to probe the interactions occurring between the organic dyes and the SWNT over a wide range of concentrations. Raman spectroscopy was employed to demonstrate debundling and to investigate structurally selective processing.

The concentration dependence of the quenching of the dye fluorescence in the presence of SWNT was employed to establish regions where debundling occurs. Using a simple adsorption/desorption model [2], binding energies can be calculated and subsequently correlated with molecular structure to establish structure-property relationships for the interactions of organic molecules with SWNT.

- [1] T.G. Hedderman et al, J. Phys. Chem. B, 110, 3895 (2006)
- [2] J.N.Coleman et al, J. Phys. Chem. B., 108, 3446 (2004).

### OPTICAL PROPERTIES of POLYMER FILMS with EMBEDDED SINGLE-WALL CAR-PTU BON NANOTUBES 18

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Investigations of composites of polymers and single-wall carbon nanotubes (SWNTs) during last years aimed mostly getting a light material with an ultimate mechanical strength. Another idea was to design a conducting flexible material for shielding of electro-magnetic fields and for replacing ITO contacts in microelectronic devices. Just recently such composites have been taken into consideration as an optical material with a high non-linearity. This property allows using them as ultrafast beam modulators in different laser schemes, especially, in fiber lasers. Many film parameters should be optimized for keeping the laser generation after introduction of the nanotube-containing element into resonator and for transforming the cw (continuous wave) laser output into a train of ultrashort pulses: an optical density, the film smoothness and thickness, a high beam-resistance, a low level of scattered light, a proximity of the absorption bands of the material to the laser working wavelength. In this work the results of such measurements performed by UV-VIS-NIR technique for optimization of the polymer films based on two polymers (PvA -polyvinyl alcohol and carboxymetylcellulose) incorporating SWNTs synthesized by different methods (arc, HipCO, CVD) are presented. Mechanical stress was applied for changing the positions of the film absorption bands. The work was supported by RFBR-06-02-08151.

#### Pressure response of carbon nanotube systems

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We present and compare our experimental results regarding the high pressure response of single-, double- and oligo-wall carbon nanotubes (SWCNTs, DWCNTs and OWCNTs) studied by Raman spectroscopy. The possibility to probe the innermost tubes in OWCNTs offers a unique experimental opportunity for demonstrating the consequences of shell addition and the concomitant isolation effects in the nanotube interior. Furthermore, we develop a simple phenomenological model of concentric polygonal rings in order to study the pressure response of multi-shell carbon nanotubes. Although our model does not describe realistically a carbon nanotube, it bares all of its qualitative characteristics. It is used for the interpretation of the experimental results and the discrete grouping of the normalized pressure coefficients, G parameters, for the inner tube radial breathing modes in DWCNTs. The strength of the pressure screening effect depends on the inner-outer tube spacing. Consequently, the encapsulation of any species inside a tube cannot be strictly considered as "isolation" and rather describes a reduced and selective interaction with the environment. Furthermore, the model suggests that the experimentally observed distribution of the G parameter values for the inner tubes can be in principle attributed to nanotubes of only a few specific diameters.

The financial support by the European Social Fund and National Resources (YPEPTH-EPEAK, Greece) through "Pythagoras II" is greatly acknowledged.

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#### PTU Electronic transport and optical properties of silicon and CdSe nanowires

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There is a growing interest in using semiconductor nanowires as building blocks for electronic and optoelectronic applications [1]. Silicon nanowires (SiNWs) are very attractive due to their central role in the semiconductor industry. Here, we assess the electronic transport in transistors built on multiple and single SiNW channels [2,3]. Different metal contacts and annealing procedures are studied, including Ti/Al, Ti/Au, and Ni. The presence of a Schottky barrier can be inferred in all cases [3]. We determine the metal/semiconductor band-offset by means of temperature-dependent current-voltage measurements on ambipolar SiNWs.

NWs made of direct band-gap semiconductors are front-line candidates for next-generation photovoltaic and light-emission devices [1,4]. It is thus important to correlate different optical contributions with crystal quality and morphology [4]. By probing the photoluminescence (PL) of multiple and individual CdSe NWs, we show that defect-related emission bands may arise when Au is used as a catalyst to promote NW growth. PL from individual NW synthesized without any metal catalyst indicates a better crystal quality compared to their Au-catalysed counterparts.

- [1] Y. Li et al., Materials Today 9, 18 (2006)
- [2] S. Hofmann et al., J. Appl. Phys. 94, 6005 (2003)
- [3] A. Colli et al., J. Appl. Phys. Submitted (2006)
- [4] A. Colli et al., Nanotechnology 17, 1046 (2006)

#### PTU Filling Carbon nanotubes for bio-applications

<u>Sara Costa</u><sup>1</sup>, Ryszard Kalenczuk<sup>1</sup>, Alicja Bachmatiuk<sup>1</sup>, Mark Rümmeli<sup>2</sup>, Thomas Gemming<sup>2</sup>, Ewa Borowiak-Palen<sup>1</sup>

<sup>1</sup>Centre of Knowledge Based Nanomaterials and Technologies, Institute of Chemical Engineering and Chemical Technology, Szczecin <sup>2</sup>Leibniz Institute for Solid State and Materials Research Dresden, Germany

Current efforts to produce pure Fe-MWCNT on a bulk scale are driven by the massive potential of this molecular hybrid in applications such as magnetic nano-heaters and as drug delivery systems in the medical diagnosis and therapeutic treatment at the cellular level.

In our report we present a comparative study on the synthesis of iron filled multiwalled carbon nanotubes (Fe-MWCNT). We have applied two experimental techniques namely, single step in-situ filling and synthesis via carbon vapor deposition (CVD) and filling as a post-treatment to previously produced MWCNT. A combination of techniques have been applied to characterize the quality and efficiency of these hybrid nano-structures.

#### PTU Exciton Delocalization in Structurally Sorted Single-wall Carbon Nanotube Ropes

<u>Jared Crochet</u>, Zipeng Zhu, Tobias Hertel Vanderbilt University

Diameter enriched single-walled carbon nanotube ropes are structurally sorted by ultracentrifugation using density gradients. Atomic force microscopy and structural modeling allow us to determine the average number of tubes in a rope for a specific density. The trends found in absorption and photoluminescence spectra are consistent with a gradual increase of the translational degrees of freedom, i.e. dimensionality of the lowest lying optically active exciton. This allows us to probe exciton dynamics in various dimensions with the same material and provides clues about the nature of tube-tube charge and energy transfer processes in nanotube agglomerates. Furthermore, time-resolved experiments shed light on the influence of dimensionality on trapping of the dark exciton.

#### Magnetic and optical properties of erbium-doped endohedral fullerenes

PTU

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 $^1\mathrm{Department}$  of Materials - University of Oxford - Parks Road - Oxford, OX1 3PH - UK  $^2$   $^3\mathrm{Clarendon}$  Laboratory - Department of Physics - University of Oxford - Parks Road - Oxford, OX1 3PU - UK

Er3N@C<sub>80</sub> and ErSc<sub>2</sub>N@C<sub>80</sub> endohedral fullerenes have been isolated, purified by HPLC and characterized by optical and magnetic spectroscopy. Their UV-Vis-NIR absorption spectrum reveals a good transparency of the cage in the near infra-red range and indicates that their electronic structure can be respectively written  $(\text{Er3N})^{6+}$  C<sub>80</sub><sup>6-</sup> and  $(\text{ErSc}_2\text{N})^{6+}$  C<sub>80</sub><sup>6-</sup>. Photoluminescence and photoluminescence excitation at liquid helium temperature show the characteristic Er<sup>3+</sup> emission at 1.5 um, corresponding to the 4I13/2? 4I15/2 transition. Continuous wave ESR of ErSc?2N@C<sub>80</sub> at liquid helium temperature gives a signal associated with the Er ion.

ErSc2N@C80 molecules are the only erbium-doped metallofullerenes in which we have found a relatively strong fluorescence at 1.5  $\mu$ m and an ESR signature. Thanks to these two characteristics, it should be possible to detect optically the spin state in these fullerenes, by exciting spin-selective luminescent transitions under a magnetic field, and thus to perform single spin readout of ErSc2N@C80 fullerenes for quantum computing.

#### SOLUBILISATION OF SWNT USING ORGANIC DYES

PTU

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Single walled carbon nanotubes (SWNT) have unique mechanical and optical properties which point to potential applications. But the as prepared SWNT are obtained in bundled form and are impure which is a major problem in the field of carbon nanotube research. Organic dyes have been shown to interact with and solubilise SWNT [1].

Here we report the solubilization of SWNT in toluene in the presence of the two oligomic series naphthalene, anthracene, 2, 3-benzanthracene and bi-phenyl, p-terphenyl, p-quarterphenyl. UV/VIS/NIR and Luminescence spectroscopies were employed to probe the interactions occurring between the organic dyes and the SWNT over a wide range of concentrations. Raman spectroscopy was employed to demonstrate debundling and to investigate structurally selective processing.

The concentration dependence of the quenching of the dye fluorescence in the presence of SWNT was employed to establish regions where debundling occurs. Using a simple adsorption/desorption model [2], binding energies can be calculated and subsequently correlated with molecular structure to establish structure-property relationships for the interactions of organic molecules with SWNT.

- [1] T.G. Hedderman et al, J. Phys. Chem. B, 110, 3895 (2006)
- [2] J.N.Coleman et al, J. Phys. Chem. B., 108, 3446 (2004).

#### Testing of SWNTs for day sensitized solar cells

PTU

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A random carbon nanotube network is considered as alternative for applications where low sheet resistance and high optical transparency in the visible and infrared spectral range are essential. We investigated such transparent thin films of SWNTs on various substrates with the intention of using them as conducting electrodes. Such networks have been prepared on glass, on FTO coated glass and on flexible PET foil by the air-brush technique. However, the thin nanotube films are not mechanically stable and can easily be scraped off the surface. The adhesion to the substrate can be improved by using a PVA cover layer. The nanotube networks show the surface resistivity in the range of 200 - 600 Ohm/sq. Exposure to the 0.5 M LiI/0.05 M I2 solution in acetonitrile, which is the solution used in the active solar Graetzel cell, does not change the electrical properties of the protected nanotube films. They are mechanically and chemically stable in iodine solution in acetonitrile even during heating up to 50 °C. In addition, we prepared conducting carbon nanotube lines which are supposed to help collecting the photo-generated charges. Leads based on epoxy composite (UHU glue) show volume resistivity in the range 1-7 kOhmcm and are stable in iodine solution.

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#### PTU Novel Organometallic Fullerne Complexes for Vehicular Hydrogen Storage

Anne Dillon, Erin Whitney, Calvin Curtis, Chaiwat Engtrakul, Philip Parilla, Yanfa Yan, Tining Su, Kim Jones, Lin Simpson, Michael Heben, Yufeng Zhao, Yon-Hyun Kim, Shenbai Zhang National Renewable Energy Laboratory

Theoretical studies have predicted scandium will complex with the twelve five-membered rings in  $C_{60}$ . It is then possible to stabilize four H2 dihydrogen ligands on each Sc atom with a binding energy of  $\approx$  30 kJ/mol, ideal for vehicular hydrogen storage. The resulting  $C_{60}[ScH2(H2)4]12$  complex is predicted to be a minimum energy structure with  $\approx$ 7.0 wt% reversible hydrogen capacity. However, wet chemical synthesis of the calculated ?5 coordinated fullerene complex is unprecedented. The chemistry of  $C_{60}$  is generally olefinic (i.e., ?2 coordination, in which the metal is coordinated to two carbon atoms contributing two electrons to the bonding). Furthermore, stabilization of multiple dihydrogen ligands on a single transition metal has not been demonstrated. Recently we have probed new synthesis techniques in which  $C_{60}$  is coordinated with either Fe, Sc, Cr, Co or Li. The new compounds were characterized with 13C solid-state nuclear magnetic resonance, Raman spectroscopy, electron paramagnetic spin resonance, transmission electron microscopy and nanoprobe electron energy loss spectroscopy. Structures for the new compounds have been proposed. All of the structures were found to have unique binding sites for dihydrogen molecules. The synthesis of these novel organometallic fullerene structures and their potential for vehicular hydrogen storage applications will be presented.

#### PTU Growth and electrical caracterisation of one-dimensional nanostructures

 $\frac{\text{Martial Duchamp}^1, \text{ Gerit Kulik}^1, \text{ Arnaud Magrez}^1, \text{ Benjamin Dwir}^2, \text{ Jin Won Seo}^1, \text{ László Forró}^1}{^1\text{EPFL-SB-IMPC-LNNME}}$   $^2\text{EPFL-SB-IPEQ-LPN}$ 

We investigated the growth of ZnO nanowires by vapor-liquid-solid process. Mono dispersed gold colloids were used as catalyst. The narrow diameter distribution in size leads to a narrow distribution of the nanowire diameter (1). Hence, we modified the surface of silicon wafer by silanization in order to strengthen the bonding of the gold particles onto the substrate surface(2).

KNbO3 nanowires were prepared by a hydrothermal route. The results indicate that highly uniform single-crystalline nanowires form(3). Home made multi-walled carbon nanotubes produced by arc-disharge method are contacted for measuring electrical properties of a single nanotube.

The deposition of individual nanowires and nanotubes was performed by electrophoresis adapting design and electrical parameters. Four metallic contact lines of chromium or gold palladium alloy were patterned by e-beam lithography and lift-off technic. Additionally, the pressure and temperature dependance of electrical properties of multi-walled CNTs were performed.

- (1) Hui Zhang et al. J. Phys. Chem. B 2006,110,827
- (2) Frens G et al. Nat. Phys. Sci. 1972, 241, 20
- (3) A. Magrez et al. J. Phys. Chem., 2006, 110, 58

#### PTU Morphological effects of catalyst on carbon nanomaterial in CVD process

Ahu Dumanli, Yuda Yürüm Sabanci University

Carbon nanostructures take the interest of many researchers all over the world because of their interesting structural, electronic and mechanical properties. Chemical vapor deposition (CVD) method was chosen for synthesis the carbon nanostructures in this study, since controlling the metal catalyst properties allows controlling the properties of the CNF formed. Our goal in synthesizing carbon nanostructures was to control diameter and morphology at the same time. In order to achieve such control, a detailed research for the catalyst such as, its activity, surface and thermal properties has to be done. In this study, transition metal based organometallic catalysts were synthesized by using different metallic precursors. The structural, surface and chemical properties, thermal stability of the catalysts have been investigated using XRD, SEM-EDS, FTIR, BET and TGA methods. A correlation between catalyst properties and

the morphology of CNFs produced thus was made.

### Investigation of electrochemical Ni and Fe catalyst nanoparticle formation on thin SiO2 PTU gate oxide for SWNT growth 29

<u>Durrer Lukas,</u> Matthias Muoth, Ricardo Santos Roque, Christofer Hierold  $^{1}\mathrm{ETH}$  Zürich

Single-walled carbon nanotubes (SWNTs) have shown remarkable properties for their use in sensor applications. However, for the building of reproducible CNT based devises, investigations towards better control of CNT growth by chemical vapor deposition (CVD) have to be done. It has been shown, that catalyst diameter and densities have evident influences on the CNT diameter and the CNT surface density. There exist many different ways of catalyst formation. By taking advantage of the electron tunneling through thin SiO2 layers, we propose and investigated for the first time, chronoamperometric and chronopotentiometric Ni and Fe catalyst formation on Si/SiO2 surfaces. These enabled us, the growth of individual SWNTs by low pressure chemical vapor deposition (LPCVD) on electrochemically formed catalyst. Potential pulse and current pulse Ni and Fe seed crystal formation in electrolyte solution, have the advantages of a fast, controllable and low cost particle formation processes. Since electrochemical deposition demands for conductive surfaces and SWNTs growth supporting surfaces are mostly dielectical, it has only been possible to grow multi-walled carbon nanotubes (MWNT) on electrochemically formed catalyst nanoparticles, so fare [1].

[1] Y. Tu, ZP. Huang, DZ. Wang, JG. Wen, ZF. Ren, Applied Physics Letters, 2002, 80, 4018

### Langmuir-Blodgett thin films preparation and AFM study of $C_{60}$ and $C_{60}O$ fullerenes. Aneta Dybek<sup>1</sup>, Cong Yan<sup>2</sup>, Karina Schulte<sup>2</sup>, <u>John Dennis</u><sup>1</sup>, Philip Moriarty<sup>2</sup>

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The Langmuir-Blodgett (LB) technique is currently widely used for an ultra-thin films preparation of various chemical compounds. LB films of fullerene molecules are attractive for many device related applications. Recently, the study on  $C_{60}$  LB films has become a focus of considerable interest. However, it is difficult to fabricate high quality LB films of pure  $C_{60}$  fullerene due to its hydrophobicity which occurs in molecular aggregation in solution. This prevents formation of  $C_{60}$  monolayer. Introduction of hydrophilic groups to fullerene cage can reduce the aggregation process. Thus,  $C_{60}$ O was used for LB film preparation.

We report here the preparation of micrometre-scale monolayer islands of  $C_{60}$  and  $C_{60}$ O via the Langmuir-Blodgett technique on plasma cleaned (hydrophilic) Si(111) substrates.

#### Potential Barrier Formation in Graphene by Electrostatic Doping

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Graphene is integrated into a silicon CMOS process flow to fabricate Field-Effect Devices (FEDs). Topand back-gate electric fields are used to create potential barriers (n-p-n junctions) in graphene. The electronic properties of the electrically doped graphene and the degree of control via the gates are investigated by I-V measurements. Charge carrier mobilities of "sandwiched" graphene with two graphene / silicon dioxide interfaces are compared to uncovered material with only one interface. Finally, graphene FEDs are compared to silicon MOSFETs and its potential for next generation nanoelectronic devices is evaluated.

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#### PTU Preparation of inorganic-organic ultra-thin layer systems

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We report on the preparation of inorganic-organic bilayer systems consisting of sputter grown indium-tin-oxide (ITO) on vacuum thermal deposited Zn-phthalocyanine substrate. The chemical stability of the organic material in the layer system was investigated by means of attenuated total reflection Fourier transform infrared spectroscopy. Structural stability of the film was investigated by x-ray diffraction (XRD) measurements.

The molecular organic layer turned out to be remarkable stable in the reactive ITO sputter process. Neither significant dissociation products of the ZnPc molecules, nor new crystalline phases were detected in the infrared spectra and XRD, respectively. Possible mechanisms for the observed material reduction are discussed.

### PTU Structural properties and electrochemical behaviour of CNT – TiO2 nanocrystal heterostructures

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Different methods of preparation of carbon nanotubes – TiO2 (anatase) heterostructures have been tested in order to obtain information on the relationship between the preparation method, resulting structure of the material and its electrochemical behaviour. Firstly, SWCNTs in the form of a buckypaper have been covered electrochemically with anatase nanocrystals from aqueous solution of TiCl3. Raman measurements have indicated changes of the vibrational modes of anatase and SWCNT. The HR-TEM observation accompanied by SAED and EDX analyses showed that SWCNT bundles are covered with anatase nanocrystals of approximate size of 8 nm. Electrochemical measurements of Li+ insertion into TiO2 (anatase) lattice to form LixTiO2 showed x=0.42 (corresponding to charge capacity of 507 Cg-1) with 0.98 insertion/extraction charge ratio. Secondly, CNTs have been covered by pure TiO2 anatase nanocrystals of average size about 30 nm by hydrolysis from Ti-butoxide in ethanol dispersion of CNTs. Electrochemical Li+ insertion showed x=0.54 (corresponding to charge capacity of 652 Cg-1). Thirdly, Pluronic P123 templated anatase – CNT thin films have been prepared by dip-coating of F-doped SnO2 (FTO)-slides in the solution of Pluronic P123 with F-ethoxide mixed with various concentration of CNTs. The CNTs in this case act as a cross-linking network for the anatase thin films.

#### PTU Covalently functionalized carbon nanotubes as macroinitiators for polymerization

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The sidewall chemical modification of carbon nanotubes has shown a great potential in improving their solubility and processability. The covalent functionalization strategies have opened a wide range of chemical reactions which can be performed onto the graphitic surface of tubes. Furthermore a number of recent reports have concentrated on the supramolecular modification of carbon nanotubes, especially with polymers. Until now, covalent attachment of polymer chains to carbon nanotubes has been mainly accomplished by the "grafting to" method. This work attempts to explore the growth of polymeric structures onto the sidewalls of carbon nanotubes by the "grafting from" method. The whole reaction is carried out in two steps; firstly, polymerization initiators are covalently attached onto the graphitic network and, then, secondly, the nanotube-based macroinitiators are reacting with vinyl monomers to form long macromolecules. Due to the small size of monomers, it is expected that a higher incorporation of polymeric functionalities can be achieved, compared to the "grafting to" approach.

To test the above polymerization route, we have chosen to investigate a novel functionalization scheme, the ceric ion-induced redox polymerization. This approach represents an example of green chemistry, since the grafting reactions take place in aqueous media. Detailed characterization of the starting and functionalized materials has been performed by means of Raman, SEM, TEM and XPS techniques.

#### Mechanical detection of carbon nanotube resonator vibrations

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Bending-mode vibrations of carbon nanotube resonator devices were mechanically detected in air at atmospheric pressure by means of a novel scanning force microscopy method. The fundamental and higher order bending eigenmodes of multi-wall nanotubes were imaged up to 3.1GHz. The corresponding resonance frequencies are found to be consistent with elastic beam theory for a doubly clamped beam. On the other hand, single-wall nanotube resonators are shown to be ultra sensitive to stress, slack or contamination. Our results point out that mechanical detection offers great promise for future developments of nanoelectromechanics.

#### Theoretical Study of DNA-wrapped Carbon Nanotubes

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Carbon nanotubes embedded in single-stranded DNA (CNT@DNA) were investigated by self-consistent density-functional-based tight-binding calculations (DFTB). A phenomenological model for the stability was derived, which gives the CNT-DNA interaction energy as a function of the nanotube radii and the number of DNA chains. Single CNTs are readily complexed by the DNA, but for CNT bundles an essential energy gain is only obtained, if multiple chains wrap around the tubes. Hence, the destruction of the CNT bundles, e.g. by sonication, can promote the CNT@DNA complex formation. Pyrimidine-based homopolymeric DNA more effectively wraps the DNA, whereas purine-based DNA exhibits the larger radius selectivity. The CNT-DNA interaction is not a genuine Van-der-Waals interaction. In general, the electronic structure is close to the superposition of the DOS curves of the "free" DNA and CNT fragments, but the most strongly bonding systems are characterized by a number of the mixed electronic states below Fermi level. Hence, magic matching occurs in conjunction with remarkable charge transfer.

# Ta-based Adhesion Layers for Cu coated Carbon Nanotubes Siegfried Menzel<sup>1</sup>, Silke Hampel<sup>1</sup>, Matthias Albert<sup>2</sup>, Thomas Gemming<sup>1</sup> IFW Dresden <sup>2</sup>TU Dresden

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The incorporation of nanotubes into metal matrices is a promising approach to form composite structures to enhance e.g. microelectronic or microacoustic properties of matrix materials. Carbon nanotubes (CNTs) are considered to enhance electrical, mechanical, or thermal properties of different thin film materials. However, the advanced properties of composite films strongly depend on type, quality, and incorporation principle of CNTs.

We investigated copper-matrix multiwall CNT (MWCNT) composite layers. The adhesion behavior of the matrix material on the CNTs predominantly determines the properties of composite films. In the case of copper an important fabrication problem exists because of the low interaction strength of copper with carbon. Therefore, we developed a preparation technique to enhance copper adhesion on CNTs for efficient fabrication of copper matrix-CNTs composites. A very thin Ta-based adhesion layer was deposited on chemical vapor deposited CNTs by using a plasma enhanced atomic layer deposition (PEALD) technique. Various pre-treatment steps of the nanotubes are investigated for enhancing the adhesion and quality of the ALD layers. Investigations by using SEM, TEM, and EDXS as well as other analytical methods show that a suitable wetting of thin Ta(N,C,O) layers on the MWCNTs surface can be obtained that suggests an enhanced copper plating or metal organic CVD process on CNTs.

#### PTU Sonication of porphyrin-nanotube composites: a cautionary tale

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Functionalization of nanotubes is extremely important as it couples the mechanical and structural strength of the carbon skeleton with desirable optical properties imparted by the molecules that are used to decorate the carbon exo-surface. Porphyrins represent one such family of functional molecules with potential applications as sensitizers for photoactive switches, light-harvesting systems, in cancer photodynamic therapy and electronics. Porphyrins are also particularly important as suitable partners of carbon nanotubes in nanocomposites due to their (electro) luminescence and photovoltaic properties as well as to their biocompatibility. Regardless of the functional molecule, sonication is a key step in the dispersion of single-walled carbon nanotubes (SWNT) when making composite solutions, and chloroform is frequently the solvent of choice. However, sonication of a variety of halogenated solvents may produce degradation products that can react with moieties on the composite thus hampering and complicating both characterization and function of the resulting material. In this work we demonstrate that spectroscopic changes of porphyrins in nanocomposite solutions are due to protonation of the porphyrin resulting from sonolysis of a variety of chlorinated solvents. Therefore, extreme care must be taken when working with carbon nanotube composite solutions in halogenated solvents as protonation of acid sensitive molecules may take place, changing their physicochemical properties.

Mhuircheartaigh E. N., Giordani S. and Blau W.J. (2007) Chem. Comm., submitted.

#### PTU Carbon nanotube double-slit interferometer: Synthesis pathway and electronic properties Daniel Grimm<sup>1</sup>, Pedro Venezuela<sup>1</sup>, Andrea Latge<sup>1</sup>, Mauricio Terrones<sup>2</sup>, Thomas Pichler<sup>3</sup>, Bernd Büchner<sup>3</sup> <sup>1</sup>UFF, Niteroi, Brazil <sup>2</sup>IPICyT, San Luis Potosi, Mexico <sup>3</sup>IFW Dresden, Germany

We report on the realization of double-slit interferometers made purely of single walled carbon nanotubes. We state the first time observation of such a ring-like structure naturally connected to nanotube leads using transmission electron microscopy. The merging process of the asymmetric ring into a symmetric one is investigated in situ under electron beam irradiation at high-temperatures of 800°C.

The electronic properties of the systems are studied using Monte Carlo simulations and environment dependent tight binding calculations adopting real-space Greens function formalisms. We address the possibility of standing waves formation and dispersion inside the ring and define the associated wave numbers. Moreover, we observe both the aperture of conductance channels by defect induced tunnelling as well as transport reduction and suppression due to quantum interference processes of counter-propagating electron waves.

#### PTU Structure and Electronic Properties of Nanobuds

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We present microscopic investigation of carbon nanobuds material where fullerenes molecules are attached to single wall carbon nanotubes (SWCNTs). The interaction of fullerenes molecules with the sidewall of SWCNTs has been studied with high-resolution transmission electron microscopy (HRTEM), low temperature scanning tunneling microscopy (STM) and spectroscopy. Unlike physisorbed fullerenes, which are highly mobile under TEM observation, HRTEM images show stationary fullerenes indicating strong bonding with SWCNTs. Based on HRTEM images we identified  $C_{60}$  molecules as the predominant fullerenes species. Topographic STM images show also cage structure of fullerene molecules on SWCNTs that are stable against high bias imaging. Current tunneling imaging spectroscopy displays variation in the electronic properties in the vicinity of the fullerenes. The variation is strongly localized that SWCNT electronic states at 1.5 nm away are unaffected by the fullerenes attachment. We take this as indication that the overall electronic properties of SWCNTs are unaltered by the presence of fullerenes and therefore nanobud material may offers an excellent opportunity to chemically activate SWCNTs without compromising their electrical behavior. We will discuss possible functionalization routes to selectively decorate nanobud with active chemical groups to allow easily further chemical processing.

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#### Dynamic Effects of Individual Semiconducting SWNT ChemFETs to NO2

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We present transport measurements on carbon nanotube chemical field effect transistors (CNT-ChemFETs) made of LPCVD grown individual single-walled carbon nanotubes (SWNTs) exposed to NO<sub>2</sub> gas.

We analyze the electrical transient response (i.e. the time dependent change of drain current ( $I_d$ ) for a constant source-drain and gate voltage ( $V_g$ )) of semiconducting SWNTs (S-SWNTs) measured at different applied NO<sub>2</sub> concentrations (6 - 120ppm) in dry air. While some S-SWNT show slow response times (few min) other S-SWNTs exhibit fast response times (few seconds) for NO2 concentrations as low as 6ppm, crucially depending on the intrinsic threshold level. It is noteworthy that the fast response has not yet been reported on individual non functionalized S-SWNTs. Additionally, gate charecteristic measurements of  $I_d$  ( $V_g$ ) on the CNT-ChemFET show a broad hysteresis due to trap charges in the vicinity of the SWNT before exposure to NO<sub>2</sub> that is further broadened and shifted towards positive gate voltage after exposure to NO<sub>2</sub>. We discuss the response of the CNT-ChemFET with respect to hysteresis and analyte adsorption. Based on our analysis we conclude with a strategy for minimizing response time in CNT-ChemFETs.

#### Characterization of 1-D NanoSiC-Derived Nanoporous Carbon

PTU

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Porous structures with their high surface areas have found applications in different fields. Nanofibers, with their large surface-to-volume ratio, have the potential for use in various applications where high porosity is desirable. SiC nanofibres (of 98% purity) produced using combustion synthesis technique [1] were used to make nanoporous amorphous carbon by etching the carbide with chlorine gas at elevated (1000-1100 oC) temperature. Resulting carbon material was evaluated by powder XRD and low-temperature nitrogen sorption methods. Electrical double layer characteristics were evaluated and compared with the ordinary alfa-SiC and beta-SiC derived carbon powders. All SiC-derived materials of this study have uniform pore size distribution of micropores with the peak nanopore size of carbon samples well below 1 nm. XRD analysis of SiC-nanofibres confirms the beta-SiC crystal structure. XRD patterns of carbon from SiC nanofibres show that the carbide was almost completely transformed into amorphous carbon in chlorination reaction. The cyclic voltammograms and the electrochemical impedance spectroscopy show that the electrical double layer performance of SiC nanofibres-derived amorphous carbon is good (better than most of the common pyrolytically made carbons).

This work was supported by the Ministry of Science and Education through the Department of Chemistry, Warsaw University, under Grant No. 3 T08D 012 28.

[1] A. Huczko et al., 20th IWEPNM, Kirchberg 2006, Abstract Book, p. 56.

#### Indium ions emission from carbon nanotube fibres

PTU

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The manufacturing of a carbon nanotube based liquid metal ion source is introduced. This includes assembling of carbon nanotubes on a metallic tip, wetting with a liquid metal and ion emission from nanotubes' surface in a high electric field.

MWNTs are first attached dielectrophoretically to the tip of a tungsten needle forming a single fibre several tens of mm long and a few mm in diameter. A simple method has been found enabling to cover the nanotube fibres with a thin layer (1–2  $\mu$ m) of indium. The nanotube/indium fibres were then placed about 1mm away from the grounded extractor electrode in a vacuum chamber and biased positively. Once heated above the melting temperature of indium, an emission of indium ions from the fibres was observed.

The onset voltage is much lower than that for a conventional indium covered tungsten needle. However, the nanotube fibres may degrade rapidly at higher voltages and disappear from the needle.

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#### PTU Nanotube Epitaxy

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A review is presented of the organization of carbon nanotubes by substrate-directed growth on crystal surfaces. The production of ordered carbon nanotube arrays on surfaces is a critical prerequisite for their large-scale integration into nanocircuits. We have recently elaborated a series of surface-directed mechanisms of carbon nanotube growth, which can be classified as different modes of "nanotube epitaxy". These epitaxial modes of carbon nanotube growth include "lattice-directed epitaxy" (by atomic rows), "ledge-directed epitaxy" (by atomic steps) [1], and "graphoepitaxy" (by nanofacets) [2]. Some of these epitaxial modes can be simultaneously combined with electric-field directed growth [3] for the orthogonal self-assembly of carbon nanotube crossbar architectures [4]. Nanotube epitaxy with different crystal surfaces yields unprecedented carbon nanotube array morphologies, including highly straight, kinked, wavy, crossbar, serpentine [5], and more.

- [1] Ismach, et al., Angew. Chem. Int. Ed. 2004, 43, 6140.
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- [4] Ismach et al. Nano. Lett. 2006, 6, 1706.
- [5] Ismach et al., in preparation.

## PTU Photoluminescence Microscopy and Scanning Probe Microscopy of SWNTs on Sapphire Stefan Jester<sup>1</sup>, Oliver Kiowski<sup>2</sup>, Frank Hennrich<sup>2</sup>, Sergei Lebedkin<sup>2</sup>, Manfred Kappes<sup>3</sup> Universität Karlsruhe <sup>2</sup>Forschungszentrum Karlsruhe <sup>3</sup>

Length separated Single Walled Carbon Nanotubes (SWNTs) are examined by means of Photoluminescence Spectroscopy and Scanning Probe Microscopy. The SWNTs are localized near markers prepared by electron beam lithography to allow their reproducible relocation. The photoluminescence spectra show features of individual SWNTs. The SWNT positions relative to a marker are determined by photoluminescence images and confirmed by Scanning Probe Microscope images. Further examination is in progress.

#### PTU Growth Of SWNT by Redox Reactions in Solution

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Despite some progress leading to nanotube growth, the unknown growth mechanism and accompanied lack of a large-scale synthesis of single-walled carbon nanotubes (SWCNT) is still one of the major obstacles confronting the whole nanotube field. Experiments show that nanotube nucleation and nanotube growth proceed by different chemical reactions, with completely different catalysts required on each side. On the growth side, the nanotube growth is exclusively catalysed by a large variety of trivalent catalysts: metals, non-metals and also gases. Even ppm-concentrations of a growth catalyst can effectively catalyse the SWCNT growth by a condensed-phase based scooter mechanism. Chemical redox reactions in molten nanoparticles are the root cause for the catalysed, highly selective growth of SWCNT in combination with recognition-like effects.

#### Colloidal Processing as an effective Technique to Prepare Functional Polymer/Carbon Nan- $\,{ m PTU}$ otube Composite Films and Adhesives 47

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Colloidal processing provides a facile and effective technique to mix phases at sub-micron length scales. Moreover, the use of colloids in polymer film formation is an already an established method to control structure on the scale of nanometers. Here, we report a novel and facile methodology to disperse single wall carbon nanotubes [SWNTs] in an aqueous dispersion of colloidal polymer particles. By careful control of the inter-phase between the individual polymer particles and the surface of the nanotubes via wrapping with polymers or surfactant, we are able to form nanocomposites films with controlled morphology and markedly enhanced physical properties. We show that extremely low percolation thresholds (<0.1) can be achieved by tailoring the polymer glass transition and particle size respectively. Utilizing our colloidal processing technique, we have also created a new type of waterborne pressure sensitive nanocomposite adhesives based on poly (butyl acrylate) and SWNTs. At the percolation threshold abrupt changes in the adhesive characteristics are observed with the tack energy increasing by approximately an order of magnitude. The markedly increased adhesion energy is discussed in relation to the polymer/nanotube interphase.

### In-situ Raman monitoring of individual suspended SWNTs under uniaxial load

PTU

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Microactuators were fabricated and individual suspended single-walled carbon nanotubes were embedded into them by a simple maskless CVD process [1]. The actuators were designed to apply nanoscale tensile elongations to the individual tube. As a consequence in-situ investigations of individual singlewalled carbon nanotubes at given elongations were enabled. We present SEM recordings on the failure of individual tubes. Previous studies allowed for chirality determination of specific tubes by Raman scattering from a single laser excitation [2]. We show the first Raman spectra of continuously loaded freestanding nanotubes at different strains. Complementary, we demonstrate reversibility of the Raman line-shifts by cycling the applied strain.

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#### The specific spectroelectrochemical response of TG mode of different chemically doped PTU carbon nanotube structures. 49

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Recently, the filling of the interior space of carbon nanotubes has attracted considerable interest of a broad chemical and physical audience. Among a simple nanotube filling without any charge transfer between the host and guest, the simultaneous redox doping of carbon nanotubes has been shown to lead to significant changes of the electronic properties. Here we present an easy and new method based on in-situ Raman spectroelectrochemistry which allows an identification of potassium as a dopant inside carbon nanostructures. We have studied the state of chemical dopants in the inner space of potassium vapour treated SWCNT, DWCNT and C<sub>60</sub> fullerene peapods. The presence of potassium inside the carbon nanostructures was found to be associated with a characteristic response of the tangential (TG) mode to electrochemical doping. Our study confirmed the presence of residual potassium in peapods even after treatment with water. On the other hand, potassium was not found in the interior of water treated DWCNT and SWCNT. Our results also bring new hints towards the long lasting and confusing discussions about the shifts of TG mode in Raman spectra upon charge-transfer doping.

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### PTU The effect of single walled carbon nanotube films and nano-diamonds on human osteoblast-50 like cells

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Nanomaterials, specifically nano-diamonds (ND) and carbon nanotubes (CNT) were recently proposed for biomedical application due to their many similarities with components of biological units (e.g. bone) as well as due to their unique properties (ND - high hardness, low coefficient of friction, chemical inertness and good corrosion and wear resistance; CNT - fibrous character, good conductivity, high stiffness). They also offer numerous possibilities for surface modifications (increased hydrophilicity, covalent linkage to proteins (e.g. extracellular matrix, growth factors) and to DNA or RNA (for DNA transport into cell or for diagnostic purpose), various patterning on substrate.

In the present study we have investigated the influence of SWCNT films on osteogenic ability of human osteoblasts as well as the influence of ND deposited on Ti6Al4V alloy in different thickness on viability and adherence of these cells. Our results demonstrated a different influence of SWCNT films and ND layers on investigated human cells and used materials embody promising properties for their future usage in orthopaedic/dental implant design research.

### PTU Real-time global Raman imaging of carbon nanotubes

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Optically imaging carbon nanotubes is rapid and non-destructive and allows the study of nanotube dynamics. We demonstrate direct global Raman imaging (GRI) of carbon nanotubes based on the detection of the G-band using a charge coupled detector. In contrast to more conventional raster scanning Raman imaging methods, individual carbon nanotubes and ensembles are observed in real time over a large area using a defocused laser spot for global illumination. The method is complementary to Raman spectroscopy and enables both ex situ and in situ observations down to the single nanotube level.

We apply GRI to detect and image nanotubes in real time during growth, even at very high temperatures during CVD growth. The evolution of the imaging and spectroscopy signals during CVD gives insight into the growth dynamics. The first optical images of individual nanotubes captured during growth are presented. This technique has great promise as a tool in the quest for control over nanotube synthesis as it allows non-invasive *in situ* detection and Raman characterization of individual nanotubes and ensembles while imposing minimal constraints on the synthesis method.

Funding for this project was provided by JST-CREST, as a part of the Nano-factory project lead by Y. Homma.

### PTU Polyyne to graphene conversion promoted by nanodiamond

<u>Ladislav Kavan</u><sup>1</sup>, Marketa Zukalova<sup>1</sup>, Martin Kalbac<sup>1</sup>, Eiji Osawa<sup>2</sup>, Lothar Dunsch<sup>3</sup>

Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejkova 3, 18223 Prague 8, Czech Re <sup>2</sup>NanoCarbon Research Institute, Ltd. Rm301, Toudai Ventura Plaza, 5/4/19 Kashiwa-no-ha, Kashiwa, Chiba 277-0882, Japan <sup>3</sup>Leibniz Institute of Solid State and Materials Research, Helmholtzstr. 20, D - 01069 Dresden, Germany

Polyyne to graphene conversion is ubiquitous process due to extreme chemical reactivity of polyyne. Raman spectroscopy confirms that the sp-carbon chains, which are produced by reductive carbonization of polytetrafluoroethylene (PTFE) are almost completely quenched by the presence of 10-20% of nanodiamond in the precursor mixture. The in-situ produced sp-carbon chains from PTFE readily react with the nanodiamond to form graphene (sp2 carbon), but the conversion of sp to sp3 was not observed. This reaction occurs at mild conditions (100-150oC for several hours). The nanodiamond acts as a catalyst for the sp/sp2 conversion, but a growth neither of diamond nor of sp-carbon crystals occurs at the used experimental conditions.

### Electron transport in bundles of metallic single-walled carbon nanotubes

PTU 53

Ines Klugius<sup>1</sup>, Christoph Marquardt<sup>1</sup>, Frank Hennrich<sup>1</sup>, Hilbert von Löhneysen<sup>2</sup>, Krupke Ralph<sup>1</sup>

Forschungszentrum Karlsruhe, Institut für Nanotechnologie <sup>2</sup>Universität Karlsruhe, Physikalisches Institut; Forschungszentrum Karlsruhe, Institut für Festkörperphysik

Electron transport in individual metallic single-walled carbon nanotube (SWNT) has been described within a Luttinger liquid model (LL) which can explain the power law behaviour found in the temperature dependent conductance, as well as in the voltage dependent differential conductance [1]. In heterogeneous bundles of SWNTs, that are composites of metallic and semiconducting tubes, similar power law behaviour has been observed [2], which implies, that the metallic tubes in a heterogeneous bundle are well decoupled from each other by the semiconducting nanotube matrix.

During the fabrication of carbon nanotubes both metallic and semicon-ducting ones are produced. Using dielectrophoresis as a method to separate these types [3], we are able to prepare samples of bundles of exclusively metallic SWNTs, i.e. without the semiconducting nanotube matrix. In this configuration, the SWNTs are still surrounded by the sur-factant that is necessary for the separation process.

On such samples we measure the transport characteristics and antici-pate a deviation from the LL behaviour due to enhanced intertube cou-pling. To enforce the coupling, we anneal the samples assuming that in this manner, the amount of surfactant in-between the tubes is abated and the tube-tube distance is reduced.

- [1] M. Bockrath et al., Nature 397 (1999) 598
- [2] R. Krupke et al., Nano Lett. 3 (2003) 1019
- [3] R. Krupke et al., Science 301 (2003) 344

#### Anisotropic dielectric response and local field effects in SWCNT

PTU

<u>Christian Kramberger</u><sup>1</sup>, Thomas Pichler<sup>1</sup>, Martin Knupfer<sup>1</sup>, Bernd Büchner<sup>1</sup>, Erik Einarsson<sup>2</sup>, Shigeo **54** Maruyama<sup>2</sup>

<sup>1</sup>IFW Dresden, D-01171 Dresden, Germany <sup>2</sup>Dept. of Mechanical Engineering, The University of Tokyo, Tokyo 113-8656, Japan

SWCNT are archetypical 1D systems, with peculiar anisotropic electronic properties. The depolarization effects concomitant with dielectric screening of electronic transitions are crucial in optical probes like Raman, optical absorption and luminescence. Only recently ?m thick freestanding films of vertically aligned SWCNT became available and were characterized regarding the polarization dependent optical response[1]. The plasmon response in electron energy loss spectroscopy is a direct access to the full energy and momentum dependent dielectric function. The full plasmon dispersion allows distinguishing between the effective dielectric screening and depolarization effects. The sparse morphology of the aligned freestanding mats gives rise to a substantial increase in local field corrections as compared to earlier studies on bulk aligned SWCNT[2]. The aligned nature of the SWCNT mats allows realizing experimental scattering geometries selecting specific momentum transfers parallel and normal to the axis of the SWCNT. We find two distinct branches in the ? and ? plasmon, respectively. Varying the effective transverse and parallel momentum transfer conclusively identifies the dispersive branches as parallel and non dispersive branches as perpendicular with respect to the SWCNT axis. These novel findings provide an unprecedented experimental insight into local field effects in strongly anisotropic electronic systems.

- [1] Y. Murakami et.al. Phys. Rev. Lett. 94, 087402 (2005)
- [2] X. Liu et al. Synth. Met. 121, 1183 (2001)

# PTU Nickel nanoparticle catalysed formation of fullerene like carbon nanostructures - a Raman analysis

<u>Matthias Krause</u>, Gintautas Abrasonis, Andreas Kolitsch, Arndt Mücklich, Wolfhard Möller Forschungszentrum Dresden-Rossendorf

The catalytic effect of nickel nanoparticles on the formation and on the structure of fullerene-like carbon nanostructures prepared by ion beam sputtering at different temperatures was studied by wavelength dependent Raman spectroscopy. Compared to nickel-free reference films the formation of carbon nanostructures is enhanced in the whole range of deposition temperatures from  $25^{\circ}\mathrm{C} <= \mathrm{T} <= 500^{\circ}\mathrm{C}$ . Several phases characterized by different ratios of amorphous and graphite-like carbon, a different film transparency, and a different elastic Raman background intensity, were observed. Amorphous carbon structures are preferentially formed at lower deposition temperatures, whereas graphitic structures are dominant for higher growth temperatures. Based on data for different excitation wavelengths and using difference spectroscopy, a quantitative model for the composition of these nanostructured carbon materials is developed. The results are in full agreement with those obtained by TEM, XANES and XRD analysis.[1] The model might be used as well for the analysis of other pure carbon or carbon based composite materials like CN and BCN films.

[1] G. Abrasonis, A. Mücklich, K. Küpper, M. Krause, U. Kreissig, A. Kolitsch, W. Möller, K. Sedlackova, G. Radnoczi, R. Torres, and I. Jimenez, "Morphology and bonding structure of fullerene-like nanocomposite C:Ni (≈30 at%.) thin films grown by ion beam sputtering", to be presented on XXI. IWEPNM, Kirchberg, 2007

# PTU Different orientation of metallic and semiconducting carbon nanotubes in thin films 56 Sabine Blatt<sup>1</sup>, Christoph Marquardt<sup>2</sup>, Aravind Vijayaraghavan<sup>2</sup>, Frank Hennrich<sup>2</sup>, Ralph Krupke<sup>2</sup> <sup>1</sup>Institut für Nanotechnologie, Forschungszentrum Karlsruhe, 76021 Karlsruhe, Germany <sup>2</sup>

We studied the composition and orientation of thin films of single-walled carbon nanotubes (SWNTs) by polarisation dependent optical absorptionspectroscopy and Ramanspectroscopy\*, and imaged the film morphology by scanning electron microscopy [1].

The SWNT films were produced with a novel radio-frequency dielectrophoresis setup, which generates very large dielectrophoretic force fields and allows dielectrophoretic assembling of nanotube films up to 100 nm thickness.

Exposing SWNTs, which are dispersed in aqueous surfactant solution, to such fields at moderate field frequency, produces nanotube films that are composed of metallic and semiconducting SWNTs, however with only the metallic SWNTs aligned parallel to the electric field lines.

We will discuss the experimental evidence and provide a theoretical explanation for the unexpected observations.

\* Raman data provided by L.M. Moreira and M.A. Pimenta.

[1] R. Krupke, S. Linden, M. Rapp, F. Hennrich, Adv. Mat. 18 (2006) 1468-1470.

## PTU CURVATURE EFFECTS IN D\* BAND OF SMALL DIAMETER CARBON NANOTUBES

<u>Jenő Kürti</u><sup>1</sup>, Viktor Zólyomi<sup>2</sup>, Janos Koltai<sup>1</sup>, Ferenc Simon<sup>3</sup>, Rudolf Pfeiffer<sup>3</sup>, Hans Kuzmany<sup>3</sup>

<sup>1</sup>Dept. of Biological Physics, Eotvos University Budapest, Hungary <sup>2</sup>Res. Institute for Solid State Physics and Optics of HAS, Budapest, Hungary <sup>3</sup>Institut fur Materialphysik, Universitat Wien, Austria

The energy dispersion of the D\* band (overtone of the disorder induced D band) shows a strong diameter dependence according to Raman measurements on double walled carbon nanotubes. The Raman shift of the small diameter inner tubes shows an average softening. There is an oscillation around a linear behavior with 100 cm-1/eV and 85 cm-1/eV for the outer and inner tubes, respectively. We show that the experimental observation can be reproduced by simple model calculations if the curvature effects are taken into account. The results are compared with first principles calculations.

On the morphology and transport properties of HDPE – titanate nanowire nanocomposites PTU Jozsef Szel, Endre Horvath, Andras Sapi, Akos Kukovecz, Zoltan Konya, Imre Kiricsi 58 University of Szeged, Dept. of Applied Chemistry

High aspect ratio TiO2 and titanate nanostructures and their composites are intensively studied at present because of their promising photoelectrical, biomedical and Li+ and H2 storage properties. Our recent work in this field involved studies on the formation mechanism and photosensitization of trititanate nanotubes and nanowires. In this contribution we report on the properties of high densitity polyethylene - nanowire composite materials. The morphology of the samples was investigated by SEM, their thermal conductivity and thermal diffusivity was measured simultaneously using the periodic thermal excitation method and their electronic transport properties were studied by dielectric spectroscopy. We shall present a coherent interpretation of these measurements and discuss the practical applicability of these new nanocomposites.

### Pressure-induced phenomena in single-walled carbon

PTU

C. Kuntscher<sup>1</sup>, K. Thirunavukkuarasu<sup>1</sup>, Á. Pekker<sup>2</sup>, K. Kamarás<sup>3</sup>, F. Hennrich<sup>4</sup>, M. Kappes<sup>5</sup>, Y. Iwasa<sup>6</sup> <sup>1</sup>Experimentalphysik II, Universität Augsburg, D-86159 Augsburg, Germany <sup>2</sup>Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, P.O.Box 49, Budapest, Hungary H 1525 <sup>3</sup>1 <sup>4</sup>Institut für Nanotechnologie, Forschungzentrum Karlsruhe, D-76021 Karlsruhe, Germany <sup>5</sup>3, Institut für Physikalische Chemie, Universität Karlsruhe, D-76128 Karlsruhe, Germany <sup>6</sup>Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

The study of single-walled carbon nanotubes (SWNTs) under high pressure has attracted much interest recently as the application of pressure induces structural deformations of the SWNTs and also tunes the intertube interactions by changing the distances between the tubes. Both should significantly affect the properties of the SWNTs.

We studied the optical response of thin films of both unoriented and oriented SWNTs over a broad frequency range (IR-VIS) and for pressures up to 8 GPa. The effect of pressure on oriented nanotubes caused major changes in the optical properties only for the polarization along the nanotube axis. We will discuss in detail the effect of pressure on the electronic properties like interband transitions for the different SWNT films.

Supported by the DFG, Emmy Noether-program. Provision of beamtime at the ANKA Angströmquelle Karlsruhe is acknowledged.

### Nanostructuring of a C<sub>60</sub>-uNanostructuring of a C<sub>60</sub>-uracil Adduct and 2-Aminopurine com- PTU plex in Langmuir Films by Crick-Watson Base

60

Francis D'Souza<sup>1</sup>, Suresh Gadde<sup>1</sup>, Krzysztof Noworyta<sup>2</sup>, Jerzy Karpiuk<sup>2</sup>, Ievgen Obraztsov<sup>2</sup>, Wlodzimierz Kutner<sup>2</sup>

<sup>1</sup>Department of Chemistry, Wichita State University, 1845 Fairmount, Wichita, KS 67260-0051, USA <sup>2</sup>Institute of Physical of Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

An adduct of  $C_{60}$  and uracil ( $C_{60}$ ur), capable of formation of hydrogen bonds with 2-aminopurine (2-AP) in non-aqueous solvent solutions via Crick-Watson pairing of complimentary nucleic acid bases, was able to molecularly recognize 2-AP in the air-solution interface. That is, "expanded liquid" Langmuir films of a relatively stable  $C_{60}$ ur:(2-AP) complex were formed. The films were characterized by simultaneously recorded isotherms of both surface pressure and surface potential versus area per molecule as well as imaged by the Brewster angle microscopy (BAM). For all systems, BAM imaging indicated co-existence of gaseous and condensed phases even at zero surface pressure. For infinite adduct dilution in the film, the area per molecule was much higher in the presence than that in the absence of 2-AP in the subphase solution, as expected for the complex formation. Comparison of the determined and calculated values of area per molecule as well as those of dipole moment components normal to the air-solution interface indicated prevailing horizontal orientation of the complex in the film. The Langmuir films were transferred, by using the Langmuir-Blodgett technique, onto quartz slides and characterized by the UV-vis and fluorescence spectroscopy.

## PTU Thermodynamic analysis of nucleation of boron nitride nanotubes on metal particles.

<u>Vladimir Kuznetsov</u><sup>1</sup>, Ilya Mazov<sup>1</sup>, Artem Delidovich<sup>1</sup>, Elena Obraztsova<sup>2</sup>, Annick Loiseau<sup>3</sup>

<sup>1</sup>Boreskov Institute of Catalysis, Novosibirsk, Russia <sup>2</sup>Prokhorov General Physics Institute, Moscow, Russia <sup>3</sup>Office National d'Etudes et de Recherches Aérospatiales & Centre National de la Recherche Scientifique, Chatillon, France.

By considering the catalytic processes of BN nanotubes (BNT) formation (arc-discharge, laser ablation, CVD processes) we conclude that these processes include some common steps. The most important are: the formation of metal particle alloys oversaturated with boron and nitrogen atoms, the nucleation of corresponding deposits on the metal catalyst surface and BN deposit growth via migration of B and N atoms to the interface of metal particle and growing BN deposit (nanotubes).

A thermodynamic analysis of the BNT nucleation on the catalysts surface was performed. We have used AM1 and PM3 semiempirical calculations for a detailed study of the geometry, structure, and energetics of BNT nucleus. The master equations for the dependence of critical size of BN nucleus on reaction parameters, such as reaction temperature, supersaturation degree of catalyst particles with B and N, work of adhesion of catalyst to BN, were obtained. These equations combined with the phase diagram approach can be used for the description of different scenarios of BN deposits formation and for the development of the main principles of catalysts design. The calculated values of BN nucleus critical size are compared with experimental data and conditions for the formation of BNT on metal particles are analyzed.

## PTU Construction of carbon nanotube junctions

62 <u>Istvan Laszlo</u>

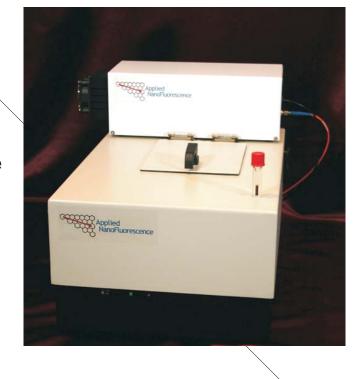
Department of Theoretical Physics, Institute of Physics, Budapest University of Technology and Economics H-1521 Budapest, Hungary

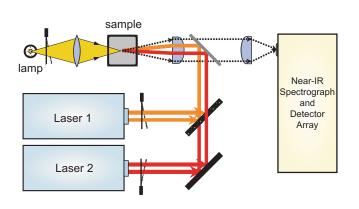
Carbon-nanotube-based electronics offers significant potential as a nanoscale alternative to silicon-based devices for molecular electronics technologies. Using nanotube junctions a truly nanoelectronic architecture can be realized where both devices and interconnects are based on carbon nanotubes. Although there are various theoretical propositions for nanotube junctions, all of them are applied for non chiral nanotubes. We have recently presented an algorithm for constructing junctions between single wall nanotubes of any chirality and diameter. This method is based on Geometric Intersection of Cylinders and it can describe most of the Y and T junctions obtained by the To-Doped Vapour Catalyst method. Namely in this method new nanotube branches are attached to already developed nanotubes. In the present work a new method will be presented for constructing nanotube junctions between three nanotubes of any chirality.

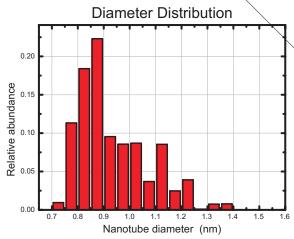
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### Nanotube Growth

### 8:30-9:00 S. HOFMANN, US

In-situ observations of catalyst dynamics during surface-bound carbon nanotube nucleation

9:00 - 9:30 S. IIJIMA, JP

Science and Technology of Single-Walled Carbon Nanotubes

9:30 - 10:00 D. GEOHEGAN, US

In situ time-resolved measurements of carbon nanotube and nanohorn growth

10:00-10:30 Coffee break

### 10:30 – 11:00 R. PFEIFFER, AT

Growth mechanisms of inner-shell tubes in double-wall carbon nanotubes

### **ANNOUNCEMENTS**

### 11:00 – 11:30 H. KATAURA, JP

Filling up Metallic Valley on Photoluminescence Map by Organic Molecules Encapsulated in Single-Wall Carbon Nanotubes

11:30 – 12:00 M. CALAME, NL

From individual molecular junctions to networks

12:00 – 17:00 Mini Workshops

17:00 - 18:30 Dinner

### Noncarbon Nanotubes

18:30 - 19:00 A. LOISEAU, FR

Luminescence properties of Boron Nitride Nanotubes

19:00 - 19:30 A. RUBIO, ES

Optical properties of graphite, h-BN and nanotubes: coherent excitations

19:30 - 20:00 C. GADERMAIER, SI

Equilibrium and non-equilibrium optical properties of MoSI nanowires

### Poster II (PTH)

## 8:30 NTG

1

# In-situ observations of catalyst dynamics during surface-bound carbon nanotube nucleation Stephan Hofmann

Centre for Advanced Photonics and Electronics, University of Cambridge, Cambridge CB3 0FA, UK

An accurate model of catalytic carbon nanotube nucleation relies heavily on the quality of direct experimental observation. We present atomic-scale environmental transmission electron microscopy and in-situ time-resolved X-ray photoelectron spectroscopy (XPS) of dynamic effects before and during catalyst assisted CVD of SWNTs and CNFs [1]. We focus on acetylene decomposition over SiOx supported Ni and Fe catalyst films at gas dilutions and pressures similar to those during our normal CVD experiments [2,3], so we can draw realistic conclusions about what determines structural selectivity.

We observe that the core of a transition metal catalyst nano-particle remains crystalline, whereas its surface continuously reshapes during nanotube formation. Our XPS results suggest a rapid transition from initial chemisorbed carbon on a metallic Fe catalyst surface to a sp2 graphitic carbon network. A SWNT nucleates by lift-off of a carbon cap. Cap stabilization and nanotube growth involve the dynamic reshaping of the catalyst nano-crystal itself. For a CNF, the graphene layer stacking is determined by the successive elongation and contraction of the catalyst nano-particle at its tip.

- [1] Hofmann S., Sharma R., Ducati C., Du G., Mattevi C., Cepek C., Cantoro M., Pisana S., Parvez A., Ferrari A. C., Dunin-Borkowski R., Lizzit S., Petaccia L., Goldoni A., Robertson J., submitted (2006)
- [2] Cantoro et al., Nano Lett. 6, 1107 (2006)
- [3] Hofmann et al., Phys. Rev. Lett. 95, 036101 (2005)

## 9:00 NTG

2

### Science and Technology of Single-Walled Carbon Nanotubes

S. Iijima

AIST, Research Center for Advanced Carbon Materials, Meijo University and NEC

Many unique properties of CNTs depend on their structures and morphologies. When come to detailed comparisons between experiment and theory, well-controlled and characterized specimens (diameter, length, quantity, chirality, structural perfection, impurity, homogeneity) will be eventually needed. This is also true for their industrial applications to match their requirements. Recently two important breakthroughs in single-wall carbon nanotube (SWCNT) growth were made in our laboratories at AIST (1). One is a floating catalyst-assisted CVD method of growing SWCNTs. The method can provide controlled tube diameters and extremely high purity tubes with high production yield according to optical spectroscopic characterization. The other is the "Super-Growth2 of CNTs, which grow vertically on various substrates including metal foils as high as one centimeter. Here we emphasize recent developments on these two SWCNTs towards industrial largescale production and applications.

Secondly, the importance of characterization of nano-structured materials will be discussed by showing the latest observation on individual carbon atoms, local atomic defects and their dynamic behaviors of SWCNTs, which have been carried out by an ultra-high resolution TEM with a spherical aberration corrector. Furthermore, it will be demonstrated that the inside nano-spaces of SWCNT are an ideal support for individual atoms and some organic molecules for atomic resolution TEM microscopy.

- (1) T. Saito, et al., J. Phys. Chem. B, 109, 10647-10652 (2005). D. Futaba et al., Science 306, 1362-1364 (2004). D. Futaba et al., Phys. Rev. Lett. 95, 056104 (1)-(4) (2005 D. Futaba et al., Science 306, 1362-1364 (2004). D. Futaba et al., Nature Materials 5, 987-994 (2006).
- (2) A. Hashimoto, et al., Nature, 430, 870-873 (2004). K. Urita, et al., Phys. Rev. Lett., 94, 155502(2005). Z. Liu, et al., Phys. Rev. Lett., 95, 187406(1)-(4) (2005). Y. Sato, et al., Phys. Rev. B, 73, 233409(2006).

### IN SITU TIME-RESOLVED MEASUREMENTS OF CARBON NANOTUBE AND NANOHORN GROWTH

9:30 NTG

3

David Geohegan, Alex Puretzy, Gyula Eres, David Styers-Barnett, Chris Rouleau, Zuqin Liu, Ilia Ivanov, Jeremy Jackson, Richard Wood, Sreekanth Pannala, Jack Wells, Meng-Dawn Cheng, Hongtao Cui, Hui Hu, Bin Zhao, Mina Yoon, Kai Xiao, Matthew Garrett Oak Ridge National Laboratory

Time-resolved, in situ imaging and spectroscopic investigations of the growth mechanisms and kinetics of carbon nanotubes and nanohorns are described, and the effects of their resulting nanostructure on their properties. Growth conditions for high-yield, laser vaporization production of single-wall carbon nanotubes and nanohorns (SWNHs) using a high-power industrial Nd:YAG laser with tunable, ms-pulse widths were investigated by high-speed videography and pyrometry. SWNHs are found to grow at rates comparable to SWNTs without the need for a metal catalyst. In situ optical interferometry and timeresolved imaging are used to directly measure the height of vertically-aligned nanotube arrays (VANTAs) during CVD synthesis to understand their nucleation and growth kinetics, reasons for their coordinated growth and growth termination, and methods to maximize SWNT content in multi-millimeter-long arrays. A kinetic model is proposed to explain Raman microscopy and TEM observations that the number of walls and the diameters of nanotubes appear to change during VANTA growth to multimillimeter heights. The high thermal diffusivity of VANTAs and their application as thermal interface materials will be described. Synthesis science supported by the U.S. DOE-BES, DMSE with characterization facilities supported at the Center for Nanophase Materials Sciences by the Scientific User Facility Division, DOE-BES.

#### Growth mechanisms of inner-shell tubes in double-wall carbon nanotubes

10:30 4

Rudolf Pfeiffer<sup>1</sup>, M. Holzweber<sup>1</sup>, H. Peterlik<sup>1</sup>, H. Kuzmany<sup>1</sup>, H. Shiozawa<sup>2</sup>, A. Grüneis<sup>2</sup>, T. Pichler<sup>2</sup>, H. NTG Kataura<sup>3</sup>

<sup>1</sup>Fakultät für Physik, Universität Wien, Austria <sup>2</sup>IFW Dresden, Germany <sup>3</sup>AIST, Japan

We report on detailed growth studies on the growth of inner-shell tubes in DWCNTs. The used precursor materials were C<sub>60</sub> fullerenes and ferrocene (FeCp<sub>2</sub>) filled tubes. The samples were characterized with Raman spectroscopy and x-ray diffraction.

In the case of the C<sub>60</sub> peapods it is shown that the starting fullerenes decay with a half-lifetime of 2.9(5) min at 1250 °C. However, the periodicity of the 1D chain formed inside the outer tubes persists almost five times longer. I.e., the initial fullerenes decay into an intermediate phase but do not completely disintegrate into C<sub>2</sub> units. The growth of the small diameter inner tubes agrees well with the decay of the 1D chain but the large diameter inner tubes reach their maximum growth rate long after the initial fullerenes and the 1D chain were already destroyed.

The FeCp<sub>2</sub> based inner tubes grow already at 600; °C in about 1 hour. The inner tubes RBM frequencies are the same as for the  $C_{60}$  based tubes but the intensities are different. I.e., even for the same starting SWCNTs material the distribution of inner-outer tube pairs is different. Thus, the growth mechanism of the FeCp<sub>2</sub> based tubes is different from the peapods route. In the FeCp<sub>2</sub> case Fe<sub>3</sub>C particles are formed that act similar to the catalysator particles for CVD grown nanotubes.

### Filling up Metallic Valley on Photoluminescence Map by Organic Molecules Encapsulated 11:00 in Single-Wall Carbon Nanotubes

NTG

Hiromichi Kataura, Kazuhiro Yanagi

Nanotechnology Research Institute, AIST, Tsukuba 305-8562, Japan

5

Single-wall carbon nanotubes (SWCNTs) exhibit excitonic optical absorptions corresponding E11 and E22 transitions of semiconductors and E11 of metals. Semiconducting SWCNTs show strong E11 photoluminescence (PL) for E22 excitations and we can produce a PL map for a specific sample. However, of course, no PL is observed for E11 excitation of metallic SWCNTs, which is so-called "metallic valley". In this work, we demonstrate a new PL peak just on the metallic valley of the PL map simply by encapsulating squarylium dye molecules in SWCNTs. The squarylium dye has strong optical absorption at the E11 transition of metallic SWCNTs used in this work. The new PL peak is caused by efficient energy transfer from the dye molecules to semiconducting SWCNTs. Enhancement of E11 transient absorption saturation of the semiconducting SWCNTs was observed after the excitation of the encapsulated dye, which indicates ultrafast (< 190 fs) energy transfer from the dye to the SWCNTs. These results suggest that we can modify the optical response of the SWCNTs by encapsulating molecules inside.

### 11:30 From individual molecular junctions to networks

NTG
Michel Calame<sup>1</sup>, Maria González<sup>1</sup>, Jianhui Liao<sup>1</sup>, Roman Huber<sup>1</sup>, Songmei Wu<sup>2</sup>, Laetitia Bernard<sup>2</sup>,
Sense van der Molen<sup>2</sup>, Christian Schönenberger<sup>2</sup>

<sup>1</sup>University of Basel, Switzerland <sup>2</sup>

The shrinking of components dimensions in electronic circuits has triggered the exploration of alternative routes to fabricate electronic devices. As fundamentally interesting and practically promising, devices where the electronic function shall be realized by a single molecule are currently being intensively investigated.

We prepare and characterize individual molecular junctions using a mechanically controllable break junction technique working in a liquid environment. We studied in particular the electrical transport properties of fullerene derivatives and n-alkanedithiols with this technique. The large number of possible microscopic arrangements during the formation of a metal-molecule-metal junction requires a careful statistical analysis of the data. We proposed recently a simple and robust physical criterion allowing the extraction of the molecular signature from the tunneling background without performing any data selection.

As a complementary approach, we are developing a new scheme for the preparation of networks of molecular junctions based on the self-assembly and stamping of metallic nanoparticles. Thiolated conjugated molecules can be inserted within such arrays via chemical exchange to form a network of molecular junctions. This methodology permits the fabrication of a large number of junctions in parallel and represents a valuable test platform for the development of molecular circuits.

#### Luminescence properties of Boron Nitride Nanotubes

18:30

Perine Jaffrennou<sup>1</sup>, Julien Barjon<sup>2</sup>, S. Sonderreger<sup>3</sup>, Jean-Sébastien Lauret<sup>4</sup>, J.-D. Ganière<sup>3</sup>, Brigitte **NCN** Attal-Trétout<sup>5</sup>, François Ducastelle<sup>1</sup>, <u>Annick Loiseau</u><sup>1</sup>

<sup>1</sup>LEM, ONERA-CNRS, BP72, 92322 Châtillon Cedex, France <sup>2</sup>GEMC, Université Versailles-ST Quentin, Meudon, France <sup>3</sup>IPEQ, EPFL, Lausanne, Switzerland <sup>4</sup>LPQM, ENS Cachan, Cachan, France <sup>5</sup>ONERA, Chemin de la Hunière, 91761 Palaiseau Cedex, France

Boron nitride nanotubes are wide band gap semiconductors, expected to strongly emit in the UV range and to display strong excitonic effects.

Thanks to the vaporization laser route developed at Onera, we have performed the very first absorption measurements on BN-SWNT assemblies, which revealed the existence of three bands in the UV range

In order to analyse the nature of these bands, we have undertaken two kinds of optical measurements on isolated tubes. First the dielectric response in low energy loss spectroscopy provided the first measure of the optical gap close to 5.8 eV [2].

The second approach, detailed in this talk, consists in coupling cathodoluminescence spectroscopy and imaging of individual BNNT [3]. The luminescence is composed of two emission bands in the 3 to 6.2 eV range. The first band is centered at 5.3 eV and is attributed to quasi-Frenkel excitons. The second band is centered at 3.9 eV and is shown to be due to defect centers [4]. Time-resolved cathodoluminescence in the picosecond range confirms this interpretation.

- [1] J. S. Lauret, et al Phys. Rev. Lett. 94, 037405 (2005).
- [2] R. Arenal, et al, Phys. Rev. Lett. 95, 127601 (2005).
- [3] P. Jaffrennou et al., submitted to Nanoletters (2007)
- [4] M. Silly et al, Phys. Rev B, in press (2007).

### Optical properties of graphite, h-BN and nanotubes: coherent excitations Angel Rubio

19:00 NCN

Universidad del Pais Vasco UPV/EHU, San Sebastian Spain

In this talk we will present and analysis of the excited state properties of hexagonal structures, in particular graphite/graphene and h-BN. Then we will transport those studies to understand the response of the corresponding nanotubes. We will concentrate on the electronic properties and optical response (dominated by strongly bound excitons) as well as Raman for tube characterisation, including the coherent excitation of phonons by strong short-laser pulses. Some future lines of research will be addressed at the end of the talk.

Work done within the Network of Excellence NANOQUANTA and within the European Theoretical Spectroscopy Facility (ETSF) in collaboration with L. Wirtz, A. Marini, H. Petek, I. Kunie, J. Serrano.

#### Equilibrium and non-equilibrium optical properties of MoSI nanowires

19:30

Christoph Gadermaier<sup>1</sup>, Primoz Kusar<sup>2</sup>, Damjan Vengust<sup>2</sup>, Leonardo Degiorgi<sup>3</sup>, Igor Vilfan<sup>2</sup>, Dragan NCN Mihailovic<sup>2</sup>

<sup>1</sup>Department of Complex Matter, Jozef Stefan Institute, Ljubljana, Slovenia <sup>2</sup> <sup>3</sup>Laboratorium fuer Festkoerperphysik, ETH Zurich, Switzerland

MoSI nanowires are the one-dimensional systems with the weakest known interaction with their neighbours. Therefore they are expected to show most clearly the effects of one-dimensionality. We studied equilibrium and non-equilibrium optical properties via optical reflectivity and absorbance as well as femto second pump-probe spectra of oriented MoSI nanowire thin films. The results are compared with density functional theory calculations for light polarisation parallel and perpendicular to the nanowire

Absorption of light polarised parallel to the axis of orientation shows a series of resonances that are absent for perpendicular polarisation. The pattern of these resonances is in excellent agreement with the calculations. The sharp Van Hove features expected from the highly one-dimensional character of the material and the narrow valence and conduction bands of predominantly Mo-d and S-p character are not observed, partly because of the large density of electron sub-bands and partly because of electron energy damping.

Femtosecond studies presented will be discussed in terms of electronic structure, one-dimensional relaxation behaviour and propagation of impulsive mechanical strain.

### Phase Coherent Charge Transport in Single and Bi-layer Graphene

PTH

Feng Miao, Sitara Wijeratne, Ulas Coskun, Yong Zhang, Chun Ning Lau University of California, Riverside

1

We experimentally investigate electrical transport properties of graphene, which is a two dimensional (2D) conductor with relativistic energy dispersion relation. By investigating single- and bi-layer graphene devices with different aspect ratios, we confirm that the minimum conductivity in wide and short graphene strips approaches the theoretical value of  $4e^2/ph$ . At low temperatures, quantum interference of multiply-reflected waves of electrons and holes in graphene give rise to periodic conductance oscillations. Thus graphene acts as a quantum billiard, a 2D ballistic, phase coherent electron system with long phase coherence length that exceeds 5  $\mu$ m. Additional features in differential conductance emerge when graphene is coupled to superconducting electrodes. We observe proximity-induced enhanced conductance at low bias, and conductance dips at energy scales far above the superconducting gap of the electrodes. The latter provides preliminary evidence for a novel superconducting material that consists of graphene coated with metallic atoms.

# Body emission characteristics from lateral single-walled carbon nanotube emitters

PTH

2

Wei-Yang Lee

National Tsing Hua University

The uniform body emission properties of lateral single-walled carbon nanotubes (SWNTs) emitters grown by chemical vapor deposition are reported. Lateral SWNTs lying on the substrate were found to possess a turn-on field of at least 1.67 V/ $\mu$ m and a field enhancement factor of 5223 at most. A flat panel display requiring 1mA/cm2 was carried out at 4.7 V/ $\mu$ m. The large area uniform luminescence was obtained due to the uniform electrical field intensities throughout the body of SWNTs according to a calculation of electrical field distribution. Good field emission characteristics with a simple process could be more applicable for display applications.

### Carbon nanotubes inorganic glass composites

PTH

3

Mônica Jung de Andrade<sup>1</sup>, Márcio Dias Lima<sup>1</sup>, Carlos Pérez Bergmann<sup>2</sup>, Siegmar Roth<sup>3</sup>

<sup>1</sup>Federal University of Rio Grande do Sul (Brazil) and Max-Planck Institut for Solid State Research (Germany) <sup>2</sup>Federal University of Rio Grande do Sul (Brazil) <sup>3</sup>Max-Planck Institut for Solid State Research (Germany)

Since the early nineties the unique physical and chemical properties of carbon nanotubes (CNTs) have attracted the attention of worldwide research, yielding to more than 202400 publications. CNTs offer scope for the development of fundamentally new composite materials with several applications in different areas. Although more than 1940 works on CNT composites have already been reported, less than 4% are concerned on CNTs ceramic matrices composites. Great part of this lack is probably due to the poor interaction already achieved and to the difficulty of densification of the final composites. In the present work, different compositions of inorganic glasses were evaluated through Raman spectroscopy, X-ray diffraction and electron microscopy. The main focus in this work was to study the interaction between the matrix and carbon nanotubes. As it was expected, boron and silica contributed for a good wettability between the host matrix and the CNTs.

# PTH Development of catalysts for large scale production of single and double walled carbon nanotubes

Marcio Lima<sup>1</sup>, Monica de Andrade<sup>1</sup>, Carlos Bergmann<sup>2</sup>, Siegmar Roth<sup>1</sup>

<sup>1</sup>Max Planck Institute for Solid State Research <sup>2</sup>Federal University of Rio Grande do Sul

Great attention has been focused on Thermal Chemical Vapour Deposition (TCVD) due to its great potential for scale-up the synthesis of carbon nanotubes (CNTs) with powder catalysts. The main purpose of this work is to optimize the production of Fe-Mo/MgO Single Walled Carbon Nanotubes (SWNTs) and Double Walled Carbon Nanotubes (DWCNT) through TCVD. In order to that, the composition of the catalyst (Fe:Mo precursos ratio), the catalyst preparation route and synthesis conditions were evaluated (temperature, time and carbon source). Ethanol and Hexane were tested as carbon sources. The catalysts were tested in a large capacity fluidized bed CVD reactor. Iron and molybdenum oxides dispersed in magnesium oxide (MgO) matrix form an inexpensive CNT catalyst and the easily dissolution of the MgO in mild acids facilitates the purification process. In situ characterization by electrical conductivity of the catalysts were also used to evaluated the effect of several synthesis parameters. The diameter of the nanotubes were not significantly affected by the carbon source. Higher yields of SWCTs were obtained using hexane but also more deposition of amorphous carbon was observed. It was found that molybdenum addition in small amount (Fe:Mo?20) causes an increasing in the G/D ratio and yields SWCNTs, but higher amount causes an increase in the number of walls of CNTs and also the production of undesirable carbon nanostructures (nanofibers and carbon onions).

# PTH SOLUBILIZATION OF SINGLE-WALL CARBON NANOTUBES IN SOLUTIONS OF CALIX[4]RESORCINARENE DERIVATIVES

Anatoly Lobach<sup>1</sup>, Irina Ryzhkina<sup>2</sup>, Nataliya Spitsina<sup>1</sup>, Elena Obraztsova<sup>3</sup>

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Chemical covalent and noncovalent functionalization of single-wall carbon nanotubes (SWNT) is very important for development technological applications of nanotubes. The present work reports on investigations of noncovalent interaction process of pristine and purified SWNT\_arc and SWNT\_HiPco with various types surfactants [1], functionalized macrocyclic compounds – calix[4]resorcinarene derivatives [2] and polymers: carboxymethylcellulose, polyvinyl alcohol and their mixture in water and organic solvents. Solubilization of SWNT in solvents were successively characterized using UV-vis-NIR and Raman spectroscopy. We find for the first time that calix[4]resorcinarene derivatives solutions forms stable dispersion of individual nanotubes at less concentration detergent than common surfactants. High dispersion of SWNT in surfactant or/and calix[4]resorcinarene-polymer and polymer solutions were used for preparation of freestanding transparent thin films for photonic devices[3].

The work is supported by RFBR 05-03-33132, 06-02-08151 grants.

- 1. W. Wenseleers et al., Adv. Funct. Mater., 14, 1105 (2004).
- 2. I.S. Ryzhkina et al., Russ. Chem. Bull., Int. Ed., 7, 1470 (2004).
- 3. A.V. Tausenev, E.D. Obraztsova, A.S. Lobach et al., Quantum Electronics, submitted (2007).

### PTH Generation of femtosecond electron bunches from CVD nano-graphite

Dmitry Lyashenko<sup>1</sup>, Elena Obraztsova<sup>2</sup>, Alexander Obraztsov<sup>3</sup>, Yuri Svirko<sup>1</sup>

<sup>1</sup>Department of Physics and Mathematics, University of Joensuu, PO Box 111, Joensuu, 80101, Finland <sup>2</sup>Natural Sciences Center of General Physics Institute, 38 Vavilov street, 119991, Moscow, Russia <sup>3</sup>Physics Department, Moscow State University, 119992, Moscow, Russia

Nano-graphite (NG) has recently emerged as a promising material for manufacturing of cathodes for both field and thermioninc electron sources. In this work, we demonstrate that under irradiation by femtosecond laser pulses, CVD NG films produce dense electron bunches opening new horizons in development novel X-ray and UV sources.

In this experiment we measured charge of emitted electrons as a function of the applied voltage U and the energy density W of the incident laser pulse (wavelength is 800 nm, pulse length is 50 fs, laser spot size is about 8 mm2). The threshold energy density was as low as Wth = 5 mJ/cm2 and showed a weak dependence on U. At W > Wth, the emitted charge was found to be a linear function of the laser energy density. In particular, at W = 20 mJ/cm2, the emitted charge changes from 0.004 nC to 0.2 nC at U = 0 and U=500 V, respectively. If we assume that electrons are emitted only in the presence of the laser pulse, the emission current in the femtosecond regime is as high as 1000 A/cm2. This makes the laser-assisted field emission to be a prospective method of the generation of dense electron bunches.

### An Equimolar C2H2-CO2 Reaction in the Synthesis of Carbon Nanotubes.

PTH

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Arnaud Magrez<sup>1</sup>, Jin Won Seo<sup>1</sup>, Vladimir Kuznetsov<sup>2</sup>, László Forró<sup>1</sup>

<sup>1</sup>Ecole Polytechnique Fédérale de Lausanne, Switzerland <sup>2</sup>Boreskov Institute of Catalysis, Russia

Chemical vapor deposition is considered to be the most viable process for the production of nanotubes i) in large scale, ii) in-situ when integrated into a device. Regardless of the carbon source, carbon synthesis is limited to classical decomposition reactions (i.e. C2H2? 2C +H2). Recent results have shown that the presence of a small amount of a species that contains oxygen atoms in addition to the carbon source dramatically improves the yield of the reaction. Amorphous carbon is effectively etched by H2O[1], O2[2] and/or CO2[3] which preserves and stimulates catalyst activity. Herein, we report a reaction between acetylene and CO2, mixed in an equimolar ratio[4], to produce carbon nanotubes. A dramatic enhancement of the CNT yield compared with those of previous syntheses has been observed. Furthermore, the lifetime of the catalyst is considerably extended and the initial growth rate is enhanced compared with those of classical decomposition reactions.

- [1] K. Hata et al, Science 2004, 306, 1362–1364.
- [2] G. Zhang et al, Proc. Natl. Acad. Sci. USA 2005, 102, 16141–16145.
- [3] A. G. Nasibulin et al, Chem. Phys. Lett. 2006, 417, 179–184.
- [4] A. Magrez et al, Angew. Chem. Int. Ed. Accepted (2007)

### Chirality dependence in the absorption and Rayleigh spectra of carbon nanotubes

PTH

Ermin Malic<sup>1</sup>, Matthias Hirtschulz<sup>2</sup>, Frank Milde<sup>2</sup>, Andreas Knorr<sup>2</sup>, Stephanie Reich<sup>3</sup>

<sup>1</sup>Massachusetts Institute of Technology, and Technische Universität Berlin, Institut für Theoretische Physik <sup>2</sup>Technische Universität Berlin, Institut für Theoretische Physik <sup>3</sup>Massachusetts Institute of Technology, Department of Materials Science and Engineering

We studied optical absorption and Rayleigh scattering in single-walled carbon nanotubes using the density matrix formalism and the tight-binding approximation. We obtain analytical results for the matrix elements of arbitrary nanotubes; in the special case of zigzag nanotubes even the absorption coefficient can be expressed analytically. We analyze the chiral angle and family dependence of the optical spectra. The absorption increases up to 10% from the zigzag to the armchair configuration, which originates from the combined chirality dependence of the optical matrix element and the electronic density of states. We show that metallic nanotubes have an optical gap regardless of their chiral angle. Our calculated Rayleigh spectra are in good agreement with experiment. Metallic nanotubes have a double-peak structure in their Rayleigh spectra, where the low energy peak is weaker in intensity than the high-energy transition. This intensity ratio can be explained from the dependence of the optical matrix elements on the wave vector in graphite. Our method for describing optical absorption in nanotubes allows the inclusion of electronelectron and electron-hole interaction. We discuss how this affects the optical spectra and the chirality dependence of the optical absorption.

#### Fabrication of Nanogaps in Individual Metallic Single-Walled Carbon Nanotubes

PTH

Christoph Marquardt<sup>1</sup>, Aravind Vijayaraghavan<sup>1</sup>, Simone Dehm<sup>1</sup>, Frank Hennrich<sup>1</sup>, Hilbert von Löhney- 9 sen<sup>2</sup>, Ralph Krupke<sup>1</sup>

<sup>1</sup>Forschungszentrum Karlsruhe, Institut für Nanotechnologie, 76021 Karlsruhe, Germany <sup>2</sup>Universität Karlsruhe, Physikalisches Institut, 76128 Karlsruhe, Germany

We investigate the formation of nanoscale gaps in individual metallic single-walled carbon nanotubes (SWNTs) for the purpose of using them as molecular leads. Individual metallic SWNTs were deposited on large arrays of lithographically designed metal electrodes [1] using the technique of dielectrophoresis [2, 3]. The contacted tubes were biased in a way that current-induced electrical breakdown occured [4] and a gap was generated.

Due to the large number of devices, we are able to investigate statistically the formation of nanogaps under different conditions and to study the influence of the tube surrounding such as the substrate or a liquid.

On this poster we report on our first results in the nanogap fabrication.

- [1] see poster of A.Vijaraghavan: "Ultra-large Scale Directed Assemly of Single-Walled Carbon Nanotube Devices."
- [2] R. Krupke, Science 301 (2003) 344
- [3] R. Krupke, Nano Letters 3 (2003) 1019
- [4] P. G. Collins, Science 292 (2001) 706

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### PTH Kohn anomalies in doped carbon nanotubes

Nicolas Caudal, A. Saitta, Michele Lazzeri,  $\underline{\text{Francesco Mauri}}$  IMPMC

The tangential vibrational modes of metallic single-walled carbon nanotubes (SWNTs) are thought to be characterized by Kohn anomalies resulting from the combination of their intrinsic one-dimensional nature and a significant electron-phonon coupling. These properties are modified by the doping-induced tuning of the Fermi energy level Ef, obtained through the intercalation of SWNTs with alkali atoms or the application of a gate potential. We present a Density-Functional Theory (DFT) study of the vibrational properties of a (9,9) metallic SWNT as a function of electronic doping. For such study, we use, as in standard DFT calculations of vibrational properties, the Born-Oppenheimer approximation, but we also use time-dependent perturbation theory to explore non-adiabatic effects beyond this approximation. We compare our results with existing measurements and suggest features to be explored in future experiments.

# PTH A charge-dipole model to compute the polarization properties of carbon nanotubes and fullerenes

Alexandre Mayer, Rachel Langlet, Philippe Lambin Facultés Universitaires Notre-Dame de la Paix

We present an electrostatic model for the calculation of the polarization properties of fullerenes and carbon nanotubes. This model describes each atom by both a net electric charge and a dipole. The consideration of electric charges enables one to account for the displacement of free electrons in structures subject to an external field. It also enables one to account for the accumulation of additional charges. By expressing the electrostatic interactions in terms of normalized propagators, the model achieves a better consistency as well as an improved stability. In its most elementary form, the model depends on a single adjustable parameter and provides static polarization properties that are in excellent agreement with other experimental/theoretical data. The next step in the development of this methodology consists in the consideration of oscillating fields. This step is achieved by including the kinetic energy of the moving charges as well as damping forces in the model. This extended version of our model gives then access to the dynamic polarization properties of fullerenes and carbon nanotubes, which include their absorption spectrum. The results presented in this poster include the polarization properties of fullerenes ranging from the C20 to the C3840. The poster also presents results related to the polarization properties of metallic nanotubes.

### PTH NO gas sensors based on functionalized carbon nanotubes

<u>Tero Mustonen,</u> Jani Mäklin, Krisztián Kordás, Sami Saukko, Jouko Vähäkangas Microelectronics and Materials Physics Laboratories, Department of Electrical and Information Engineering, University of Oulu, P

Aqueous solutions of carboxyl functionalized single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) were deposited between gold electrodes of a gap size of 200  $\mu$ m on alumina wafers. The sensors were equipped with integrated heater elements on the back side of the substrates. The resistive nanotube sensors were tested in a 2-point setup at different temperatures and NO gas concentrations up to 100 ppm in synthetic air and Ar buffer. When exposed to NO, the conductivity of the sensors changed up to 40% for SWCNTs; however, the response was found to be fairly independent on the concentration of the gas in the investigated regime. Both types of sensors could be recovered after measurements by applying short heat pulses on the samples. The sensors showed practically instantaneous gas response with a concentration dependent saturation time of a few tens of minutes. Since all the electrodes and the active materials can be printed on various substrates, our components have potential for scaleable production of NO sensors, and also open new possibilities towards other gas sensing applications.

### Resonant Raman Scattering on Chemically Functionalized Carbon Nanotubes

PTH

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Matthias Müller<sup>1</sup>, Janina Maultzsch<sup>2</sup>, Christian Thomsen<sup>1</sup>, David Wunderlich<sup>3</sup>, Andreas Hirsch<sup>4</sup>

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<sup>4</sup>Inst. für Organ. Chemie, Univ. Erlangen-Nürnberg[1.5ex] We present resonant Raman scattering on carbon nanotubes functionalized with alkenes at various degrees of functionalization. From the resonance profiles of the radial breathing mode (RBM) we assign the chiral indices of the tubes [1] in order to study the behavior of metallic and semiconducting tube species. Both the RBM intensity and the transition energy change with functionalization.

We discuss the influence of the functionalization on the transition energies of the tubes and a possible selectivity of tube species to the chemical reaction, as has been observed for several reactants [2,3].

- [1] J. Maultzsch et al., Phys. Rev. B 72, 205438 (2005).
- [2] M. Strano et al., Science 301, 1519 (2003).
- [3] R. Graupner et al., J. Am. Chem. Soc. 128, 6683 (2006).

# Nanotube field and orientational properties of $\mathbf{C}_{70}$ molecules in carbon nanotubes K.H. Michel

PTH 14

University of Antwerp

The orientation of a  $C_{70}$  fullerene molecule encapsulated in a single-walled carbon nanotube (SWCNT) depends on the tube radius. First we confirm that chirality effects do not affect the orientation as well by comparing discrete atomistic calculations with the results of a continuous tube approximation for a variety of SWCNTs. The molecular and the tube symmetry are exploited by using symmetry-adapted rotator functions. We accurately determine the optimal molecular orientation as a function of the tube radius; for low (< 7 A) and high (> 7.2 A) tube radii, lying and standing molecular orientations are recovered, respectively. In between, we observe a transition regime. In addition, we consider off-axis. We perform a one-dimensional liquid description of a chain of on-axis  $C_{70}$  molecules inside a SWCNT. All results agree well with recent x-ray diffraction experiments.

#### Chirality Dependent Oxidation of Single-Wall Carbon Nanotubes

PTH

<u>Yasumitsu Miyata</u><sup>1</sup>, Takazumi Kawai<sup>2</sup>, Yoshiyuki Miyamoto<sup>2</sup>, Kazuhiro Yanagi<sup>3</sup>, Yutaka Maniwa<sup>1</sup>, Hi- **15** romichi Kataura<sup>3</sup>

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It is often said that the oxidation reactivity of single-wall carbon nanotube (SWCNT) depends on its diameter. However, detailed experimental analysis has not been reported so far. In this work, we have investigated a chirality dependent combustion of SWCNTs by using photoluminescence (PL) spectroscopy. Chirality distributions of semiconducting SWCNTs were measured before and after a thermal oxidation in air. After the heat treatment, PL signal from thin SWCNTs disappeared as reported previously. Farther, interestingly, the lower chiral angle SWCNTs showed the stronger PL in the remained sample. This means that the smaller diameter and the higher chiral angle SWCNTs were decomposed more rapidly. The detailed reaction rate analysis revealed that the oxidation reactivity decreased monotonously as a function of the shortest "bond curvature radius" that is defined as a local curvature radius along with each C-C bond. This simple rule can explain both the diameter and the chirality dependent combustion. Reaction barriers for C-C bond breaking by a singlet oxygen molecule on several SWCNTs were estimated by the first-principle calculations. The barrier heights were depending on the shortest "bond curvature radius" of the SWCNT, which is consistent with the present experimental results.

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# PTH Optical absorption and photoluminescence excitation spectroscopy of SWNTs in UV-Vis

Yuhei Miyauchi, Zhengyi Zhang, Shigeo Maruyama

Department of Mechanical Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

In our previous study [1], we have found that some PL peaks for cross-polarized excitation to the nanotube axis can be clearly observed in the PLE spectra of isolated SWNTs.

In this study, we focus on optical absorption and polarized PLE spectra for UV-Vis range. In Vis to UV range, there exist small but nonzero intensity tails for perpendicular excitation above the distinct peaks of parallel (E22) excitation. The PL intensities corresponding to the perpendicular excitation were almost comparable to those for the parallel excitation in a certain energy region.

In addition, we studied details of optical absorption of SWNTs in UV range by comparing optical absorption and PLE spectroscopy. In an optical absorption spectrum of SWNTs in UV range, there are two major peaks corresponding to parallel ( $\approx 4.5~\rm eV$ ) and perpendicular ( $\approx 5.25~\rm eV$ ) excitations. We compared absorption and PLE spectra and found there is no feature corresponding to  $\approx 4.5~\rm eV$  peak in the PLE spectra. Since only semiconducting SWNTs contribute to PLE spectra, this result suggests that the  $\approx 4.5~\rm eV$  peak is only for metallic nanotubes.

[1] Y. Miyauchi, M. Oba, S. Maruyama, Phys. Rev. B 74, (2006) 205440.

### PTH Mixing of the $A_1$ -modes in carbon nanotubes

Marcel Mohr<sup>1</sup>, Maria Machón<sup>1</sup>, Christian Thomsen<sup>1</sup>, Ivanka Milošević<sup>2</sup>, Milan Damnjanović<sup>2</sup>

<sup>1</sup>Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

<sup>2</sup>Faculty of Physics, University of Belgrade, POB 368, 11011 Belgrade, Serbia

Electron-phonon coupling (EPC) is a key magnitude in carbon materials like graphite or nanotubes, with important consequences on electronic transport or Raman intensities. In nanotubes, symmetry allows a mixing of the radial-breathing mode (RBM) and the high-energy modes (HEMs), often regarded as independent otherwise. This mixing has considerable effects on the electron-phonon coupling of carbon nanotubes. We compare electron-phonon coupling matrix elements  $\mathcal{M}_{e-ph}$  obtained from ideal and mixed modes. The ideal RBM is purely radial and the ideal HEMs are directly derived from the  $E_{2g}$ -mode of graphene. We obtain the degree of mixing by a variational approach based on density-functional theory calculations. We find that the actual RBMs and HEMs differ from the ideal, irrespective of the nanotube chirality. Calculations of  $\mathcal{M}_{e-ph}$  for the ideal RBM leads to deviations of up to 60 % showing the importance of a correct calculation of the eigenvectors. Since the observed intensity of Raman peaks is proportional to  $|\mathcal{M}_{e-ph}|^2$  this effect is relevant for the optical characterization of nanotube abundance. The mixing also influences the calculation of phonon frequencies: while the frequency of the RBM is only slightly changed, we find deviations up to 50 cm<sup>-1</sup> for the HEM.

### PTH Disorder and mesoscopic transport in few-layer graphene

<u>Françoise Molitor</u><sup>1</sup>, Davy Graf<sup>1</sup>, Thomas Ihn<sup>1</sup>, Klaus Ensslin<sup>1</sup>, Christoph Stampfer<sup>2</sup>, Alain Jungen<sup>2</sup>, Christofer Hierold<sup>2</sup>

<sup>1</sup>Solid State Physics Laboratory, ETH Zurich, 8093 Zurich, Switzerland <sup>2</sup>Micro and Nanosystems, ETH Zurich, 8092 Zurich, Switzerland

We investigate effects of disorder in few-layer graphene observed by Raman spectroscopy and transport measurements.

At the transition from few-layer to single-layer graphene flakes, the G line of the Raman spectrum shifts to higher wave numbers [1]. This shift in the G peak position is, however, not constant in space but fluctuates within a given section. This can be attributed to inhomogeneities in the flake possibly related to doping variations leading to the shift [2,3].

Additionally we report on transport measurements on a few-layer graphene wire with a phase coherence length at low temperatures larger than the wire width, but comparable to the wire length [4]. By analyzing the weak localization peak in the one-dimensional dirty-metal regime, we find a density dependence of the quantum corrections to the conductivity. Side gates allow us to tune the Fermi energy locally and to change the disorder configuration for a fixed Fermi level.

- [1] D. Graf et al., Nano Lett., accepted, cond-mat/0607562
- [2] D. Graf, F. Molitor, K. Ensslin, C. Stampfer, A. Jungen, C. Hierold and L. Wirtz, submitted
- [3] S. Pisana et al., cond-mat/0611714
- [4] D. Graf, F. Molitor, T. Ihn and K. Ensslin, in preparation

#### Improving macroscopical physical and mechanical properties of thick layers of aligned mul- PTH tiwall carbon nanotubes by annealing 19

Simone Musso<sup>1</sup>, Mauro Giorcelli<sup>1</sup>, Alberto Tagliaferro<sup>1</sup>, Matteo Pavese<sup>2</sup>

<sup>1</sup>Dipartimento di Fisica, Politecnico di Torino, Torino, Italy <sup>2</sup>Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, Torino, Italy

We report about the growth and properties of thick layers of aligned MWNTs (average diameter 50nm, average length 2mm). Such MWNT blocks were synthesized, at 850°C, on uncoated silicon by an easyto-scale thermal-CVD system involving the co-evaporation of camphor and ferrocene in a nitrogen gas flow. The growth rate reached 0.5 mm/s and the mass production rate exceeded 1 g/h, with a conversion rate of reagents over 30% in weight.

The availability of self-standing large area blocks of MWNTs allowed us to perform a macroscopic investigation of the mechanical and physical properties, avoiding the drawbacks suffered by works in which microscopic measurements give little information on what can be expected for large-scale systems.

The thick layers of as-grown MWNTs showed interesting mechanical properties and impressive hydrophobic behavior previously reported for functionalized non self standing nanotubes only.

Several annealing treatments were carried out on pristine MWNT chunks in nitrogen gas, in order to obtain an improvement in properties as a consequence of the lattice defect removal. Investigation was carried out on as-deposited and annealed material by scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermo-gravimetric analysis, and mechanical characterization.

### Vortex Nernst effect in a quasi-two-dimensional organic superconductor Moon-Sun Nam, Arzhang Ardavan, Stephen Blundell Department of Physics, University of Oxford

PTH 20

The Nernst effect is the appearance of a voltage transverse to an applied temperature gradient in the presence of a magnetic field (the equivalent of the Hall effect for thermoelectric voltages). In most normal metals the Nernst coefficient is small, but a large signal can be generated by vortices diffusing down a temperature gradient in a type-II superconductor. This effect offers a unique probe of the vortex physics and nature of the superconducting transition.

 $\kappa$ -(ET)<sub>2</sub>Cu(NCS)<sub>2</sub> ( $T_c = 12$  K,  $B_{c2} \approx 6$  T) is the most extensively studied of the quasi-two-dimensional organic superconductors. Owing to its large unit cell size it has a low superfluid density, and a correspondingly small phase stiffness. Our measurements of the vortex Nernst effect reveal a large signal in the vortex liquid state. For small magnetic fields, the vortex Nernst onset and peak are essentially independent of magnetic field strength. This is strong evidence that the transition is not conventional and mean-field-like, but rather it is associated with a "melting" of the phase of the superfluid as has been proposed for low-superfluid-density superconductors [Emery and Kivelson, Nature 374, 434 (1995)].

#### CORRELATION OF CRYSTAL AND STRUCTURE PROPERTIES OF EPITAXIALLY PTH GROWN C<sub>60</sub> THIN-FILMS WITH CHARGE CARRIER MOBILITY 21

Birendra Singh<sup>1</sup>, H. Yang<sup>2</sup>, Birgit Plochberger<sup>3</sup>, L. Yang<sup>4</sup>, Helmut Sitter<sup>3</sup>, Helmut Neugebauer<sup>1</sup>, Serdar Sariciftci<sup>1</sup>

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Recent investigations on organic field-effect transistor performance using C<sub>60</sub> films as semiconductor shows a strong dependence of the charge carrier mobility on the film morphology, influenced by the growth conditions and the choice of the gate dielectric. The origin of this dependence is generally attributed to crystal grain boundaries originating mainly from interactions of the semiconductor with the gate dielectric. The morphology and therefore the charge carrier mobility are highly correlated with the substrate temperature for film growth. Recent work on transistors with  $C_{60}$  films, grown by hot wall epitaxy at high substrate temperature, showed carrier mobilities up to 6 cm2/Vs, an order of magnitude higher compared with films grown at room temperature. In the present paper, we present studies on film morphology and crystallinity of the fullerene films using atomic force microscopy and grazing-incidence Xray diffraction. A correlation of the crystallinity of the film and the charge carrier mobility is established. Higher substrate temperatures lead to singe crystal-like faceted fullerene crystals. The highly crystalline film structure brings a drastic improvement in the charge carrier mobility. Gate voltage independent mobility is also observed in these devices which can be attributed to the highly ordered nature of the fullerene thin film.

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### PTH NanoCogs: Vanadium Oxide Nanostructures with Six-Fold Rotational Symmetry

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Although there are numerous reports describing a wide range of  $V_2O_5$ -based nanostructures, the majority or reports focus on low-dimensional systems such as tubes, ribbons, blades, belts and wires. In this work we report the first observation of unique hierarchical six-fold rotational symmetrical vanadium oxide based nanocomposite synthesized by a simple chemical route. Each cog-like structure is composed of six spokelike platelets of equal dimensions and crystal orientation. Given the high surface area, their application as charge storage materials is promising since Li incorporation into vanadate is well understood and controllable. Their unique structure allows also for cog-like resistive-type gas sensoring applications by addition of  $SnO_2$  as a dopant. The form adopted plays a major role in determining the basic properties, for example, isotropic or anisotropic behaviour and region-dependent surface reactivity. The overall structure has six-fold rotational symmetry and the synthesis results in the unique observation of this one characteristic and uniform structure, even in quantities of the order of grams and they have potential application for Li-based charge storage devices.

# PTH Excitonic transition energies in single-walled carbon nanotubes: Dependence on environmental dielectric constant

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Optical transition energies in SWNTs are affected by environmental dielectric constant ( $\epsilon$ ) because the electric field regarding carrier-carrier interactions spreads outside the SWNTs. In this work, we have investigated the environmental  $\epsilon$  dependence of excitonic transition energies in the range of  $\epsilon$  from 1.0 to 37.5 by soaking SWNTs suspended on gratings in various liquids.

The SWNTs were grown on a grated quartz substrate by alcohol CVD. Both period and depth of the grating were  $2\,\mu\mathrm{m}$ . The density of SWNTs was less than  $1\,\mu\mathrm{m}^{-1}$  along a groove. PL and PLE maps were measured using a CW Ti/Sapphire laser, a 25-cm monochromator, and a L-N<sub>2</sub>-cooled InGaAs PMT. The sample was mounted in a vessel with a quartz window, and soaked in various solvent.

The excitonic transition energies showed a clear  $\epsilon$  dependence; a redshift with increasing  $\epsilon$ , which can be expressed by a simple empirical form as  $E = A\epsilon^{-\alpha} + E_0$ . The redshift can be explained by dielectric screening of e-e repulsion interaction.

### PTH ELECTRONIC STRUCTURE OF ARTIFICIAL AND COSMIC NANODIAMONDS

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X-ray absorption and X-ray photoelectron spectroscopy has been used for comparative study of the electronic state of carbon constituted the detonation nanodiamonds (ND) and that occurred in various carbonaceous chondrite meteorites. The fractions of the detonation ND purified using different oxidative treatments were studied. The treatment of detonation soot with a mixture of nitric and sulfuric acids followed by ion exchange and ultrafiltration of hydrosol obtained was found to result in developing of ND surface coverage consisting of a few graphitic-like layers and oxidized carbon species, which electronic state is close to that of strongly oxidized graphite. The deeper purification of ND was demonstrated to allow cleaning of ND particles from the graphitic-like component and the most of oxidized carbon contaminations. Carbon exiting in the meteorites studied (Staroe Boriskovo, Isna, Murray, Murchison, Orgueil, Allende, Kainsaz, and Mighei) is mainly presented by diamond and graphitic-like species; the latter component could be developed in the result of meteorites irradiation.

### Model exact two-band tunneling formula for real oligomers

PTH

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An accurate description of through-molecule tunneling must take into account the electron states from both the valence and conduction bands. The Franz two-band model,  $k^2 = 2m^*\hbar^{-2}E(1 + E/E_g)$ , gives the relationship between the absolute value of imaginary wave vector k and electron energy E within the band gap interval  $E_g$ ,  $-E_g \le E \le 0$ . Hence, it provides us with a relevant exponential factor that governs tunneling through long molecules, e.g., organic oligomers, which possess semiconductor- or insulator-like electronic structure. However, because the effective mass  $m^*$  is a phenomenological parameter, the use of the above formula says little about the role of the molecular structure in determining the tunneling probability. In our earlier work, exploiting established model Hamiltonians, the band structure of real oligomers was obtained in an analytical form. Different aspects of tunneling through oligomers were then discussed in subsequent publications. Here, we present an analogue of the Franz two-band formula derived from the model exact dispersion relation. It specifies the k on E dependence in terms of  $E_g$  and the width of the valence and conduction bands; the latter are expressed in terms of the Hamiltonian parameters. Implications of our tunneling formula are discussed in the context of recent experiments on metal-molecule-metal contacts.

# Computer modeling of electronic structure of single-wall carbon nanotubes affected by PTH pressure 26

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In this paper, a principal calculation of the electronic structure of single-wall carbon nanotubes at different pressure values has been performed. The simulations have been done for nanotubes aggregated in ropes. The pressure has been modeled by changing the distances between neighbor nanotubes in the rope. The results of the calculations show that the pressure increase leads to the decrease of energy of allowed optical transitions in nanotubes. This result corresponds to the experimental data published [1].

1. Terekhov S.V., Obraztsova E.D., Hochheimer H.D., Teresedai P., Yarger J.L., Osadchy A.V. "Raman scattering as a probe of electronic structure of single-wall carbon nanotubes affected by pressure". Book

1. Tereknov S.V., Obraztsova E.D., Hochneimer H.D., Teresedal P., Yarger J.L., Osadchy A.V. "Raman scattering as a probe of electronic structure of single-wall carbon nanotubes affected by pressure", Book of abstracts of "XIX International Winterschool on electronic properties of novel materials", Kirchberg (Austria), March 2005, p.107.

# High Pressure Raman study of the Second-Order Vibrational modes of Carbon Nanotubes PTH K. Papagelis<sup>1</sup>, K.S. Andrikopoulos<sup>2</sup>, J. Arvanitidis<sup>2</sup>, D. Christofilos<sup>2</sup>, C. Galiotis<sup>1,3</sup>, S. Ves<sup>4</sup>, G.A. Kourouk-**27** lis<sup>2</sup>, T. Takenobu<sup>5</sup>, Y. Iwasa<sup>5</sup>, H. Kataura<sup>6</sup>

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In the current work, Raman spectroscopy is employed in a comparative study of the second order vibrational modes and their response to hydrostatic pressure for both double wall (DWCNTs) and their parent single wall carbon nanotubes (SWCNTs). The observation of the second order bands with pressure is facilitated by their high intensity due to double resonance processes and allows their use as sensitive probe for the characterization of these materials. The pressure dependence of the observed bands allows their assignment and accentuates the different pressure response of the inner and outer shells as indicated by their respective normalized pressure coefficients ( $\Gamma$  parameters) that can be used as input for theoretical calculations. The  $\Gamma$  parameter values related to the second order vibrational modes of the inner shells are smaller than the respective ones of SWCNTs. Moreover, the second order vibrational modes of the inner shells seem to follow a superlinear behaviour while the corresponding behaviour of the outer shell modes is sublinear, in accordance with the pressure response of the first order Raman modes. These observations demonstrate the pressure screening in the interior of carbon nanotubes. Finally, it must be noted that the  $\Gamma_i$  parameter values for the outer shells are greater than the corresponding ones for the parent SWCNTs, which should be ascribed to the inner-outer tube interaction.

# PTH Structural and Electrical Characterization of Low Temperature CVD Single Wall Carbon Nanotubes

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Low temperature growth of single wall carbon nanotubes (SWNTs) is highly desirable for bottom-up fabrication of next generation hybrid electronics compatible with current CMOS fabrication techniques (temperatures lower than 450C). We have recently reported the growth of SWNTs at substrate temperatures lower than 500C in a cold wall CVD system. The process does not require higher temperature pre-treatments and it allows for surface bound nucleation at specific locations by means of patterning catalyst films using conventional lithography.

It is important at this point to establish whether SWNTs grown at low temperature are of good electrical quality. In this work we compare the electrical characteristics of individual SWNTs and mats grown at low temperature, using a back-gated FET configuration, with top- and back-gated high-temperature-grown devices. We further report on suspended SWNT devices on TEM transparent substrates, where the electrical and structural characterization can be performed on the same nanostructure.

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### PTH Non-adiabatic lattice dynamics and Raman spectra of metallic nanotubes

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The decoupling between the motion of ions and electrons is the main assumption of the adiabatic Born-Oppenheimer approximation, and the basis of the lattice dynamics theory. In semiconductors, this decoupling is ensured by the presence of an energy gap between the occupied and empty electronic states. On the contrary, the coupling between ionic and electronic degrees of freedom cannot be excluded a priori in materials where the electronic gap is of the same order or smaller than the phonons energy. Nevertheless, in almost all cases the lattice dynamics of metals is well described within the adiabatic Born-Oppenheimer framework.

Here we show that metallic single wall carbon nanotubes (SWNTs) are a major exception. We prove that the correct description of Kohn anomalies in metallic SWNTs can be obtained only by including non-adiabatic contributions, which account for the dynamic, time dependent nature of phonons. This allows the definitive assignment of the Raman G+ and G- peaks of metallic SWNTs to TO (circumferential) and LO (axial) modes, the opposite of semiconducting SWNTs. Finally, we report the temperature dependent Raman spectra of metallic and semiconducting nanotubes and show that they can only be explained within a non-adiabatic framework.

### Non-adiabatic lattice dynamics and Raman spectra of metallic nanotubes

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We report on the preparation and subsequent Raman analysis of nanotube peapods, using the fullerene  $C_{60}$  and its heterofullerene derivative  $(C_{59}N)_2$  as filling materials. The filling with  $(C_{59}N)_2$  was done from liquid solution at room temperature and from the gas phase at 650 °C. The success of the encapsulation procedure is confirmed through the identification of fingerprint Raman modes and the conversion to double-wall nanotubes through heating to 1250 °C. The G' mode of double-wall nanotubes made from  $(C_{59}N)_2$  peapods is observed to be downshifted compared to the same mode in double wall nanotubes made from  $C_{60}$  peapods. We interpret this downshift as an evidence for the integration of the nitrogen into the lattice of the inner tube.

Work supported by Fonds zur Förderung der wiss. Forschung Austria, Projekt 17345.

#### Synthesis and Characterisation of Cationic Fullerides

PTH

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We present our recent results in the preparation of the cationic fulleride  $C_{60}(AsF_6)_x$ . In this compound,  $C_{60}$  molecule is oxidized by the conjugated base of the superacid HAsF<sub>6</sub>. The importance of studying the cationic fullerides in solid state form is related to the rather higher  $T_c$  expected in a hypothetical "hole" doped superconductor, as predicted by the theories of superconductivity developed for highly correlated systems (Migdal-Eliasberg and non-adiabatic approach). The compounds were characterized by employing several techniques, as laboratory X-ray diffraction, SQUID magnetometry, solid state NMR and Raman spectroscopy. The presence of the counter-ion HAsF<sub>6</sub> in the sample was confirmed by spectroscopic data, though no superconducting behavior was observed. This is probably due to the low symmetric structure of the as prepared compound, which could be compatible with the polymerization of  $C_{60}$  units. Further confirmations of this fact arise from the NMR detection of  $sp^3$  hybridized carbons, and from the splitting of the Raman-active intermolecular modes of C<sub>60</sub>. Preliminary laboratory X-ray diffraction performed during a moderate thermal treatment allowed us to find out two irreversible phase transitions in the sample, respectively at 120°C and at 175°C, which are still under investigation.

#### Modelling high-frequency nanotube mixers

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We have fabricated gate-tuneable carbon nanotube resonators and detected their bending mode vibration at room temperature using frequency mixing. To analyse these measurements, a continuum model is developed, which includes electrostatic driving forces, residual- and gate induced tension. The displacement dependence of the gate capacitance makes it possible to use an ac voltage to drive the high frequency resonator. The scaling of the resonance frequency, the tension in the tube and the down-mixed current has been studied. We generally find a good agreement between the model calculations and our measurements on doubly-clamped suspended nanotubes. It is shown that in contrast to top-down fabricated NEMS devices, non-linearities arise only from the tension and not from the capacitance.

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### PTH Synthesis of Novel Fullerene Dimers

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Fullerenes have attracted considerable interest as materials for next-generation electronic devices. Considerable effort has been focused on the chemical functionalization of fullerenes. Fullerene dimers possess interesting photophysical effects. Here we present our latest efforts on the synthesis and characterization of different types of fullerene dimers such as a novel  $C_{60}/C_{70}$  asymmetric dimer and a short chain  $C_{60}$  dimer from reaction with 2,3-bis-(bromomethyl)-1,4-dibromo-2-butene. By choosing the bridge-molecule we can control the interfullerene spacing and thus tune the electronic interaction between the fullerenes.

### PTH Excitonic Effects in Carbon Nanoribbons

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Recent advances in the synthesis of single layered graphite have focused the attention on novel quasione-dimensional carbon-based systems, i.e. carbon nanoribbons (CNRs). In particular, the possibility of patterning graphene sheets in a controllable manner opens exciting opportunities for future nanoscale optoelectronics applications.

As in the case of carbon nanotubes, the spatial confinement is expected to strongly affect both their electronic and optical properties, giving rise to peculiar features similar to those observed for nanotubes. We present a first principles study of the optical properties of CNRs with the inclusion of both self-energy corrections to the single-particle energies and excitonic effects within the GW-BSE scheme. We focus our attention on nanometer sized systems with armchair edges.

The inclusion of many-body corrections is shown to be crucial in determining both peak positions and lineshapes for all our cases.

The optical spectra are characterised by strongly bound excitons with binding energies of the order of the eV, as for nanotubes of the same size. A clear family behaviour can be recognised in the optical spectra, suggesting the possibility of tailoring the optical features varying the structural properties.

### PTH Mg5C<sub>60</sub>: A stable 2D conducting polymer

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We synthesized a series of  $Mg_xC_{60}$  samples with nominal composition of x between 1 and 6 via solid state reaction between  $C_{60}$  and Mg powder. The samples are multi phased except for x=5. For this stoichiometry a two dimensional alkali fulleride structure was found by powder X-ray diffraction. ESR studies at frequencies of 9 and 225 GHz confirm the phase purity of  $Mg_5C_{60}$ , but reveal small fluctuations in the Mg ion distribution, which broadens the absorption line at the higher ESR frequency. The polymer phase is unusually stable up to high temperatures, it remains unchanged at 823 K for 20 minutes as confirmed by ESR. The mid-infrared absorption spectrum in the range of 780-850 cm<sup>-1</sup> suggests that the polymer sheets contain single bonded fulleride ions. Both the spin susceptibility determined by ESR and microwave conductivity measurements show that  $Mg_5C_{60}$  is metallic above room temperature. Around 200 K the conductivity has a broad maximum and decreases continuously at lower temperatures. This transition from metallic to insulating states at low temperatures may be attributed to Anderson localization.

# In situ Raman spectroelectrochemistry on SWNTs at higher doping levels: evidence for a PTH transition to intercalative doping 36

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We studied the transition from a double-layer charging regime to intercalative doping of SWNT buckypaper in KCl aqueous solution. For this purpose we used higher doping levels by applying constant potentials above 1 V approaching and slightly exceeding the oxidation potential for Cl<sup>-</sup> ions. At each potential Raman measurements were performed of the radial breathing mode (RBM), the high-energy tangential mode (HEM) and the disorder-induced (D) mode. From a comparative analysis of the Raman spectra we conclude that above 1 V a significant penetration of chlorine species into the interstitial channels of the SWNT bundles and possible functionalization of the SWNTs take place.

# Functionalization of SWCNTs by Aliphatic Amides Studied by Raman and Photoelectron PTH Spectroscopy 37

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The covalent side wall functionalization of SWCNTs is of uttermost interest as SWCNTs so treated show improved solubility and processibility. Recently, we have shown that the reaction of  $^t$ BuLi with SWCNTs leads to functionalized tubes decorated with covalently attached  $^t$ Bu-groups. The nucleophilic addition of the  $^t$ Bu-anion to the sp<sup>2</sup>- $\pi$  system of the nanotubes leads to a rehybridization of one carbon atom to sp<sup>3</sup> and to the injection of a negative charge into the nanotube surface. These charged nanotubes ( $^t$ Bu-SWCNT<sup>n-</sup>) debundle due to charge repulsion and a homogeneous solution is formed. Oxidation of the charged intermediates with air leads to uncharged functionalized system of the type  $^t$ Bu<sub>n</sub>-SWCNT. This elegant reaction sequence should be expandable to other nucleophiles with high reactivity. We therefore investigate the reaction of SWCNTs with aliphatic amides.

Characterization of the reaction intermediates and products is performed by AFM, Raman spectroscopy and XPS. By using different excitation wavelengths for Raman spectroscopy it is investigated whether preferential reactions of a certain subset of the SWCNTs occur. The charge transfer between the amide ions and the SWCNTs and the degree of functionalization is studied by XPS. Preliminary results show that amide ions attack SWCNT in a similar fashion as charged C-nucleophiles.

### Recovering the metallic behaviour in Li4C<sub>60</sub> monomer phase

PTH

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In recent years the competition between Coulomb repulsion, kinetic energy, Jahn-Teller effect, and Hund's coupling rules has been subject of intensive research in the domain of alkali-doped fullerenes. Apparently, most of the phenomena, including high-Tc superconductivity in  $A_3C_{60}$ , seem to be relatively well understood. Nevertheless, the reason why  $A_4C_{60}$  are in general nonmagnetic insulators is still puzzling and remains subject of strong controversy. The restoration of metallicity in the high-temperature, cubic phase of  $\text{Li}_4C_{60}$  represents a remarkable feature for a member of the  $A_4C_{60}$  family (A = alkali metal), invariably found to be insulators. Structural and resonance technique investigations on  $\text{Li}_4C_{60}$  at T > 600 K, show that its fcc structure is associated with a complete (4e) charge transfer to  $C_{60}$  and a sparsely populated Fermi level. These findings not only emphasize the crucial role played by lattice symmetry in fulleride transport properties, but also re-evaluate the role of Jahn-Teller effects in band structure determination.

# PTH High-Yield Synthesis of Single-Walled Carbon Nanotubes With A Pulsed Arc-discharge Technique

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This contribution deals with the synthesis of single walled carbon nanotubes (SWCNT) with a novel pulsed arc-discharge technique. Pulsed arc-discharge is a very interesting technique because it is similar to the well-known Laser-evaporation technique for the synthesis of SWCNT and should allow a scale-up to reach at an SWCNT volume production. We performed a number of experiments to find optimal conditions for the arc-based SWCNT synthesis. The obtained data have been compared with known results from Laser-evaporation synthesis of SWCNT. The results indicate that it is possible to get specifically optimized synthesis conditions for the arc-discharge method that are very similar to that of the laser evaporation synthesis. Both methods allow to get similar nanotube qualities (high yield, narrow diameter distribution). We discuss similarities in the formation mechanisms between both methods.

### PTH Catalyst size and carbon feed-rate constraints for single wall carbon nanotube synthesis

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Systematic spectroscopic and microscopic studies on single-walled carbon nanotubes synthesized via laser evaporation were conducted. Our findings show upper and lower diameter limits that represent a nanotube nucleation window, which can be attributed to the catalyst particle volume to surface area constraints. However, the precipitating carbon saturated cluster size distribution depends solely on thermal aspects. SWCNT are only obtained when both the nucleation window and the catalyst size distribution crossover. The degree to which these two windows overlap establishes the diameter distribution of the obtained SWCNT. Further the developed model points not only to catalyst geometrical constraints but also to the carbon feed rate to the catalyst. CVD experiments with pre-defined catalysts highlight the carbon feed-rate constraint.

# PTH Population inversion and negative dynamic conductivity in nonequilibrium two-dimensional electron-hole systems in graphene struc

Maxim Ryzhii, Victor Ryzhii University of Aizu

We find the electron and hole distribution functions and calculate the dynamic conductivity of nonequilibrium two-dimensional electron-hole systems in graphene-based structures under optical pumping (with the emission of a cascade of optical phonons) and injection conditions (in the electrically-induced p-n junction).

Both the intraband transitions and intraband transitions associated with the electron and hole scattering on impurities and acoustic phonons are considered. It is shown that under sufficiently strong pumping the population inversion may result in the negative net dynamic conductivity in a certain range of photon frequencies. Since the frequencies corresponding to the negative conductivity fall into the terahertz range, the predicted effects might be used in coherent sources of terahertz radiation.

### Carbon nanotubes for ultrafast photonics

PTH

42

<u>V. Scardaci</u>, A. Rozhin, P. Tan, F. Wang, I. White, W. Milne, A.C. Ferrari University of Cambridge, Engineering Department

Carbon nanotubes (CNTs) saturable absorbtion properties have great potential for applications in photonics [1,2]. The performance of CNTs based saturable absorbers strongly depends on the CNTs concentration, size of CNT bundles, and transparency of the matrix where CNTs are dispersed [3].

CNTs based saturable absorbers are prepared as follows. First, we use strong ultrasonication to obtain CNT solutions. Such solutions with different nanotube bundles size are then studied by photoluminescence excitation spectroscopy [4]. We find that exciton energy transfer between semiconducting CNTs is an efficient carrier relaxation channel in the bundles [4]. This fingerprints and quantifies the presence of small bundles and allows us to optimise the solutions used for preparation of CNT-polymer composites. The saturable absorption properties of such composites are studied with a femtosecond laser. We find that the lowest value of saturation intensity for CNTs is 6 MW/cm2. We then demonstrate picosecond pulse generation in a nanotube mode-locked waveguide laser [2], as well as 600 fs generation in an erbium doped fiber laser [3].

- 1. A.G. Rozhin et al. Chem. Phys. Lett. 405, 288 (2005)
- 2. G. Della Valle, Appl. Phys. Lett. 89, 231115 (2006)
- 3. A. G. Rozhin et al. J. Appl. Phys. submitted (2006).
- 4. P. H. Tan et al. submitted (2006).

# ANTHRACENE@SWCNT AND THE TRANSFORMATION TO DOUBLE WALL CNTS PTH

Christoph Schaman

**43** 

University of Vienna

We present an investigation of anthracene ( $C_{14}H_{10}$ ) in SWCNTs and the subsequent transformation into DWCNTs by means of Raman spectroscopy and X-ray scattering. The encapsulation is demonstrated by using open and closed SWCNTs. The anthracene molecules undergo a dramatic change upon entering the CNTs. This change is analyzed by resonant Raman scattering and X-ray diffraction, and modeled with an *ab initio* code provided in the SIESTA 2.0 package.

The anthracene@SWCNT system can then be transformed into DWCNTs at conditions similar to  $C_{60}$  peapods, but much longer transformation times are required. A similar, but not identical DWCNT distribution is obtained, as demonstrated by resonant Raman spectroscopy. The final concentration of DWCNTs is lower than for peapod-grown material. There is a remarkable change in outer CNT resonances found before and after filling/transformation. Possible reasons are discussed in detail.

#### Catalytic reaction in a single-wall carbon nano-test tube

PTH

<u>Hidetsugu Shiozawa</u><sup>1</sup>, Thomas Pichler<sup>1</sup>, Alexander Grüneis<sup>1</sup>, Rudolf Pfeiffer<sup>2</sup>, Hans Kuzmany<sup>2</sup>, Zheng **44** Liu<sup>3</sup>, Kazu Suenaga<sup>4</sup>, Hiromichi Kataura<sup>5</sup>

<sup>1</sup>IFW Dresden, Germany <sup>2</sup>Universität Wien, Austria <sup>3</sup> <sup>4</sup> <sup>5</sup>AIST, Japan

We report on a novel route to explore new chemistry within the confined nanospace of single-wall carbon nanotube. A chemical reaction inside this nano-test tube is explored with the example of subsequent growth of inner tubes from encapsulated ferrocene molecules which double act as a catalyst and carbon source. Evolution of intermediate iron carbide phases accompanying with the formation of functionalized inner tubes is traced by photoemission spectroscopy, Raman spectroscopy and high-resolution transmission electron microscopy. The final products are double-wall carbon nanotubes with a defined pattern of inner/outer tube couples and controlled doping with iron nanoparticles. Given the large variety of organometallic precursors, this process paves the way to engineer purpose-built nanoscale devices for spintronics, nanoelectronics and bioelectronics.

#### PTHCharge transport in carbon nanotubes through high frequency electric fields. 45

V. Siegle

MPI für Festkörperforschung

The need of devices able of quantized charge transport on nanoampere scale with very high precision led to several developments in low-dimensional structures. The majority of cases is based on a GaAs-2DEG where the electrons are confined by the electrical potential of the applied surface acoustic wave (SAW). In several recent publications a new SAW-related effect has been predicted and investigated. An individual single-walled carbon nanotube functions as a 1D conducting channel. The SAW is induced through the the piezoelectric effect. For this purpose lithographically generated metallic interdigital transducers (IDT) are used. The coupling of SAW's electrical part to the electrons is given by the electron structure in the nanotubes. In addition, a second SWNT-based approach will be introduced. By defining a QD on a carbon nanotube by side- or top-gates a turnstile-device can be fabricated. Similar devices are capable of producing high precision currents. The devices suitable for detecting the predicted effect will be presented and the experimental progress will be reported.

#### PTH Electron transport and IFM features in Raman spectra in ion-irradiated single-wall carbon nanotube networks 46

<u>Viera Skákalová</u><sup>1</sup>, Alan B. Kaiser<sup>1</sup>, Janina Maultzsch<sup>2</sup>, Zoltán Osváth<sup>3</sup>, László Biró<sup>3</sup>, Siegmar Roth<sup>1</sup> <sup>1</sup>Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany <sup>2</sup>Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany <sup>3</sup>Research Institute for Technical Physics and Materials Science, Hungarian Academy of Sciences MFA, P.O. Box 49, H-1525 Budapest, Hungary

We have measured how irradiation by Ar+ and N+ ions modifies electronic conduction in single-wall carbon nanotube (SWNT) networks of different thickness, making a detailed analysis of the temperaturedependent conductance. For thick networks (SWNT paper) showing metallic conductivity, we demonstrate that thermal annealing extending beyond the range of the irradiating ions can cause an increase in conductivity for low doses of irradiation, and show how this effect depends on the morphology of the samples. For very thin transparent networks, however, irradiation increases localization of charge carriers and strongly reduces the variable-range hopping conductivity.

We also have studied the effect of Ar+ irradiation on the intermediate frequency modes (IFM) in Raman spectra of single-wall carbon nanotubes using 633 nm excitation wavelength. We observe new features in the intermediate frequency region from 386 to 635 cm-1 as the defect concentration increases, whereas at the same time there is a decrease of other IFM modes. After annealing in vacuum, the IFM modes recover and become similar to those of the nanotubes before irradiation. We interpret the new features in Raman spectra as originating from the phonon density of states that becomes visible in the Raman process due to the presence of defects.

#### PTH AC conductivity recovery in carbon nanotube-polymer composites after transient shear Ingo Alig<sup>1</sup>, Martin Engel<sup>1</sup>, Dirk Lellinger<sup>1</sup>, Tatyana Skipa<sup>1</sup>, Sven Pegel<sup>2</sup>, Petra Pötschke<sup>2</sup> 47

<sup>1</sup>Deutsches Kunststoff-Institut, Schloßgartenstraße 6, 64289 Darmstadt, Germany <sup>2</sup>Leibniz Institute of Polymer Research Dresden, Hohe Str. 6, 01069 Dresden, Germany

Frequency dependent investigations of conductivity and dielectric permittivity have been performed on polycarbonate (PC) and polypropylene (PP) containing multi-walled carbon nanotubes (MWNT) in a rheometer (plate-plate geometry), where the plates act as capacitor plates for dielectric spectroscopy. The time dependent recovery of AC conductivity and the related complex permittivity were recorded in the frequency range between 20 Hz to 1 MHz in the rest time after transient shear (shear rate of 1/s, times of 0.1 -10 s). For samples with a MWCNT content close to the percolation threshold the AC conductivity and the permittivity show a tremendous increase with time after shearing. This conductivity recovery is explained by the reorganization of the conducting MWNT-network, which was partially destroyed by the shear. The reformation kinetics of MWNT-clusters is considered as a cooperative cluster-cluster aggregation coupled to electrical percolation of conductive MWNTs. Reorganization of the percolation network can be related to reformation of local contact regions between the nanotubes as well as to reorganization and reorientation of nanotubes on larger length and time-scales. The recovery of DC conductivity is consistently expressed in the conductivity and permittivity spectra and can be explained in a simple model combining cluster-cluster aggregation and electrical percolation.

# Buckypaper gas chromatograph: evaporation profile based identification of liquid analytes $\,^{ m PTH}$ using multi-wall carbon nanotube films $\,^{ m 48}$

Rita Smajda, Akos Kukovecz, Henrik Haspel, Zoltan Konya, Imre Kiricsi University of Szeged

Sensorics is a rapidly expanding field of carbon nanotube applications. We report on the applicability of heated multi-wall carbon nanotube films obtained by dead-end filtration as contact sensors for common laboratory solvents. The films were characterized by measuring their filtration characteristics, morphology (using scanning electron microscopy), gas permeability and electrical resistance. The shape of the resistance vs. time curve (the evaporation profile) is characteristic of the solvent dropped onto the nanotube film. The evaporation profiles can be evaluated using either artificial neural networks or fundamental diffusion equations. We succeeded in reproducibly identifying 15 different solvents using the same buckypaper filtered from the DMF suspension of CVD-grown multi-wall carbon nanotubes. The presented results could serve as a basis for the development of a very simple, carbon nanotube based process gas chromatograph.

# RAMAN IMAGING OF INDIVIDUAL CARBON NANOTUBES AND GRAPHENE FLAKES

PTH 49

C. Stampfer<sup>1</sup>, A. Buerli<sup>1</sup>, A. Jungen<sup>1</sup>, D. Graf<sup>2</sup>, F. Molitor<sup>2</sup>, K. Ensslin<sup>2</sup>, C. Hierold<sup>1</sup>  $\overline{}^{1}$ Micro and Nanosystems, ETH Zurich, 8092 Zurich, Switzerland <sup>2</sup>Solid State Physics Laboratory, ETH Zurich, 8093 Zurich, Switzerland

We present Raman spectroscopy measurements of individual electrically contacted, suspended and non-suspended single-walled carbon nanotubes. Using a scanning confocal technique we collect spectral data with spatial resolution, which allows us to directly compare Raman spectra (and images) of distinct individual single-walled carbon nanotubes before and after electrically contacting and (HF) releasing. We show that suspended nanotubes show stronger RBM signals than not-suspended nanotubes and we show that HF treatment leads to an enhanced (defect induced) D line. Additionally, we report on the influence of the back gate voltage on the Raman spectra of single-walled carbon nanotubes integrated in a transistor configuration. Moreover, we present Raman spectroscopy measurements on single- and few-layer graphene flakes. We show that the edge of the graphene flakes leads to a strongly enhanced D line and single-layer graphene can be distinguished from double-and few-layer by the width of the D\* line: the single peak for single-layer graphene splits into different peaks for the double-layer [1].

[1] D. Graf, F. Molitor, K. Ensslin, C. Stampfer, A. Jungen, C. Hierold and L.Wirtz, "Spatially Resolved

[1] D. Graf, F. Molitor, K. Ensslin, C. Stampfer, A. Jungen, C. Hierold and L.Wirtz, "Spatially Resolved Raman Spectroscopy of Single- and Few-Layer Graphene", Nano Letters, accepted, cond-mat/0607562v1, (2006)

### Single Electron Charge Detection in Carbon Nanotubes

PTH 50

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Detection of single electron charges on quantum dots opens up new regimes of measurement where currents through the devices are too small to be measured. Charge detection in carbon nanotube quantum dots (CNT-QDs) is challenging, however, since unlike GaAs devices, a charge detector can not be as easily integrated. We present here results from single electron charge detection in CNT-QD device by using an Aluminium Single Electron Transistor (Al-SET). Operating in DC mode, we achieve a charge sensitivity of  $10^{-4}$  e/ $\sqrt{(\mathrm{Hz})}$ . By fabricating an Al-SET beside the carbon nanotube, we directly read out the charge on a nanotube quantum dot. Sweeping the chemical potential in the CNT through the bandgap, Coulomb peaks in a simultaneous transport measurement disappear as the tunnel barriers to the QD become too opaque. However, using the Al-SET, we are able to continue to monitor electrons entering the dot by measuring the charging signal. We also observe a peculiar backaction between the Al-SET and the CNT-QD: the noise emitted from current in the CNT-QD has a dramatic effect on the SET, but the converse is absent. Work is in progress to use the Al-SET charge detector to measure spin relaxation times in CNT-QDs.

### PTH Scanning Tunneling Spectroscopy of Cerium Metallofullerenes

Anna Strozecka<sup>1</sup>, Aneta Dybek<sup>2</sup>, Josef Myslivecek<sup>1</sup>, John Dennis<sup>2</sup>, Bert Voigtländer<sup>1</sup>

<sup>1</sup>Institute of Bio- and Nanosystems, Research Centre Jülich, Leo Brandt Str. 52428 Jülich, Germany <sup>2</sup>Institute of Physics, Queen Mary University of London, Mile End Road, London, E1 4NS, UK

Endohedral metallofullerenes are novel forms of carbon-based materials with potential applications in nanotechnology and nanoelectronics. Here we present a low temperature scanning tunnelling microscopy (LT-STM) study of electronic and vibrational properties of  $Ce@C_{82}$  and  $Ce_2@C_{80}$  on Cu(111). The internal structure of the molecules was clearly resolved in the STM images and the variety of the internal patterns indicate, that the metallofullerenes can bound to the surface in different configurations. Electronic spectra for differently oriented molecules were measured by scanning tunnelling spectroscopy (STS). It was found that the orientation of the molecule on the substrate strongly influences its electronic properties. The vibrational properties the metallofullerenes were analysed using inelastic electron tunneling spectroscopy (IETS). For  $Ce@C_{82}$  only the internal vibrational modes of the  $C_{82}$  cage were resolved in the spectrum. The intensity of the vibrational signal depends on the molecular orientation, what suggests that the adsorption geometry affects the molecular electron-phonon coupling. In case of  $Ce_2@C_{80}$ , apart from the modes related to the cage, also a low frequency mode was resolved. We discuss the possibility that this low energy mode can be associated with the vibrations of encaged Ce atoms.

# PTH NANOCARBON: EFFICIENT SYNTHESIS USING NATURAL LAVA AS CATALYST AND SUPPORT

Dangsheng Su, Xaiwen Chen Fritz-Haber-Institut der MPG

Nanocarbons, especially carbon nanotubes/nanofibers (CNTs/CNFs), are the key materials in nanoscience and nanotechnology, but their applications are hampered by the production. Current processes including preparation of support, normally silica or alumina, and impregnation with catalytically active metal for hydrocarbon decomposition, are not suitable for mass production of CNTs/CNFs. We report in this brief presentation the fabrication of CNTs/CNFs on Mount Etna lavas containing natural catalysts. The minerals are used both as support and as catalyst! This is the first step for industrial production without preparation of support and its wet chemical treatment. Our method is cheaper, can be easily scaled-up and therefore opens new horizon for the application of CNTs/CNTs on a large scale, for instance, in water purification and in catalysis in which tones of immobilized CNTs/CNFs are needed.

D.S. Su, X. W. Chen, Angew. Chem. Int. Ed. in press

# PTH First and second optical transitions in single-walled carbon nanotubes: a resonant Raman study

<u>Hagen Telg</u><sup>1</sup>, Janina Maultzsch<sup>1</sup>, Stephanie Reich<sup>2</sup>, Frank Hennrich<sup>3</sup>, Yang Wu<sup>4</sup>, Tony Heinz<sup>4</sup>, Bhupesh Chandra<sup>4</sup>, James Hone<sup>4</sup>, Christian Thomsen<sup>1</sup>

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Resonant Raman spectroscopy was performed to study electron-phonon coupling and exciton lifetimes in single walled-carbon nanotubes separated in solution. By varying the excitation energy from 1.26 to 1.93 eV we obtained radial breathing mode resonance profiles of the first and second optical transitions E11 and E22 of the (9,1) and (8,3) tubes [1]. By comparing the resonance profiles of the first and second transition, we find a two times broader linewidth for the E22 transition, associated with additional fast decay channels. The intensity ratio between E11 and E22 resonances is discussed with respect to theoretical predictions. We compare these results to Raman resonance profiles from suspended individual nanotubes grown across a 100 micrometer wide slit. In addition, we find that the characteristic Fano-lineshape of the high-energy modes in metallic nanotubes varies with the resonance Raman condition, and its ependence on excitation energy will be discussed.

[1] Telg et al., Phys. Rev. B **74**, 115415 (2006).

Infrared spectroscopy on rotor-stator compounds C<sub>60</sub>-C<sub>8</sub>H<sub>8</sub> and C<sub>70</sub>-C<sub>8</sub>H<sub>8</sub> under pressure PTH Komalavalli Thirunavukkuarasu<sup>1</sup>, Christine Kuntscher<sup>2</sup>, Gyula Bényei<sup>3</sup>, István Jalsovszky<sup>2</sup>, Gyöngyi **54** Klupp<sup>4</sup>, Katalin Kamarás<sup>2</sup>, Éva Kováts<sup>2</sup>, Sándor Pekker<sup>2</sup>

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The fullerene-cubane molecular crystals  $C_{60}$ - $C_8H_8$  and  $C_{70}$ - $C_8H_8$  which were synthesized recently, are the first members of the rotor-stator crystal family [1]. Static cubane molecules occupy the octahedral voids of the face-centered-cubic structure and act as bearings for the rotating fullerene molecules. At low temperature,  $C_{60}$ - $C_8H_8$  and  $C_{70}$ - $C_8H_8$  undergo orientational ordering transitions. While the phase transition for  $C_{60}$ - $C_8H_8$  occurs at 140 K,  $C_{70}$ - $C_8H_8$  undergoes two transitions at around 390 K and 150 K. Recently, an attempt to investigate the pressure-induced phase transitions in  $C_{60}$ - $C_8H_8$  was also made [2].

Based on our earlier results, further transmittance measurements under pressure were performed on both both  $C_{60}$ - $C_8H_8$  and  $C_{70}$ - $C_8H_8$  molecular crystals and over a broader frequency range (far-infrared to visible), for pressures up to 10 GPa. We report about the changes in the vibrational modes of the fullerene and cubane molecules with increasing pressure. A further interesting issue discussed is the pressure-induced shift of the absorption edge of  $C_{60}$ - $C_8H_8$  and  $C_{70}$ - $C_8H_8$  in comparison with the parent fullerenes.

Supported by the DFG.

- [1] S. Pekker et al., Nature Materials 4, 764 (2005).
- [2] C. A. Kuntscher et al., Phys. Stat. Sol. (b) **243**, 2981 (2006).

#### Scattering in Graphene

PTH

<u>Kathryn Todd,</u> Benjamin Huard, Joseph Sulpizio, Nimrod Stander, Bo Yang, Mark Topinka, David **55** Goldhaber-Gordon Stanford University

At low energies, charge carriers in graphene are Dirac fermions, characterized by a linear dispersion relation. Graphene displays electron-hole degeneracy and charge carriers possess both a spin degree of freedom and a pseudospin, which is conserved in the absence of potentials that are sharp on the scale of the lattice spacing. These properties are predicted to give rise to an effect known as the Klein paradox, where particles incident on a barrier are capable of perfect transmission at normal angles, while particles at certain other angles can be reflected.

We use top-gating and magnetic confinement techniques to test predictions about the transmission of charge carriers through potential barriers in graphene. Additionally, we plan to use a scanning gate technique to map quasiparticle trajectories in graphene, comparing them to similar measurements in materials with more conventional scattering properties.

In our preliminary work, we have made contact to graphene flakes and observed quantum hall plateaus at 0.5\*4e2/h, characteristic of single-layer graphene. We have fabricated a top-gated device and observed a change in conductance with applied gate voltage. In the near future, we plan to fabricate devices containing quantum point contacts for use in both gated devices and scanning gate measurements.

# PTH Influence of catalyst's evolution on their activity and selectivity in nanotubes synthesis Anna Usoltseva<sup>1</sup>, Vladimir Kuznetsov<sup>1</sup>, Lyudmila Plyasova<sup>1</sup>, Miroslav Haluška<sup>2</sup>, Siegmar Roth<sup>2</sup> Boreskov Institute of catalysis <sup>2</sup>Max Planck Institute for Solid State Research

Multi-component catalysts, synthesized using polymerized complex method, were used in NTs growth via CH4 and EtOH CVD process. This method provides the formation of catalytic systems with homogeneous distribution of metallic active components (Ni, Fe, Co or bimetallic composition) in inorganic matrix (MgO, CaCO3 etc). It was shown that using the same catalyst the different types of tubular carbon deposits (carbon fibers, MWNTs and SWNTs) can be produced. We suggested that the reason of this dramatic difference of selectivity of the same catalyst is a consequence of the formation of different types of active catalyst particles which could form during catalyst "activation" procedures (such as catalyst reduction or heat treatment, sintering process). The influence of catalyst activation procedure on catalyst particles formation and thus on catalyst selectivity in NTs CVD synthesis was investigated using of XRD and TEM. It was found that catalyst reduction in mixture of CH4/H2 (or EtOH/H2) is more effective for selective SWNT growth then the reduction in pure H2. The influence of catalyst size distribution and its evolution during the reaction on NTs synthesis was studied. Obtained results were discussed using general approach which based on the thermodynamic analysis of carbon nucleation on metal surface and consideration of possible scenarios of carbon nucleus growth.

### PTH Nanotube field and orientational properties of C<sub>70</sub> molecules in carbon nanotubes 57 Bart Verberck, Karl Michel

Department of Physics, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium

The orientation of a  $C_{70}$  fullerene molecule encapsulated in a single-walled carbon nanotube (SWCNT) depends on the tube radius. First we confirm that chirality effects do not affect the orientation as well by comparing discrete atomic calculations with the results of a continuous tube approximation for a variety of SWCNTs. The molecular and the tube symmetry are exploited by using symmetry-adapted rotator functions. We accurately determine the optimal molecular orientation as a function of the tube radius; for low (< 7 A) and high (> 7.2 A) tube radii, lying and standing molecular orientations are recovered, respectively. In between, we observe a transition regime. In addition, we consider off-axis positions. We perform a one-dimensional liquid description of a chain of on-axis  $C_{70}$  molecules inside a SWCNT. All results agree well with recent x-ray diffraction experiments.

# PTH Ultra-large Scale Directed Assembly of Single-walled Carbon Nanotube Devices

Aravind Vijayaraghavan, Sabine Blatt, Matti Oron-Carl, Frank Hennrich, Horst Hahn, Ralph Krupke Institut für Nanotechnologie, Forschungszentrum Karlsruhe

Despite the rapid progress in understanding electronic transport in single-walled carbon nanotubes, the fabrication of nanotube devices remains the biggest obstacle in the way of practical realization of their enormous potential application in nano-electronics.

We demonstrate the use of A/C dielectrophoresis to fabricate individual nanotube devices at high densities of 3-4 million devices/cm2, which is three orders of magnitude higher then other methods. This is comparable to the current level of microelectronics complexity, namely Ultra-Large Scale Integration. This is a self-limiting process allowing only one nanotube to deposit between the electrodes for each device. We present numerical simulations of the dielectrophoretic force field experienced by the nanotube to illustrate self-limiting behavior. We also present a two-layer metallization which surrounds the ends of the nanotubes in metal to provide a robust way to reduce contact resistance, compared to other techniques where the nanotube lies either on top or underneath the metal. Systematic electrical characterization of our devices is also presented.

Dielectrophoresis is a universal phenomenon observed in many nanoscale objects like nanowires, nanoparticles, biomolecules and cells. The results in the presentation have universal appeal as they can be adapted to form large-scale systematic electrical contacts to a variety of nano-scale objects.

#### Resistive switching phenomena in nanoscopic gaps filled with an organic complex

PTH 59

Ralf Weitz, Alicia Forment-Aliaga, Marko Burghard, Klaus Kern Max Planck Institute for Solid State Research, Stuttgart, Germany

With recent advancements in the miniaturization of memory technology, increasing importance is being placed on the fabrication of highly integrated and yet competitively priced devices. In this context the utilization of organic materials such as charge-transfer (CT) salts offers significant promise: not only can such materials be easily tailored, but they can also usually be deposited quite cost-effectively by solution processing [ref 1]. Resistive memory switching phenomena in CT salts have been reported in sandwich devices with film thicknesses thicker than 100 nm in for example the CuDDQ (2,3-dichloro-5,6-dicyanop-benzoquinone) salt [ref 1]. In this work we present a novel approach to the miniaturization of such memory cells: Starting from AuPd electrodes forming a lateral gap of 50 nm width defined by electronbeam lithography on a SI/SiO<sub>2</sub> substrate, copper is electrodeposited selectively on one side of the gap to barely close the gap. The substrate is then immersed into a DDQ/Acetonitrile solution resulting in the growth of the complex onto the Cu-covered electrode and in the cause of which the gap is fully closed. Devices obtained in this manner can be switched between a high and a low resistance state (R<sub>high</sub>/R<sub>low</sub>  $> 10^{2}$ ) by applying voltage ramps. This fabrication method opens the possibility of fabricating organic memory cells with a size of one nanometer and below.

1 R. T. Weitz, et al., Nano Lett. 6 (12), 2810 (2006)

#### NANOCARBON-CATALYZED STYRENE SYNTHESIS AND H2 PRODUCTION

PTH 60

Jian Zhang, Dangsheng Su

Department of Inorganic Chemistry, Fritz-Haber-Institut der MPG

Here we report for the first time a systematic study on nanocarbons (e.g. nanographite, nanotube, nanodiamond) as catalysts for two important reactions, i.e. styrene synthesis by direct dehydrogenation of ethylbenzene and H2 production from NH3. This study will open a new horizon for application of novel nanostructured carbons in catalysis science.

Styrene as one of the most vital monomers is mainly synthesized via dehydrogenation of ethylbenzene. Traditional iron-based styrene industry has still been greatly hindered by catalyst deactivation. Excessive amount of steam is always required to maintain a long-time stability. We used metal-free sp2-hybridized nanographite and sp3-hybridized nanodiamond as catalyst and were delighted to observe a comparably high activity with the existing commercial Fe-based catalysts. Almost 100% atomic efficiency of feedstock could be achieved. Even without using steam, nanocarbons could stably catalyze synthesis of styrene. In another test, nanocarbons were used as the catalyst for NH3 decomposition to produce COx-free H2 for fuel cell uses. It is found that commercial carbon nanotubes possessed a superior activity to the reported commercial metal catalysts.

#### The effects of inhomogeneous isotope distribution on the vibrational properties of isotope PTH enriched double walled carbon nano

Viktor Zólyomi<sup>1</sup>, Ferenc Simon<sup>2</sup>, Adam Rusznyak<sup>3</sup>, Rudolf Pfeiffer<sup>2</sup>, H. Peterlik<sup>2</sup>, Hans Kuzmany<sup>2</sup>, Jenő

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The radial breathing mode in the Raman spectrum of <sup>13</sup>C isotope enriched single walled carbon nanotubes is inhomogeneously broadened due to the random distribution of isotopes. We study this effect theoretically using density functional theory within the local density approximation and compare the result with experiments on isotope engineered double walled carbon nanotubes in which the inner tubes were grown from a mixture of <sup>13</sup>C enriched fullerenes and natural fullerenes. As explained by the calculations, this synthesis procedure leads to an increased inhomogeneity compared to a case when only enriched fullerenes are used. The good agreement between the measurements and calculations shows the absence of carbon diffusion along the tube axis during inner tube growth, and presents a strong support of the theory that inner tube growth is governed by Stone-Wales transformations following the interconnection of fullerenes.

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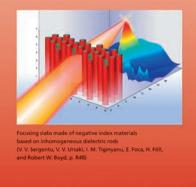
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Print ISSN 1862-6254 Online ISSN 1862-6270 2007. Volume 1, 6 issues.

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#### Transport

8:30-9:00 J. APPENZELLER, US

Carbon nanotube field-effect transistors as tunneling devices

9:00 - 9:30 Z. CHEN, US

Graphene ribbon electronics

9:30 - 10:00 B. RAQUET, FR

Aharonov-Bohm conductance modulation in Ballistic Carbon Nanotubes

10:00-10:30 Coffee break

10:30 – 11:00 A. KAISER, NS

Changes in electronic transport in carbon nanotube networks with thickness and chemical treatment

11:00 – 11:30 H. van der ZANT, NL

Coupling electronic transport to vibrational modes in suspended nanotube resonators

11:30 – 12:00 J.-P. CLEUZIOU, FR

Carbon nanotube superconducting quantum interference device

12:30 – 17:00 Mini Workshops

#### Molecular Nanomaterials

17:00 - 17:30 H. WEBER, DE

Charge transport across single-molecule junctions

17:30 – 18:00 A. FILORAMO, FR

Self-assembly of carbon nanotubes by bio-directed approach

18:00 - 18:30 C. RICHERT, DE

DNA-carbon nanotube interactions and nanostructuring based on DNA

18:30 – 19:00 T. PICHLER, D

Summary and Concluding Remarks

#### Bauernbuffet, fare well

## 8:30 Carbon nanotube field-effect transistors as tunneling devices TRP Joerg Appenzeller

IBM T.J. Watson Research Center

1

9:30

The electrical properties of single wall carbon nanotubes have been thoroughly studied over the last couple of years and more than once novel transport properties have been uncovered. The ultra-small body of a single wall carbon nanotube "the diameter" is key for understanding the band bending situation in semiconducting carbon nanotubes in a field-effect transistor (FET) design. Under certain conditions, the impact of external fields can result in a very abrupt band profile that allows for an enhanced tunneling probability. Consequently, it has been found that tunneling processes frequently limit the device performance of carbon nanotubes (CNs) for high performance logic applications. Here we discuss the impact of electron and hole tunneling on the electrical characteristics of carbon nanotube devices and elucidate on the impact of various device layouts. We argue why a novel tunneling carbon nanotube field-effect may prove useful in the future for high performance low power applications. In particular, we discuss the implications of our experimental and simulation study on the on- as well as off-state performance of the tunneling (T)-CNFET.

# 9:00 Graphene ribbon electronics TRP Zhihong Chen, Phaedon Avouris IBM T.J. Watson Research Center

Recent experimental studies of single layer graphite - graphene - have advanced the understanding of two-dimensional systems of Dirac fermions. Three terminal transistor-like devices have been fabricated. Gate-dependent transport measurements have revealed that the carrier density in this gapless semiconductor can be changed by shifting the Fermi level with the gate bias. Less than one order of magnitude current variation has been observed at room temperature. Theoretically, a semiconducting gap can be introduced by making the width of the graphene sheet small enough and for certain carbon hexagons orientations. In this study, we have combined e-beam lithography and etching techniques to form graphene nano-ribbons of different widths. Temperature dependent measurements show that an energy gap of  $\approx 14 \text{meV}$  is indeed opened for ribbons with width of 20nm, while wider ribbons (> 50nm) behave like an unconfined two-dimensional graphene. Another important factor that needs to be taken into consideration is the new boundaries introduced by lithography and etching processes, especially in the case of the narrow ribbons. Increased resistivity of the graphene with decreasing ribbon width is observed at room-temperature and is attributed to boundary scattering effects.

#### Aharonov-Bohm conductance modulation in Ballistic Carbon Nanotubes

TRP Bertrand Raquet<sup>1</sup>, Benjamin Lassagne<sup>1</sup>, Sébastien Nanot<sup>1</sup>, Walter Escoffier<sup>1</sup>, Jean-Marc Broto<sup>1</sup>, Jean-Marc Broto<sup>1</sup>,

<sup>1</sup>Laboratoire National des Champs Magnétiques Pulsés <sup>2</sup>CEMES <sup>3</sup>CEA DSM/DRFMC/SPSMS

When a magnetic field is applied parallel to the axis of mesoscopic rings or cylinders, the phase of the wave functions for each of the ring's arms are out of phase one to each other which in turns modulates the electronic transmission coefficients of the system. This quantum phenomenon, referred as the Aharonov-Bohm effect, is responsible for  $\Phi_0 = h/e$  periodic oscillations of the conductance. In this context, systems of particular interest are ballistic carbon nanotubes (CNT) since they can be viewed as mesoscopic cylinders made from concentric rolled graphene sheets. The so-called Aharonov-Bohm effect is expected to drastically alter the allowed k-vectors along the circumference of the nanotubes resulting in a periodic energy gap modulation. We report on magneto-conductance experiments in ballistic multiwalled carbon nanotubes threaded by magnetic fields as large as 60 Tesla. In the high temperature regime (100K), giant quantum flux modulations of the conductance, mediated by electrostatic gating, are unveiled. Evidence is given for an unambiguous manifestation of the Aharonov-Bohm modulation of the electronic band structure. We infer an energy gap opening for the external shell from a simple tight binding calculation. A quantitative interpretation of experimental data is achieved by computing the electronic transmission properties within the Landauer/Büttiker theoretical framework and assuming a field dependent band bending profile at the nonatube/metal interface.

#### Changes in electronic transport in carbon nanotube networks with thickness and chemical 10:30 treatment TRP

<u>Alan Kaiser</u><sup>1</sup>, Viera Skákalová<sup>2</sup>, Siegmar Roth<sup>2</sup>

<sup>1</sup>MacDiarmid Institute, SCPS, Victoria University of Wellington <sup>2</sup>Max-Planck-Institut FKF, Stuttgart

Thin transparent SWNT networks show a conductance that varies with gate voltage and follows variablerange hopping behaviour [1]. For thicker SWNT networks, conductance becomes metallic: it is still relatively large in the zero-temperature limit, and shows a decrease at higher temperatures consistent with backscattering by zone-boundary phonons of energies around 160 meV. When thick SWNT networks are exposed to different types of molecule, systematic correlated changes are observed in the magnitude and temperature dependence of conductivity, far-IR absorbance and Raman frequencies that are largely determined by changes in free carrier density [2], with metallic behaviour retained (in contrast to the effect of reducing thickness). We also analyze conduction in individual MWNTs (which show mixed metallic/nonmetallic behaviour) [1], and investigate the effects of ion irradiation on the conductivity of SWNT networks.

- [1] V. Skakalova, A.B. Kaiser, Y.-S. Woo and S. Roth, Phys. Rev. B, 74, 085403 (2006).
- [2] V. Skakalova, A.B. Kaiser, U. Detlaff-Weglikowska, K. Hrncarikova and S. Roth, J. Phys. Chem. B, 109, 7174-7181 (2005).

#### Coupling electronic transport to vibrational modes in suspended nanotube resonators Herre van der Zant

Delft University of Technology

11:00 TRP

4

At room temperature, suspended semiconducting nanotubes can be used as frequency mixers to detect their mechanical motion. Employing this mixing technique, we have measured a single gate-dependent resonance, which is attributed to the bending mode vibration of the suspended tube [1]. A continuum model [2] describes the gate-dependence of the resonance frequency very well. The analysis shows that our devices do not exhibit slack and that by applying a gate voltage, the nanotube can be tuned from a regime without strain to a regime where it behaves as a vibrating string under tension. Non-linear behavior of the nanotube resonator and indications for Euler buckling are also observed. At low temperatures, the suspended nanotubes act as quantum dots. Phonon-assisted tunneling mediated by longitudinal vibration modes has been measured [3] in agreement with a Franck-Condon-based model with a rather strong electron-phonon coupling factor of order unity. Recent work on short tubes indicates a complete blockade of the current at all gate voltages (phonon blockade).

- [1] S. Sapmaz, P. Jarillo-Herrero, Ya. M. Blanter, C. Dekker and H.S.J. van der Zant, Physical Review Letters 96 (2006) 026801.
- [2] S. Sapmaz, Ya. M. Blanter, L. Gurevich, and H.S.J. van der Zant, Phys. Rev. B. 67 (2003) 235414.
- [3] B. Witkamp, M. Poot and H.S.J. van der Zant, Nano Lett. 6 (2006) 2904.

#### Carbon nanotube superconducting quantum interference device

<u>Jean-Pierre Cleuziou</u><sup>1</sup>, Wolfgang Wernsdorfer<sup>2</sup>, Vincent Bouchiat<sup>3</sup>, Thierry Ondarçuhu<sup>1</sup>, Marc Mon-**TRP**  $thioux^1$ 

<sup>1</sup>CEMES-CNRS Toulouse <sup>2</sup>LLN-CNRS Grenoble <sup>3</sup>CRTBT-CNRS Grenoble

Recent progress in improving the contact of single-walled carbon nanotubes (SWNTs) to superconducting nanoelectrodes showed that such molecules can accommodate a superconducting current and behave as gate-controlled Josephson junctions.

We report the study of a superconducting quantum interference device (SQUID) with SWNTs Josephson junctions. Quantum confinement in each junction induces a discrete quantum dot (QD) energy level structure, which can be controlled with two lateral electrostatic gates. In addition, a backgate electrode can vary the transparency of the QD barriers. The gates are also used to directly tune the quantum phase interference of the Cooper pairs circulating in the SQUID ring. Optimal modulation of the switching current with magnetic flux is achieved when both QD junctions are in the "on" or "off" state. In particular, the SQUID design establishes that these carbon nanotube Josephson junctions can be used as gate-controlled pi-junctions, that is, the sign of the current-phase relation across the SWNTs junctions can be tuned with a gate voltage.

The carbon nanotube SQUIDs are sensitive local magnetometers, which are very promising to study the magnetisation reversal of an individual magnetic particle or molecule placed on one of the two carbon nanotube Josephson junctions.

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11:30

#### 17:00 Charge transport across single-molecule junctions

MNM Heiko Weber

University of Erlangen

I will report on recent progress in the field of single-molecule junctions, employing the break junction technique. In particular, I will show results obtained with a donor-acceptor like molecule, which diplayed diode-like current-voltage characteristics. In contrast to the traditional Aviram-Ratner picture, charge reconfiguration of the electronic structure under applied bias is the driving source for the electric asymmetry. Moreover, the role of molecular vibrations is investigated. We find indications for bias-induced reconfigurations in the noise spectra.

#### 17:30 Self-assembly of carbon nanotubes by bio-directed approach

MNM

1

<u>Arianna Filoramo</u>, Khoa Nguyen, Sebastien Lyonnais, Stephane Streiff, Laurence Goux-Capes, Marcelo Goffman, Jean-Philippe Bourgoin

Laboratoire d'electronique moleculaire — SPEC-CEA Saclay

Single wall carbon nanotubes (SWNTs) occupy a special place within molecular electronics. The future of SWNT-based devices is to a large extent related to the development of a bottom-up self-assembly technique.

Here, we will briefly compare the current state of the fabrication of devices made of carbon nanotubes by using self-assembly. Then, we will focus on DNA-directed approaches: construction of the DNA scaffold, DNA-nanotube chemistry and DNA metallisation. This bio-directed method constitutes a genuine and complete molecular-scale bottom-up method, since it relies on recognition properties inherent to biological entities and can be employed without using any standard nanolithography technique.

Indeed, the exceptional recognition properties of DNA molecule make it an ideal candidate for realizing a site-controlled implementation of nanocomponents and its engineering is currently investigated to both create scaffolds and self-assemble nanomaterials. We will present a simple and versatile method for linking SWNT to DNA by non-covalent chemistry using streptavidin-biotin recognition complex. We will discuss also the covalent approach and show how the site specificity can be controlled. Finally, to fully utilize DNA not only as a positioning scaffold for nanodevices but also as a conducting element, we will show how to metallise DNA by electroless plating techniques.

### 18:00 DNA-Carbon Nanotube Interactions and Nanostructuring Based on DNA

MNM 3 Stephanie Vogel<sup>1</sup>, Ulrich Plutowski<sup>1</sup>, Manfred Kappes<sup>2</sup>, Clemens Richert<sup>1</sup>

<sup>1</sup>Inst. of Organ. Chem., University of Karlsruhe (TH) <sup>2</sup>Inst. of Phys. Chem., University of Karlsruhe (TH)

Single-walled carbon nanotubes (SWCNTs) are fascinating molecules of unusual shape, strength and thermal stability. They form bundles of exceptional stability, making it difficult to handle them like common organic compounds. This complicates attempts to generate homogeneous samples. An unlikely "detergent2 shown to be particularly effective in solubilizing SWCNTs is DNA. Sequences with alternating dG and dT residues with a length between 20 and 90 bases were described as best suited for the separation of nanotubes. Intuitively, one would expect longer DNA to be more effective in solubilizing SWCNTs than short DNA, based on multivalent binding. One would also expect Watson-Crick helices to be incompatible with SWCNT binding, because they bury the lipophilic bases inside and generate a stiff structure without obvious shape complementarity. We found the optimum for concentrated suspension to be a mixture of the short, complementary sequences d(GT)3 and d(AC)3. But, the kinetic stability of SWCNT-DNA suspensions increases with increasing chain length. So, the mixture of hexamers allows for efficient solubilization and controlled deposition of SWCNTs. Possible scenarios for DNA-mediated structuring utilizing both DNA-wrapped SWCNTs and DNA-coated metallic nanoparticles will be discussed.

18:30Concluding Remarks CORE

Thomas Pichler
Leibniz Institute for Solid State and Materials Research Dresden, IFW Dresden, P.O. Box 27016 D-64979;01171 Dresden, Germany

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## **Manager of Hotel Sonnalp** and their staff



Josef R. Jurgeit

1987- 1996



Harald Gradnizer

1996 - 2002



**Edith** Mayer

from 2002 on













