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Verein zur Förderung der Internationalen Winterschulen in Kirchberg Austria

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Financial assistance from the sponsors and supporters is greatly acknowledged.



Dear Friend:

Welcome to the 24<sup>th</sup> International Winterscholl on:  
**Electronic Properties of Novel Materials: "Molecular nanostructures"**

This Winterscholl is a sequel of twenty-three previous meetings held in Kirchberg in the last decades 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 runs on an informal level.

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:

Janina Maultzsch	program
Matthias Mller, Matthias Staiger	accommodation
Nils Rosenkranz, Jan Laudenbach	registration, finance
Marcel Mohr, Katharina Brose	video transfer and recording, internet
Hagen Telg, Sevak Khachadorian	general assistance
Harald Scheel	receipts, technical assistance
Dirk Heinrich	technical assistance
Norman Tschirner, Niculina Peica	computer, internet, e-payment
Patrick May	sponsoring, photography

Also the managers of the hotel, Mrs. Mayer and her son Mr. Mayer, and their staff promised to help us wherever they can. We want to acknowledge their help and also that of Sabine Morgner in preparing this abstract booklet for the IWEPM 2010.

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

Sincerely yours, Christian, Peter, Hans, Stephanie, and Siegmar

## Chairmen

C. Thomsen (Berlin)  
P. Dinse (Darmstadt)  
H. Kuzmany (Vienna)  
S. Reich (Berlin)  
S. Roth (Stuttgart)

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A. Loiseau (FR)	C. Thomsen (DE)
F. Mauri (FR)	A. Zettl (US)

## 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: • Materials science of graphene and nanoribbons • Carbon nanotube optics and electronics • Graphene and Carbon nanotube growth and selection • Single-molecule experiments • Applications of molecular nanostructures • Theory of molecular nanostructures • Biomolecule physics and applications • Nanostructure spintronics



## INFORMATION FOR PARTICIPANTS

### Time and location

The IWEPNM 2010 starts on Saturday, 6 March, evening, at the hotel Sonnalp in Kirchberg/Tirol, Austria and extends to Saturday, 13 March, breakfast. There will be a reception party on 6 March, after dinner, and a farewell party including dinner on Friday, 12 March.

### Transport

The hotel Sonnalp can be reached by private car from downtown Kirchberg by driving about one kilometer towards Aschau. Participants 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 2010, Hotel Sonnalp, A-6365 Kirchberg/Tirol, Austria

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

e-mail: [info@hotelsonnalp.info](mailto:info@hotelsonnalp.info), Web: [www.hotelsonnalp.info](http://www.hotelsonnalp.info)

All questions concerning the IWEPNM 2010 should be directed to:

Prof. Dr. Christian Thomsen,

Institut für Festkörperphysik, Technische Universität Berlin

Hardenbergstr. 36, 10623 Berlin, Germany

Tel: +49-(0)30-31423187, Fax: +49-(0)30-31427705

email: [iwepnm-info@physik.tu-berlin.de](mailto:iwepnm-info@physik.tu-berlin.de), Web: <http://www.iwepnm.org>

### Participation

Participation at the IWEPNM 2010 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 after each lecture. Video projection will be available for presentations. Presentation of video films needs prearranged confirmation. Invited speakers please test the video projection with the technical staff at the latest a few minutes before your session begins. Posters will be presented in the hall of the seminar room.

### Childcare

Childcare is provided by Michaela Kisch and her team ([michaela@kitzkids.com](mailto:michaela@kitzkids.com), Tel.: +43 664 5225265). If you need childcare during the winterschool, please contact us at the registration desk.

### Ski pass and internet connection

If you wish to buy a ticket for the ski lifts in the Kirchberg/Kitzbühel area, please ask at the hotel reception on Saturday evening.

Internet connection through WLAN is available for all participants, even if they are not accommodated at the Hotel Sonnalp. Please check at the front desk. There will be a room in the basement with fixed LAN connections, and limited number of laptops for free internet surfing.

### Proceedings

The contributions to the IWEPNM 2010 will be published by Wiley in physica status solidi. The expected date for the appearance of the proceedings is October 2010. **Contributions can only be published if they arrive before the 30 April.** 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.

### Manuscript preparation

General author instructions with links to the template, style, packages valid for pss (a), (b), and (c) are available at <http://www3.interscience.wiley.com/journal/122311674/grouphome/instruct-c08.html>. Please use either the Word or the LaTeX template, especially for publication in pss (c), since the articles will be produced from the publication-ready manuscript files. In addition, it is the easiest and most accurate way to check the page limits.

Please do not modify any pre-settings in the manuscript templates/style file such as font sizes, margins, and other formats, to avoid an incorrect layout of the publication. Manuscripts with wrong template use may be returned to the authors by the guest editors or the pss editorial office.

### Manuscript submission

URL: <http://mc.manuscriptcentral.com/pssc>

If you already have an ID and a password for this system, use them to log in. If not, register by clicking on the respective link. (right side - New User?) Please note that your login information is CASE SENSITIVE. Should you not remember your access data, use the "password help" section on the website. Once you are logged in, the Main Menu will be displayed. To submit your contribution, please click on Author Center.

### File names

Please use only Western letters for the file name, and only lower-case letters for the format extension. Please use clear, self-explaining file names, e.g. smith\_version2.doc. Please note that after submitting a manuscript, you can no longer modify it.

IWEPNM 2010  
CHAIRPERSONS FOR THE ORAL SESSIONS

The following participants are asked to support the program of the Winterschool by serving as chairperson:

Sunday, 7.03.	morning	Kuzmany
	morning, after coffee break	Prato
	evening	Dinse
Monday, 8.03.	morning	Hone
	morning, after coffee break	Obraztsov
	evening	Kaiser, Ute
Tuesday, 9.03.	morning	Jorio
	morning, after coffee break	Hertel
	evening	Luzzi
Wednesday, 10.03.	morning	Mehring
	morning, after coffee break	Freitag, Marcus
	evening	Doorn
Thursday, 11.03.	morning	Kamaras
	morning, after coffee break	Sauvajol
	evening	Kürti
Friday, 12.03.	morning	Roth
	morning, after coffee break	Akasaka
	evening	Forró

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 side-room (bar)!**

Chairpersons please remember: **For questions from the main room please ask the speaker to repeat the question. The chairperson's microphone 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

## Final Program

	Sunday 7 March	Monday 8 March	Tuesday 9 March	Wednesday 10 March	Thursday 11 March	Friday 12 March
Topics	synthesis and selection of carbon nanotubes	graphene transport, growth and characterization	carbon nanotube spectroscopy; non-carbon nanowires	graphene transport and mechanics	graphene transport, optics and theory	carbon nanotube and applications
8:30	Patterned CVD Growth of SWNTs for Device Application MARUYAMA	Heating and energy dissipation in biased graphene transistors FREITAG	Raman Spectroscopy of Chirality-Enriched Single Walled Carbon Nanotubes DOORN	Mobility and Resonant Scatterers in Graphene NOVOSELOV	Conduction in graphene: the low-temperature anomaly SKAKALOVA	Functionalization of Synthetic Carbon Allotropes HIRSCH
9:00	Dispersion, separation, and application of SWCNT KATAURA			Electronic properties of graphene ANDREI	Transport in graphene at high bias: current saturation and Klein tunneling MAURI	
9:30	DNA Sequence Motifs for Structure-Specific Recognition and Separation of CNT ZHENG	Electron-Electron Interaction in Graphene KIM	Indexing of individual single-walled carbon nanotubes from Raman spectroscopy SAUVAJOL	Electronic Spin Transport and Spin Precession in Single Graphene Layers TOMBROS	Gate-tunable band gap in bilayer graphene TSUKAGOSHI	Dispersion, separation, and reaction of single-walled carbon nanotubes MAEDA
10:00	Coffee break					
10:30	Self-assembled carbon nanotube structures and devices HANEIN	Epitaxial graphene on SiC(0001) SEYLLER	Electronic structure of carbon nanotubes with ultrahigh curvature PLANK	Nuclear spin relaxation and Korringa relation for Dirac electrons in graphene DORA	Bilayer graphene: tunable bandgap and electron-phonon Fano resonances WANG	Nanotubes see the light! GULDI
11:00	Applications of Aligned Carbon Nanotube Wafers: From MEMS to Human Motion Detection YAMADA	Epitaxial Graphene: Designing a New Electronic Material DE HEER	A high-energy spectroscopy viewpoint to access the electronic properties of metallicity selected functionalized SWCNT AYALA	Mechanics and Tribology of Graphene and Related Materials HONE	Dispersion of electrons and phonons, and electron-phonon interactions in bilayer graphene investigated by Resonance Raman scattering PIMENTA	Carbon Nanotubes: Fundamental Components for Materials Science and Bionanotechnology PRATO
11:30	High density carbon nanotubes and their applications for VLSI via interconnects AWANO	Synthesis of Graphene and Modified Graphene Using Chemical Vapour Deposition and Their Properties PARK	Electron microscopy and spectroscopy of low-dimensional materials SUENAGA	ElectroMechanical Resonators based on Nanotube and Graphene BACHTOLD	Vibrational properties of graphene nanoribbons MAULTZSCH	Towards Ultimate Scaling - Semiconducting Nanowires and Molecular Electronics RIEL

12:00-17:00	Mini workshops					
17:00 - 18:30	Dinner					17:00 Nanotube and nanotube-surface spectroscopy HERTEL
18:30	Intrinsic Superconductivity in Arrays of 4-Angstrom Carbon Nanotubes Embedded in AFI Zeolite SHENG	Graphene defects at atomic resolution MEYER	Electronic properties of single crystalline aluminium nanowires HWANG	Nano-electro-mechanical systems from arrays of graphene membranes VAN DER ZANDE	Illuminating graphene nanostructures MOLINARI	
19:00	Do fullerenes belong to the high-Tc family superconductivity universe? PRASSIDES	Electron Spin Resonance study of Graphene FORRO	Fabrication of novel low-dimensional nanomaterials using carbon nanotube nanoreactors KITAURA	Carbon nanotube mechanical resonators VAN DER ZANT	Electronic and vibrational properties of graphene under strain MOHR	17:30 Phonon assisted electroluminescence from metallic carbon nanotubes and graphene KRUPKE
19:30	Electron and nuclear spin coherence in (and outside) fullerenes MORTON	Imaging planar carbon and BN using high resolution TEM ZETTL	Semiconductor Nanowires: Growth, Mechanical and Optical Properties, and a Bendable Ceramic Fabric KORGEL	Clean carbon nanotubes: Single-electron quantum dots and strong coupling to nanomechanical motion STEELE	Conductance of doped or functionalized nanowires, nanotubes and graphene BLASE	18:00 IWEPM10 - Conference summary JORIO
20:00	Spin Relaxation in <sup>13</sup> C Nanotube Double Quantum Dots CHURCHILL	Poster I Monday	Poster II Tuesday	Production, properties and applications of graphite films of nanometer thickness OBRAZTSOV	Poster III Thursday	Bauernbuffet Farewell
20:30						
Topics	synthesis and selection of carbon nanotubes	graphene transport, growth and characterization	carbon nanotube spectroscopy; non-carbon nanowires	graphene transport and mechanics	graphene transport, optics and theory	carbon nanotube and applications
	Sunday 7 March	Monday 8 March	Tuesday 9 March	Wednesday 10 March	Thursday 11 March	Friday 12 March



**PROGRAM**

**AND**

**ABSTRACTS**



**COSMOSIL**

HPLC columns for separation of soluble carbon nanotubes

# COSMOSIL CNT

**NEW!!**

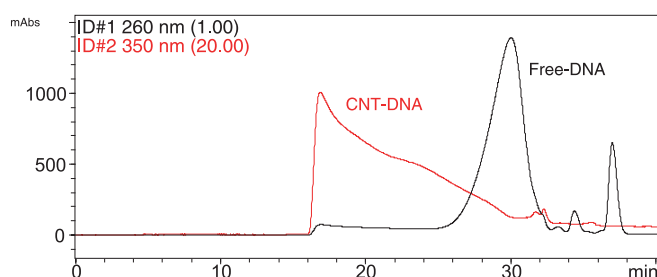


## Features of COSMOSIL CNT packed columns

- Size-based separation of soluble carbon nanotubes
- Hydrophilic group coating silica packing material
- Three types of pore sizes (300 Å, 1000 Å, 2000 Å)
- High durability

## Size-based separation of carbon nanotubes

COSMOSIL CNT packed columns offered improved separation for DNA wrapped carbon nanotubes by connecting three columns with different pore sizes.



Column COSMOSIL CNT-300 7.5 mm I.D. x 300 mm  
COSMOSIL CNT-1000 7.5 mm I.D. x 300 mm  
COSMOSIL CNT-2000 7.5 mm I.D. x 300 mm  
Mobile phase 0.5 mmol/L EDTA, 200 mmol/L NaCl, 40 mmol/L Tris-Tris HCl(pH7.0)  
Flow rate 1.0 ml/min  
Temperature 40 °C  
Detection UV 260 nm(x 1), 350 nm(x 20)  
Sample DNA-wrapped CNT(CNT-DNA)  
Injection vol. 500 µl  
Pressure 8.1 MPa

Sample courtesy of Prof. H. Shinohara, Department of Chemistry & Institute for Advanced Research, Nagoya University

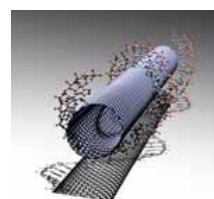


Image courtesy of Dr. Y. Ito, Univ. of Oxford

## Material characteristics

Packing material	CNT-300	CNT-1000	CNT-2000
Silica gel	high purity spherical porous silica		
Average particle size	5 µm		
Average pore size	approx. 300 Å	approx. 1000 Å	approx. 2000 Å
Stationary phase	hydrophilic group (neutral)		
pH range	2 - 7.5		
Pressure	15 MPa and below		

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Sunday, March 7

## Synthesis and selection of carbon nanotubes

- 8:30 – 9:00     **S. Maruyama, JP**  
*Patterned CVD Growth of SWNTs for Device Application*
- 9:00 – 9:30     **H. Kataura, JP**  
*Dispersion, separation, and application of single-wall carbon nanotubes*
- 9:30 – 10:00    **M. Zheng, US**  
*DNA Sequence Motifs for Structure-Specific Recognition and Separation of Carbon Nanotubes*
- 10:00 – 10:30   **Coffee break**
- 10:30 – 11:00   **Y. Hanein, IL**  
*Self-assembled carbon nanotube structures and devices*
- 11:00 – 11:30   **T. Yamada, JP**  
*Applications of Aligned Carbon Nanotube Wafers: From MEMS to Human Motion Detection*
- 11:30 – 12:00   **A. Awano, JP**  
*High density carbon nanotubes and their applications for VLSI via interconnects*
- 12:00 – 17:00   **Mini Workshops**
- 17:00 – 18:30   **Dinner**
- 18:30 – 19:00   **P. Sheng, CN**  
*Intrinsic Superconductivity in Arrays of 4-Angstrom Carbon Nanotubes Embedded in AFI Zeolite*
- 19:00 – 19:30   **K. Prassides, US**  
*Do fullerenes belong to the high- $T_c$  family superconductivity universe?*
- 19:30 – 20:00   **J. J. L. Morton, UK**  
*Electron and nuclear spin coherence in (and outside) fullerenes*
- 20:00 – 20:30   **H. Churchill, US**  
*Spin Relaxation in  $^{13}\text{C}$  Nanotube Double Quantum Dots*

Sunday, March 7

**8:30****Patterned CVD Growth of SWNTs for Device Application**

Shigeo Maruyama

Department of Mechanical Engineering, The University of Tokyo, Tokyo

The conventional concept of using SiO<sub>2</sub> patterned Si substrates to selectively grow 3D carbon nanotube structures can be applied to a dip-coating method followed by alcohol CVD growth. High-quality vertically aligned single-walled carbon nanotube (SWNT) patterns can be easily obtained by this protocol [1]. The more elaborate patterned growth is based on the control of wettability of substrates. Surface wettability strongly affects the deposition of catalyst in dip-coating process. By functionalizing the silicon surface using a classic self-assembled monolayer (SAM) and then selectively removing the SAM by ultraviolet (UV) light, the catalyst can be dip-coated onto only the hydrophilic areas of the substrate. Furthermore, by utilizing an electron beam instead of UV, the line width of an SWNT pattern can be easily reduced to 50 nm. The patterned region can be easily located and visualized under a scanning electron microscope [2]. References: [1] R. Xiang, E. Einarsson, H. Okabe, S. Chiashi, J. Shiomi, *Jpn. J. Appl. Phys.*, (2010), in press. [2] R. Xiang, T. Wu, E. Einarsson, Y. Suzuki, Y. Murakami, J. Shiomi, S. Maruyama, *J. Am. Chem. Soc.*, 131 (2009) 10344.

**9:00****Dispersion, separation, and application of single-wall carbon nanotubes**Hiromichi Kataura

Nanotechnology Research Institute, AIST, Ibaraki, Japan &amp; JST, CREST

For the practical application of single-wall carbon nanotubes (SWCNTs), metal semiconductor separation is one of the most important issues to be solved. Recently, some excellent separation methods, such as density gradient ultracentrifugation, were developed and now we can obtain high-purity semiconducting and metallic SWCNTs very easily. Our research group has also developed a new separation method using agarose gel [1] and tried to use them for field effect transistors. Semiconductor enriched SWCNTs can be used for a good source of the thin film FET without electrical breakdown process. They all showed on/off ratios higher than 10000. However, the mobility of them was still not good probably due to the defects induced in the ultrasonic dispersion process for the isolation. To solve this problem, we have developed a new method to get isolated SWCNTs with low defect density. We have also developed new separation method and FET device fabrication process. In this presentation, we would like to show total progress in dispersion, separation and application of SWCNTs in our lab.

## References

1. T. Tanaka et al., Appl. Phys. Express.2 (2009) 125002.

**9:30****DNA Sequence Motifs for Structure-Specific Recognition and Separation of Carbon Nanotubes**Ming Zheng

National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

Single walled carbon nanotubes (SWCNT) are a family of molecules that have the same cylindrical shape but different chiralities. The SWNT sorting problem, i.e., separation of a synthetic mixture of tubes into individual single-chirality components, has attracted considerable attention in recent years. A systematic and general method to purify each and every single-chirality species of the same electronic type from the synthetic mixture is highly desirable. Recently, we have reported such a method that allows purification of all 12 major single-chirality semiconducting species from a synthetic mixture, with sufficient yield for both fundamental studies and application development (Tu et al., Nature, 406, 250, 2009). In this presentation, I will review the experimental development and mechanistic understanding of the separation process. In particular, a model of DNA wrapping structure invoking a novel secondary DNA structure motif will be discussed.

**10:30****Self-assembled carbon nanotube structures and devices**Yael Hanein

Tel-Aviv University, Tel-Aviv

Self-assembly is an attractive approach to organize elements which are either too small or too gentle to be handled by pick and place approaches. Carbon nanotube assembly is a prime example. Carbon nanotubes (CNTs) have spearheaded much of the research in the field of nanotechnology, and in particular, in the field of nanocircuits, due to their superb electrical properties, ease of fabrication and their durability. Despite extensive efforts, to date, no method has been devised that can address all four crucial aspects involved in the fabrication carbon nanotube based devices, namely: aligning the tubes in a preset pattern, positioning the nanotubes in a desired location, selecting or identifying the chirality of each of the individual CNTs, and finally, the ability to integrate CNT in an integrated circuit (IC) compatible environment. Using a novel self-assembly approach we can arrange CNTs in a distinct pattern and integrate them into functional electrical and electro-mechanical devices. The underlying mechanical principles of the assembly and the devices will be described.

**11:00****Applications of Aligned Carbon Nanotube Wafers: From MEMS to Human Motion Detection**Takeo Yamada

Nanotube Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki

Motivated to realize reproducible, uniform, and reliable carbon nanotube (CNT) based devices, we developed an approach centered on the use of aligned and closely-packed CNT films, called “CNT wafers” [1]. Through this approach an assembly of a predetermined, massive quantity of aligned CNTs, grown by the super-grown method [2], could be placed at prescribed locations and orientations, which then could be controllably fabricated into well-defined configurations. In this way, functional components with higher structural diversity and complexity could be fabricated and serve as building blocks for device systems. In this presentation, I will present our recent progress on the development of applications based on carbon nanotube wafer technology. After providing an introduction to the concept of the CNT wafer and our motivations, I will present the fundamental obstacles we face. Finally, I will highlight some current examples of applications, which represents length scales both small [1] and large [3] and underscores the unique properties of the CNT wafer. 1. Y. Hayamizu, et al. Nature Nanotech. 3, 289 (2008) 2. K. Hata, et al. Science 306, 1362 (2004) 3. T. Yamada, et al. Submitted

**11:30****High density carbon nanotubes and their applications for VLSI via interconnects**Yuji Awano

Dept. of Electronics and Electrical Engineering, Keio University, Yokohama

Carbon-based nano-materials, such as carbon nanotubes (CNTs) and graphene, have many attractive properties, including high carrier mobility, ability to carry a high-density current, high mechanical strength and long spin relaxation time. Because of these remarkable properties, they are expected to be used in future LSIs as Emerging Research Materials (ERM). Their advantages are not only they can provide a technology platform enabling a new “Beyond CMOS” information processing paradigm, but also they potentially can have an impact on scaled MOS-FETs as an alternate channel material and an alternate wiring material. In this paper, we discuss the present status of the material technologies and some issues to be addressed for realizing CNT via interconnects (vertical wirings) as an emerging interconnect for a future LSI.

Main topics which I will report are as follows[1]:

1. High-quality multi-walled CNTs were synthesized by CVD at temperatures below 400°C.
2. CNT density reaches the order of  $1 \text{ E}12 / \text{cm}^2$ .
3. CNT vias were fabricated with a low-k dielectric layer ( $k = 2.6$ ), and also with CMOS as contact plugs.
4. Ballistic length of CNT grown at 450 °C was estimated to be 80nm, which is almost the same as the via height for 32-nm technology node and below.
5. CNT vias were not deteriorated at current density as high as  $5\text{E}6 \text{ A}/\text{cm}^2$  at 105 °C for 100 hours. Moreover, several improvements of the contacts with both the upper and the lower metal lines could withstand a high current density of  $1.7\text{E}8 \text{ A}/\text{cm}^2$  per tube of a CNT's via.

Acknowledgments: This work was completed as part of the MIRAI Project supported by NEDO.

## References:

See, for example, M. Sato, et al., SSDM 2009, M. Katagiri, et al., IEEE/IITC 2009, A. Kawabata, et al., IEEE/IITC 2008. M. Nihei et al., IEEE/IITC 2007



**18:30****Intrinsic Superconductivity in Arrays of 4-Angstrom Carbon Nanotubes Embedded in AFI Zeolite**Ping Sheng

Department of Physics, Hong Kong University of Science &amp; Technology, Hong Kong

Superconductivity in carbon nanotubes has been controversial because carbon is not known to be a superconducting element. In this talk I show that by improving the sample quality and devising strategy to make surface electrical contacts to the samples that are separated by only 100nm, repeatable observations of the superconducting resistive transition can be obtained on samples comprising 4-Angstrom carbon nanotubes embedded in AFI zeolite pores. The picture which emerges is that of a coupled Josephson array consisting of aligned nanotubes crossing over from an individually fluctuating 1D system to a coherent 3D superconductor, mediated by a Kosterlitz-Thouless (KT) transition which establishes quasi long range order in the lateral plane perpendicular to the c-axis of the nanotubes. The attainment of overall coherence across the measuring electrodes is seen at 5K and below, evidenced by the appearance of a well-defined supercurrent gap at 2K. Magnetic torque measurements, showing evidence of Hc1 as well as differences in the field-cooled and zero-field cooled data, are consistent with the above interpretation. Some preliminary theoretical simulation results will be shown.

**19:00****Do fullerenes belong to the high- $T_c$  family superconductivity universe?**Kosmas Prassides

Department of Chemistry, Durham University, Durham, United Kingdom

C60-based solids are archetypal examples of molecular superconductors with  $T_c$  as high as 33 K.  $T_c$  of the fcc  $A_3C_{60}$  ( $A$  = alkali metal) fullerenes increases monotonically with the interC60 separation, which is in turn controlled by the sizes of the  $A^+$  cations – this physical picture has remained unaltered since 1992. Pressure-induced trace superconductivity (s/c fraction  $\ll 1\%$ ) at 40 K was reported in 1995 in multiphase samples in the  $Cs_xC_{60}$  phase field. Despite numerous attempts by many groups worldwide, this remained unverified and the structure and composition of the material responsible for superconductivity unidentified. This has hindered any attempt to push  $T_c$  even higher and make contact with theory which predicts correlation-enhanced superconductivity for expanded fullerenes near the metal-insulator transition. Here I will present our recent work in this field that led to the discovery of pressure-induced bulk superconductivity emerging out of a parent antiferromagnetic insulating state at the highest  $T_c$  currently known for any molecular material [1,2].

[1] Ganin AY et al. Nature Mater. 2008, 7, 367. [2] Takabayashi Y et al. Science 2009, 323, 1585.

**19:30****Electron and nuclear spin coherence in (and outside) fullerenes**

John J. L. Morton<sup>1</sup> Richard M. Brown<sup>1</sup> Vasiliea Filidou<sup>1</sup> Yasuhiro Itoh<sup>1</sup> Steven D. Karlen<sup>1</sup> Jamie H. Warner<sup>1</sup> Alexei M. Tyryshkin<sup>2</sup> S. A. Lyon<sup>2</sup> Hisanori Shinohara<sup>3</sup> Arzhang Ardavan<sup>4</sup> G. Andrew D. Briggs<sup>1</sup>

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Electron spins can show long-lived coherent behaviour, especially within carbon nanomaterials where there is a low natural abundance of nuclear spins. Furthermore, carbon nanostructures such as nanotubes and graphene offer opportunities to interface molecular spins with nanoelectronics. We have investigated electron and nuclear spin coherence in endohedral fullerenes such as N@C<sub>60</sub> and Group III metallofullerenes (Sc-, Y- and La@C<sub>82</sub>). In all cases we have observed coherence times in excess of 200  $\mu$ s, and observed relaxation arising from molecular vibrational modes and environmental nuclear spins. We have studied the transfer of coherent states between the electron and nuclear spin in such systems in order to benefit from the longer coherence times of the nuclear spin. The measured nuclear coherence times are limited by relaxation of the electron spin, which we can seek to overcome using a transient electron spin, such as that generated through optical excitation of an (empty) fullerene which has been decorated with a set of appropriate nuclear spins. This transient electron spin can be used to polarise, entangle, and measure the attached nuclear spins.

Sunday, March 7

Synthesis and selection of carbon nanotubes

**20:00**

**Spin Relaxation in  $^{13}\text{C}$  Nanotube Double Quantum Dots**

Hugh Churchill

Department of Physics, Harvard University, Cambridge, MA

This talk will present experiments on carbon nanotube double quantum dots aimed at developing a nanotube spin qubit. The first part will describe transport measurements of Pauli blockaded, many-electron  $^{12}\text{C}$  and  $^{13}\text{C}$  double dots that examine the strength of the hyperfine interaction in this system. The second part will describe charge sensing measurements that probe the timescales of relaxation,  $T_1$ , and inhomogeneous dephasing,  $T_2^*$ , for a two-electron  $^{13}\text{C}$  double dot. The dependence of  $T_1$  on a parallel magnetic field is attributed to the spin-orbit-modified electron spectrum of carbon nanotubes.  $T_2^*$  is consistent with the hyperfine coupling strength in  $^{13}\text{C}$  nanotubes inferred from the transport measurements. New device fabrication and spin manipulation proposals will be described.

Synthesis and selection of carbon nanotubes

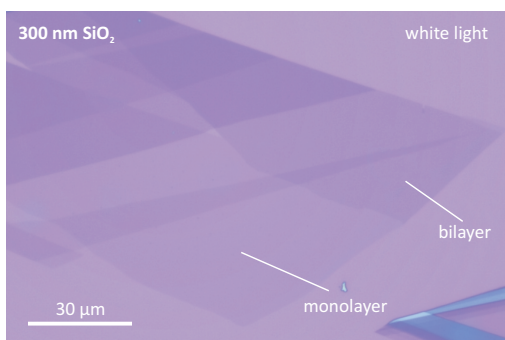
Sunday, March 7



Providing graphene flakes and devices to industry and academia

## Graphene on Si|SiO<sub>2</sub> or quartz

- We offer single, double, triple and >3-layer graphene flakes on oxidised silicon (300 nm and 90 nm SiO<sub>2</sub>) and quartz.
- 90 nm SiO<sub>2</sub> offers higher graphene contrast than the traditional 300 nm.
- Flakes are prepared from natural graphite using micro-mechanical cleavage.

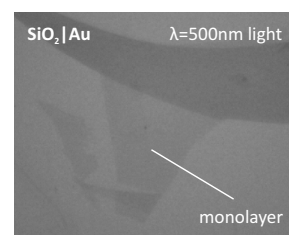
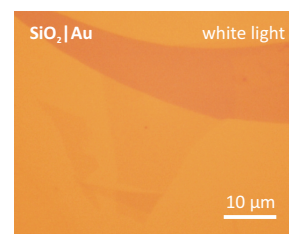


<b>Flake sizes</b>	Typically < 2000 μm <sup>2</sup> ; largest monolayer found to date: 1.5 mm <sup>2</sup>
<b>Pricing guide</b>	≈ € 0.50 per μm <sup>2</sup> area (decreases significantly for v. large flakes), with reductions if the flake is difficult to use for lithography, e.g. close to the wafer's edge
<b>Applications</b>	transistors, spintronics, gas sensors, metrology, spectroscopy, optoelectronics, AFM, STM, etc.
<b>Wafer sizes</b>	min: 5 mm × 5 mm max: 100 mm diameter circle

## Graphene on Si|SiO<sub>2</sub>|Au

- We can isolate graphene flakes on gold using optical microscopy.
- A thin layer of gold is deposited onto an oxidised silicon wafer before preparing flakes.
- The gold layer is continuous and electrically conductive, but thin enough to maintain the optical interference effect that makes graphene visible.
- Narrow band-pass filters can be used to enhance the contrast.

<b>Flake sizes</b>	Typically < 500 μm <sup>2</sup> ; largest monolayer found to date: 5000 μm <sup>2</sup>
<b>Pricing guide</b>	≈ € 3 per μm <sup>2</sup> area, with reductions for large flakes
<b>Applications</b>	STM, Raman spectroscopy
<b>Wafer sizes</b>	min: 5 mm × 5 mm; max: 25 mm × 25 mm



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Monday, March 8

## Graphene transport, growth and characterization

- 8:30 – 9:30      **M. Freitag, US**  
*Heating and energy dissipation in biased graphene transistors*
- 9:30 – 10:00    **P. Kim, US**  
*Electron-Electron Interaction in Graphene*
- 10:00 – 10:30   **Coffee break**
- 10:30 – 11:00   **T. Seyller, DE**  
*Epitaxial graphene on SiC(0001)*
- 11:00 – 11:30   **W. A. d. Heer, US**  
*Epitaxial Graphene: Designing a New Electronic Material*
- 11:30 – 12:00   **H. J. Park, DE**  
*Synthesis of Graphene and Modified Graphene Using Chemical Vapour Deposition and Their Properties*
- 12:00 – 17:00   **Mini Workshops**
- 17:00 – 18:30   **Dinner**
- 18:30 – 19:00   **J. C. Meyer, DE**  
*Graphene defects at atomic resolution*
- 19:00 – 19:30   **L. Forró, CH**  
*Electron Spin Resonance study of Graphene*
- 19:30 – 20:00   **A. Zettl, US**  
*Imaging planar carbon and BN using high resolution TEM*

Monday, March 8



**8:30**

**Heating and energy dissipation in biased graphene transistors**

Marcus Freitag

IBM, T.J. Watson Research Center, Yorktown Heights, NY

High carrier mobility and thermal conductivity are key attributes that make graphene a promising material for high-speed electronics. However, self-heating of the graphene may be an issue that limits its performance at high biases. In this talk we use several experimental methods to characterize the graphene self heating and the energy dissipation into the substrate. The interface between graphene and the underlying silicon-oxide is of particular interest, since the electrons in graphene can directly couple to surface polar phonons in the silicon-oxide, opening up an additional power-dissipation channel. This work was done in collaboration with Mathias Steiner, Vasili Perebeinos, Hsin-Ying Chiu, Yves Martin, Zhihong Chen, James Tsang, and Phaedon Avouris.

**9:30****Electron-Electron Interaction in Graphene**Philip Kim

Columbia University, New York

Electrons confined in two dimensions (2D) can exhibit strongly correlated states. Recent experimental discovery of integer and fractional quantum Hall effect in graphene amplified interest in correlated 2D electronic systems, owing to presence of the unusual topological phase associated with zero effective mass of charge carriers. In this talk, we will discuss the transport, employing both Hall bar geometry samples and Corbino geometry samples, and infrared spectroscopy results that reveal the role of the many-body effects due to the electron-electron interaction in graphene near the Dirac point. In particular, we will discuss the unusual spontaneous symmetry breaking of single particle LLs under the extreme quantum condition in single and bilayer graphene together with the appearance of unique low density insulating states and fractional quantum Hall states.

**10:30****Epitaxial graphene on SiC(0001)**Thomas SeyllerLehrstuhl für Technische Physik, Friedrich-Alexander-Universität Erlangen-Nürnberg,  
Erlangen

Graphene, the  $sp^2$ -bonded honeycomb network of carbon atoms, constitutes a very active field of research. In graphene, charge carriers are described by the Weyl-Hamiltonian for massless, relativistic Fermions. Extraordinary transport properties such as an unusual quantum Hall effect were observed with graphene samples obtained by mechanical exfoliation. A large mobility of charge carriers and prospects for room-temperature ballistic transport raise hopes for application of graphene in electronic devices. While exfoliated graphene is the material for groundbreaking studies, it offers no perspective for large scale application. In this talk I will review studies of the structural, electronic, and transport properties of graphene grown epitaxially on SiC, which offers an excellent perspective for application of graphene in electronic devices. The first part describes studies of the electronic structure and structural properties of epitaxial graphene. In the second part I demonstrate how the properties of epitaxial graphene on SiC are improved by growth in an Argon atmosphere. Finally I shall report on ongoing work related to the development of graphene transistors.

Monday, March 8

Graphene transport, growth and characterization

**11:00**

**Epitaxial Graphene: Designing a New Electronic Material**

Walt A de Heer

Physics, Georgia Institute of Technology, Atlanta

Since 2001 the Georgia Tech epitaxial graphene research team and its collaborators have developed the new field of epitaxial graphene electronics. The current status of epitaxial graphene research will be presented, including the production methods and recent results from various characterization investigations. Methods have been developed to grow continuous multilayer epitaxial graphene (MEG) on the C-face of hexagonal silicon carbide with of up to 100 graphene sheets and its extraordinary transport properties have been demonstrated, including the quantum Hall effect. Surprisingly, the properties of MEG are closely related to monolayer graphene rather than graphite, as a result of an unusual rotational stacking of the graphene layers that causes the graphene sheets to electronically decouple. Consequently the electronic band structure of MEG is composed of Dirac cones. The charge carriers are chiral and exhibit a non-trivial Berry 's phase. Weak anti-localization and quantum confinement has been demonstrated. Landau level spectroscopy further exhibits record-breaking room temperature mobilities and well resolved Landau levels below 1 T, indicating extremely low carrier densities an

**11:30****Synthesis of Graphene and Modified Graphene Using Chemical Vapour Deposition and Their Properties**Hye Jin Park<sup>1</sup> Viera Skákalová<sup>1</sup> Jannik Meyer<sup>2</sup> Takayuki Iwasaki<sup>1</sup> Siegmund Roth<sup>3</sup>Klaus v. Klitzing<sup>1</sup><sup>1</sup>Max Planck Institute for Solid State Research, Stuttgart, Germany<sup>2</sup>Electron Microscopy for Material Science, University of Ulm, Ulm, Germany<sup>3</sup>School of Electrical Engineering, WCU Flexible Nanosystems, Korea University, Seoul, Korea

We present a study of the influence of synthesis' parameters and a metal catalyst (Ni, Cu, Ni/MgO) during the chemical vapour deposition (CVD) process on growth of graphene sheets - their structure and properties, like number of layers, size of crystal domains and crystallinity, by Raman and UV/VIS optical absorption spectroscopy, SEM, XPS and HR-TEM. When ammonia was incorporated during synthesis, the grown graphene sheet contained nitrogen modifying its electronic properties. Electrical transport was measured after the sample was transferred onto a Si/SiO<sub>2</sub> substrate by 4-probe method. We show how chemical modification by nitrogen, different growth condition as well as the size of the sample varies the electrical conductivity and its response to electrostatic field applied through the back gate of the Si/SiO<sub>2</sub>-wafer.

**18:30****Graphene defects at atomic resolution**

J. C Meyer<sup>1</sup> S. Kurasch<sup>1</sup> G. Algara-Siller<sup>1</sup> A. Chuvilin<sup>1</sup> H.-J. Park<sup>2</sup> V. Skakalova<sup>2</sup>  
S. Roth<sup>3</sup> C. Gomez-Navarro<sup>2</sup> R. S. Sundaram<sup>2</sup> M. Burghard<sup>2</sup> K. Kern<sup>2</sup> U. Kaiser<sup>1</sup>

<sup>1</sup>Electron microscopy department of the materials sciences, Universität Ulm, Ulm, Germany

<sup>2</sup>Max Planck Institute for solid state research, Stuttgart, Germany

<sup>3</sup>School of Electrical Engineering, WCU Flexible Nanosystems, Korea University, Seoul, Korea

We present new insights into various aspects of defects in graphene. For example, the formation and evolution of defects under electron irradiation is observed in real time with atomic resolution. We determine the precise knock-on threshold energy and identify other radiation damage mechanisms. High-energy electron irradiation provides a continuous "randomization" of some atoms, which then allows further insights into the complicated bonding behaviour in carbon materials. The existing defects in as-synthesized CVD grown graphene and reduced graphene oxide are elucidated from atomically resolved images. In addition, we demonstrate that information on charge distribution, rather than just structural information, can be obtained from TEM measurements. The ionicity of single-layer hexagonal boron nitride is confirmed from direct images, while the same effect complicates the elemental identification. A nitrogen substitution in graphene can be detected from changes in the electronic configuration on its neighbouring carbon atoms. Further, the nitrogen defect in graphene is reactive and provides a preferred site for the trapping of ad-atoms on the graphene sheet.

**19:00****Electron Spin Resonance study of Graphene**László Forró

Inst. of Physics of Complex Matter, Ecole Polytechnique Fédérale de Lausanne, Lausanne

Electron spin resonance (ESR) is an efficient technique to study the density of states (as a function of temperature and doping) of graphene, and to detect magnetic interaction of localized spins at the edges of graphene flakes and ribbons. We have performed ESR measurements in the 4-300 K temperature range on graphene samples derived from: 1) chemical reduction of graphene oxide sheets, 2) liquid phase exfoliation of graphite (LPEG), 3) and mechanical exfoliation. The ESR signal depends very much on the method of preparation of graphene. The amount of localized spins and the Pauli component of the spin susceptibility vary from sample to sample. In some cases ferromagnetism is observed below 20 K.

Acknowledgment: The work is performed in collaboration with A. Sienkiewicz, A. Magrez, R. Nesper, J. Coleman and K. Kern and Luka Ciric. The project is partially supported by MaNEP and by the European Network IMPRESS.

Monday, March 8

Graphene transport, growth and characterization

**19:30**

**Imaging planar carbon and BN using high resolution TEM**

Alex Zettl

University of California at Berkeley and Lawrence Berkeley National Laboratory  
Berkeley, CA 94720 USA

We have used aberration-corrected transmission electron microscopy to examine the local atomic structure in vacuum-suspended low-layer-number carbon and BN sheets. Individual atoms are imaged and interesting defect structure is identified. High data acquisition rates allow movies to be compiled showing dynamics of adsorbates and motion of atoms along edges. The stability of various edge configurations (including zig-zag and armchair) is explored via model simulations. The detailed understanding of stability and dynamics of 2-D atomic sheets has much relevance to applications including graphene electronics and BN optics.



**MON 1****Sorting Single-Wall Carbon Nanotubes combining Gel Filtration and Density-Gradient Ultracentrifugation**

Daisuke Nishide<sup>1</sup> Huaping Liu<sup>2</sup> Takeshi Tanaka<sup>1</sup> Hiromichi Kataura<sup>2</sup>

<sup>1</sup>Nanotechnology Research Institute (NRI), National Institute of Advanced Industrial Science and Technology (AIST), Japan

<sup>2</sup>NRI, AIST, and JST-CREST, Japan

To investigate the intrinsic optical and electronic properties of single-wall carbon nanotubes (SWCNTs), sorting a single chirality of SWCNTs is one of the most important tasks, because pristine sample is formed by various chirality structures. Aiming at the solution, some methods for enrichment of specific SWCNTs were reported. For example, density gradient ultracentrifugation (DGU) can enrich (6,5) SWCNT using sodium cholate (SC) as a surfactant. However, it is known that obtained sample still contains small amount of metallic SWCNTs as an impurity. To solve this problem, we have combined two separation techniques, gel filtration and DGU to sort SWCNTs. Pristine SWCNTs were firstly dispersed in SC solution, then isolated and purified by ultracentrifugation. The supernatant was next filtered through gel medium to separate metallic and semiconducting SWCNTs [1]. After obtaining semiconductor-enriched SWCNTs, the solution was sorted by DGU [2]. As a result, high-purity (6,5) SWCNT was extracted from HiPco SWCNTs. Detailed protocols and characterization will be discussed. [1] T. Tanaka et al, App. Phys. Exp. 2 (2009) 125002. [2] M. S. Arnold et al, Nat. Nanotechnol. 1 (2006) 60.

**MON 2****The Effect of Atomic Nitrogen on the C<sub>60</sub> Cage**

Hidefumi Nikawa<sup>1</sup> Yasuyuki Araki<sup>2</sup> Zdenek Slanina<sup>1</sup> Takahiro Tsuchiya<sup>1</sup> Takeshi Akasaka<sup>1</sup> Takahiko Wada<sup>2</sup> Osamu Ito<sup>2</sup> Klaus-Peter Dinse<sup>3</sup> Masafumi Ata<sup>4</sup> Tatsuhisa Kato<sup>5</sup> Shigeru Nagase<sup>6</sup>

<sup>1</sup>University of Tsukuba

<sup>2</sup>Tohoku University

<sup>3</sup>Darmstadt University of Technology

<sup>4</sup>National Institute of Advanced Industrial Science and Technology

<sup>5</sup>Josai University

<sup>6</sup>Institute for Molecular Science

Quantum computing is expected as the next version of computing systems to make it possible to solve in seconds certain problems that would take the fastest existing supercomputer millions of years to complete. Several proposals for solid-state implementations of quantum computers based on electron spins are currently being investigated. Among them, N@C<sub>60</sub> is particularly promising for the realization of qubits because of its long spin relaxation time even at room temperature. This

exceptional property results from the fact that the N atom and its spin, being shielded by the C<sub>60</sub> cage, is largely immune from environmental influences. Therefore, N@C<sub>60</sub> is a key material for solid-state spin quantum computing, and much work to explore its electronic ground state properties has been carried out. In the present study we report about the investigation of N@C<sub>60</sub> exposed to laser flash excitation. For the implementation of selective read out schemes it will be important to understand the electronic excitation and deactivation pathways of N@C<sub>60</sub> because the use of optical manipulation in addition to pulsed magnetic resonance allows the quantum control on a picosecond or femtosecond timescale.

### MON 3

#### **Nucleation theory for describing kinetics of cluster formation and growth in solutions of fullerene C60**

V. L. Aksenov<sup>1</sup> M. V. Avdeev<sup>1</sup> T. V. Tropin<sup>1</sup>

<sup>1</sup>Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Moscow Region

In the present work we overlook possibilities of the nucleation theory for describing kinetics of cluster formation and growth in different types of fullerene C60 solutions. Thus, for solvents with low polarity the model of restricted cluster growth was proposed, which qualitatively describes fullerene clusters (size below 10 nm) appeared in oversaturated conditions. Its modification, which takes into account the sedimentation of larger clusters, made it possible to repeat non-monotonous behavior of C60 concentration in time when the fullerene is dissolved in carbon disulfide. Also, prospects of a similar kinetic theory of the cluster growth are considered for polar solutions such as C60/n-methyl-pyrrolidone, C60/pyridine. The kinetic equations cannot be applied directly in the same way like in the previous case because of the large size of final stable clusters (up to 500 nm) observed in these solutions. This fact requires a detailed study, from the theoretical viewpoint, of the intermediate regimes, when the size of the growing clusters is still reasonable (between 10 and 100 nm) for numerical solutions of the kinetic equations.

### MON 4

#### **Carbon Nanotube Coatings to Improve Intracortical Recording Electrodes**

Elisa Castagnola<sup>1</sup> Alberto Ansaldi<sup>1</sup> Davide Ricci<sup>1</sup>

<sup>1</sup>Italian Institute of Technology, Robotics, Brain and Cognitive Sciences Department

Via Morego 30, 16163, Genoa – Italy

Implantable electrodes are one of the most useful tools for electrophysiology research, both for acute recording of intracortical signals and for long term implants. A stable low-impedance electrode to tissue interface is fundamental to obtain reliable, long term recordings of the Central Nervous System activity. Commonly used

metal electrodes do not meet such requirements, as their surface degrades in time and have high impedance. Conductive polymers have been largely investigated as nano-structured coatings to enhance electrode surfaces for in vivo recording. With the same purpose, carbon nanotubes (CNTs) composite coatings have been obtained by chemical and electrochemical methods. In the present work we have used reference commercial electrodes for in vivo intracortical recording made from quartz insulated platinum/tungsten wires, mechanically ground, as a platform for comparing two widely different CNT deposition methods: direct in situ growth of CNTs by chemical vapour deposition and an highly selective and controllable electrochemical co-deposition of polypyrrole and CNTs. In depth analysis of their electrochemical properties and stability is presented and discussed.

## MON 5

### Diameter dependence of dielectric constant for the excitonic transition energy of single-wall carbon nanotubes

P. T. Araujo<sup>1</sup> A. Jorio<sup>1</sup> M. S. Dresselhaus<sup>2</sup> K. Sato<sup>3</sup> R. Saito<sup>4</sup>

<sup>1</sup>Departamento de Física-Instituto de Ciencias Exatas-ICEx, UFMG, Belo Horizonte, Brazil.

<sup>2</sup>Department of Electrical Engineering and Computer Science and Department of Physics, MIT, Cambridge, USA.

<sup>3</sup>Department of Mechanical Engineering, The University of Tokyo, Tokyo, Japan.

<sup>4</sup>Department of Physics, Tohoku University, Sendai, Japan.

The measured optical transition energies  $E_{ii}$  of single-wall carbon nanotubes are compared with bright exciton energy calculations, which include symmetry optimization and environmental effects. The  $E_{ii}$  differences between experiment and theory are minimized by considering a diameter-dependent dielectric constant  $\kappa$ , with different dependencies obtained for  $(E_{11}^S, E_{22}^S, E_{11}^M)$  relative to  $(E_{33}^S, E_{44}^S)$ . A changing environment changes the  $\kappa$  diameter dependence for  $(E_{11}^S, E_{22}^S, E_{11}^M)$ , but for  $(E_{33}^S, E_{44}^S)$  the environmental effects are minimal. The resulting calculated exciton energies reproduce the experimental  $E_{ii}$  values to an accuracy within  $\pm 70$  meV for  $0.7 < d_t < 3.8$  nm, and  $1.2 < E_{ii} < 2.7$  eV, thus providing a theoretical justification for  $E_{ii}$ , environmental effects and important insights on the dielectric screening in one-dimensional structures.

**MON 6****In-situ TEM studies of mechanical and electrical properties of single-walled BNNTs**R. Arenal<sup>1</sup> M.S. Wang<sup>2</sup> Z. Xu<sup>2</sup> A. Loiseau<sup>1</sup> D. Golberg<sup>2</sup><sup>1</sup>LEM, CNRS-ONERA, Chatillon, France<sup>2</sup>International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Tsukuba, Japan

Boron nitride nanotubes (BNNTs) are an emerging nanomaterial with properties complementary to those of the well-known carbon counterparts [1,2]. In this contribution we will present our studies on mechanical and electrical properties of single-walled (SW) BNNTs [3]. In order to investigate these properties, we carried out in-situ TEM experiments [4]. All these experiments indicated that SW-BNNTs are very flexible and elastic. Furthermore, we determined the Young modulus of an individual SW-BNNT. On the other hand, we carried out several experiments where I/V curves were measured on individual NTs as well as on bundles, confirming that these tubes are insulating with an overall electrical resistivity of  $> 7G\Omega$ . These studies provide very useful information that has been not acquired before and that sheds considerable light on the properties and characteristics of these inorganic SW-NTs[5]. [1] R. Arenal, X. Blase, A. Loiseau, *Advances in Physics*, in press (2010). [2] D. Golberg, et al., *Adv. Mat.*(2007). [3] R. Arenal, et al., *J. Am. Chem. Soc.*(2007). [4] D. Golberg, et al., *Appl. Phys. Lett.* (2006). [5] R. Arenal, M.S. Wang, Z. Xu, A. Loiseau, D.Golberg, submitted.

**MON 7****New nanostructures based on Carbon Nanotube – Graphene Compounds: Modelling of their energetic, elastic and electronic properties**Anastasia A Artyukh<sup>1</sup> P. Sorokin<sup>1</sup> L. Chernozatonskii<sup>1</sup><sup>1</sup>Institute of biochemical physics, Moscow

In this work, we considered new carbon materials: nanotube - graphene compounds. Recently, Kondo et al. prepared a composite from a nanotube structure coated by graphene ribbons. Boundaries of the nanotube(SWNT) and zigzag graphene nanoribbon (ZGNR) display high chemical activity, that's why we expect the formation of composite from them. We calculated bind energies of fragments and their compounds. The compounds display higher energy that their fragments. We calculated Young's moduli of some compounds. Its value grows with increasing number of attached nanoribbons. We studied electronic properties of considered structures by density functional theory method. The NT/ZGNR compounds display the semiconductor properties. Also we studied porous crystal which unit cell consist of (12,0) nanotube covalently bounded with four ZGNRs. The studied structure display metallic properties. The local DOS of the crystal shows that the metal part belongs only to nanotube part. The ZGNR parts are semiconductors

due to quantum confinement effect because they are bordered by sp<sup>3</sup> hybridized atoms. All studied structures have similar geometric parameters (bond lengths, bond angles etc.).

## MON 8

### Graphite fluoride and graphane: structure and layer interactions from computer simulations

Vasilii I. Artyukhov<sup>1</sup> Leonid A. Chernozatonskii<sup>1</sup>

<sup>1</sup>Institute of Biochemical Physics RAS, Moscow

Graphite monofluoride (CF)<sub>n</sub> and graphane are two very different materials from the practical point of view, but the basic chemical motifs of these materials are closely related. Unfortunately, experimental data on the structure of these materials is ambiguous ((CF)<sub>n</sub>) or scarce (graphane), and its interpretation is sometimes problematic.

We report a detailed computational study of structure of (CF)<sub>n</sub> and graphane, both as isolated layers and in a three-dimensional stacked arrangement, using nonlocal DFT to describe long-range correlation from first principles. We find strong similarities between the two materials in both conformational energetics (including a "gauche-chair" conformation not considered in previous studies) and layer stacking patterns. A molecular mechanics force field is derived for (CF)<sub>n</sub> that performs exceptionally well at reproducing the quantum chemical results.

Our quantum and classical simulations suggest that the unexpectedly small lattice parameter values of the materials may result from in-layer conformational disorder. Direct comparison of experimental and calculated atomic radial distributions for (CF)<sub>n</sub> confirms this possibility.

## MON 9

### Anisotropic macrostructures formed of single-wall carbon nanotubes

Natalia Arutyunyan<sup>1</sup> Alexander Chernov<sup>1</sup> Elena Obraztsova<sup>1</sup>

<sup>1</sup>A.M.Prokhorov General Physics Institute, Moscow

Nanotubes themselves possess a unique geometric structure that leads to anisotropy of optical properties, conductivity and other phenomena. However the majority of growth methods provides no alignment along the nanotube axis direction. Thus no anisotropy of the nanotube properties can be reproduced at the macro-scale.

The present investigation is focused on the formation of the macro-structures which are SWNTs aligned in a parallel way on substrates. In order to analyze and estimate the angular distribution of nanotubes the polarized Raman spectroscopy has been used.

The method of formation of anisotropic structures is based on the self-assembly process of the SWNT in a suspension (similar to nematics) [1]. During the liquid

evaporation, the nanotubes can be deposited on the substrate, vertically deepen into the enriched SWNT suspension. This procedure results in the formation of the SWNT parallel alignment within the scale of few mm. The polarization curves of Raman intensity for G-band and RBM are highly anisotropic. The angular nanotube distribution is less than 15 degrees.

The work is supported by RFBR and RAS research programs.

1. M.Engel et al., ACS Nano 2 (2008) 2445

## MON 10

### Characterization of nanometer scaled ferromagnetic contacts

H. Aurich<sup>1</sup> F. Freitag<sup>1</sup> A. Kleine<sup>1</sup> A. Baumgartner<sup>1</sup> J. Trbovic<sup>1</sup> C. Schönenberger<sup>1</sup>

<sup>1</sup>Nanoelectronics group, Departement of Physics, University of Basel

We investigate a series of ferromagnetic materials as electrical contacts in spin-transport devices based on carbon nanotubes and graphene. We discuss in detail the requirements of an ideal material, which essentially are good magnetic properties and reproducible electrical contact characteristics. In a three-step characterization procedure of the magnetic material we perform vibrating sample magnetometer (VSM) measurements of a thin film, followed by VSM measurements of a large ensemble ( $> 10^5$ ) of strips of the same dimensions as the intended contacts, e.g. of 200 nm width and 25 nm thickness. In the last step before the actual device fabrication we perform anisotropic magnetoresistance (AMR) measurements of a single strip. We demonstrate this characterization procedure for several permalloy (NiFe) contacts of different film thicknesses and contact widths and discuss its suitability for spin-valve devices. In addition we discuss Fe, Co, Ni and PdFe as contact materials.

## MON 11

### Towards to surface friendly selected-area diamond seeding

Oleg Babchenko<sup>1</sup> Alexander Kromka<sup>2</sup> Tibor Izak<sup>2</sup> Karel Hruska<sup>2</sup> Egor Ukraintsev<sup>2</sup> Milan Vanecek<sup>2</sup>

<sup>1</sup>Institute of Physics of the AS CR v.v.i., Prague, Czech Republic. Czech Technical University in Prague, Prague, Czech Republic

<sup>2</sup>Institute of Physics of the AS CR v.v.i., Prague, Czech Republic

Nano-crystalline diamond films are the most attractive materials with wide range of extraordinary physical, chemical and biological properties. Unfortunately, in procedures that determine a diamond pattern formations are commonly used the aggressive chemicals, which limit the number of substrate materials for applications. In the present work is reported a study of applying polymeric photo-resist OFPR for pre-treating the nucleation layer by 3 different strategies. Strategies: A) reactive ion etching, B) photo-lithographical processing with two layers of polymer and C) selective ultrasound seeding, avoids any damaging of substrate surface. The

diamond structures were realized by microwave enhanced chemical vapor deposition on all samples, but the densities of parasitic grains differ significantly. The most efficient pattern formation was obtained applying the strategies A) and B) together. After such procedure the density of residual diamond crystals was as low as 100000 particles per square centimeter. Proposed procedure omits any treatment in aggressive chemistries, is simple in use, applicable on large areas, and are fully compatible with standard semiconductor processes.

## MON 12

### **Searching for a spin-valve effect in a Ni(111)/Graphene/Ni junction.**

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<sup>1</sup>Surface and Thin Films, Zernike Institute for Advanced Materials, University of Groningen, Groningen (NL)

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Spin valve is an interesting spintronic device which uses the spin degree of freedom in addition to the charge of an electron. It is composed by two ferromagnetic layers separated by either a metallic or a thin insulating layer. Recently, spin transport in graphene was observed. Additionally, theoretical calculations have predicted an almost perfect spin filtering in a spin valve comprising of two transition ferromagnetic metal layers separated by a graphene layer. As a first step towards the aim of realizing a device, we have developed a protocol for depositing graphene layers on Ni(111) by cracking of ethylene and investigated how graphene layers can serve as template for Ni growth on top. (111) diffraction patterns prove graphene epitaxial growth on Ni(111) and show that Ni/graphene layers preserve the (111) orientation of Ni single crystal below.

## MON 13

### **Use of chemically modified CNTs improves performances of plastic actuators**

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Carbon nanotubes have electrical and mechanical properties that make them highly attractive for actuators. Whilst in a single carbon nanotube a relatively small strain of actuation can result in high stress generation, this is not so easily achieved when assembling them together due to sliding effects between individual CNTs. We have found the way to chemically increase interactions between tubes and stabilize

patches of Super-Growth Carbon Nanotubes (SG-CNTs) flakes derived from vertically aligned forests. These modified CNTs have been used for the preparation of bucky gel actuators by mixing them with an ionic liquid and a plastic binder. The overall effect is a significant enhancement of strain, efficiency and specific capacitance with respect to the gel based on pristine CNTs. Cyclic voltammetry shows that the charge transfer capability of bucky gels made from SG-CNTs is strongly enhanced by chemical modification resulting in a threefold increase of the specific capacitance (from 45 F/g to 135 F/g at 10 mV/s). Actuation tests show that the strain for all modified CNTs, even with a significantly lower amount of CNTs in the composite, is higher at every tested frequency.

**MON 14****Curvature stress induced ferroelectricity in nanowires**Robert Blinc

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It is shown that a ferroelectric phase with a non-zero spontaneous polarization can be induced in otherwise non-ferroelectric nanowires with a radius 1-10 nm even at room temperature. Ferroelectricity is here due to strong enough surface stresses present under the curved surface of nanowires. This effect should be observable in simple binary and other non-ferroelectric oxides as well as in properly doped carbon nanowires. The same mechanism could lead in paramagnetic materials to new high-temperature nano-magnetoelectrics. Recent experiments, where a spontaneous polarization and a magnetic field dependent dielectric constant was observed in erbium oxide nanoparticles, support this model.

**MON 15****Solubilization and Individualization of Carbon Nanotubes by Noncovalent Functionalization with Switchable Molecules**Pascal Bluemmel<sup>1</sup> Antonio Setaro<sup>1</sup> Christopher Popeney<sup>2</sup> Chandan Maity<sup>3</sup> Rainer Haag<sup>2</sup> Stefan Hecht<sup>3</sup> Stephanie Reich<sup>1</sup><sup>1</sup>Fachbereich Physik, Freie Universität, Berlin<sup>2</sup>Institut für Chemie und Biochemie, Freie Universität, Berlin<sup>3</sup>Institut für Chemie, Humboldt-Universität, Berlin

The adsorption of photo switches on individual carbon nanotubes has been used by various groups to produce field effect transistors with tunable U/I characteristics [1-2]. Functionalized tubes also have potential use for color detection as well as nanoelectronic applications.

To investigate the optical and dynamic properties of switch functionalized nanotubes and to open a path towards potential industrial use, it is necessary to obtain solutions of large quantities of functionalized, individualized tubes.

We will present our research on the solubilization and individualization of car-



bon nanotubes in THF using spiropyran and azobenzene molecules with pyrene head groups as anchors for noncovalent adsorption. We found that using pyrene-spiropyran we were able to obtain dispersions of carbon nanotubes that remained stable over several days. The individualization was verified by photoluminescence measurements. We monitored the photoisomerization by measuring the sample absorbance. We will discuss different approaches of nanotube solubilization with switchable molecules.

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[2] Simmons et al. - Physical Review Letters 98(8), 086802 (2007).

## MON 16

### Raman diagnostics of multi-wall carbon nanotubes with a small shell number

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Raman spectroscopy is one of the most informative techniques for diagnostics of single-wall carbon nanotubes. It is not so implicit in studies of multi-wall carbon nanotubes (MWNTs). One of the reasons is a difficulty to estimate the exact shell number. In this work we studied two types of MWNTs with a small controllable shell number. In the pristine nanotubes the shell number was controlled by a catalyst composition. Then the pristine samples were heated up to various temperatures (2200, 2600, 2800 C). HRTEM images of all samples have been obtained. The shell number has been estimated (for thin 3-7, thick 6-15 shells). The Raman spectra of MWNT have been registered in three spectral regions: D, G and D'-bands. A ratio of intensities  $I_{2D}/I_D$  has demonstrated almost a linear dependence on the nanotube diameter. After the heating, D (disorder induced) Raman band showed a substantial decrease in intensity. So, the Raman spectroscopy has shown its sensitivity to the structure of MWNTs of small diameter, grown with a compositional catalyst and treated afterwards with a vacuum heating. The work was supported by Grant MK-761.2009.2, RFBR 09-02-01051 and project of the RSM 02.523.12.3020

**MON 17****Physicochemical characterization of the Pd/MWCNTs catalysts for fuel cell applications**

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The multiwall carbon nanotubes (MWCNTs) supported Pd catalyst, prepared by the polyol method and reduced in 5% of H<sub>2</sub> in Ar atmosphere at temperature of 200°C, exhibits high activity in electrooxidation of formic acid, whereas, the same catalyst calcinated at temperature of 250°C in 100% of Ar is inactive. The structural and chemical properties of the catalyst surface after reducing and calcination treatments were investigated using the electron spectroscopy methods, i.e. XPS, XAES, EPES, EELS and REELS. The catalytically inactive sample indicated the larger oxygen and sp<sup>2</sup> carbon-type contents. The content of carbon and oxygen groups, i.e. carboxyl, carbonyl and acid anhydride forms was quantitatively determined for both catalysts. The analysis of XPS Pd 3d<sub>5/2</sub> binding energies (BE) indicated for active and inactive catalysts three chemical Pd forms: Pd metallic crystallites, PdO and Pd in organic matrix. For the active catalyst, larger content of metallic Pd crystallites and smaller content of PdO were observed. The differences in activity of investigated catalyst after reduction and calcination processes are discussed with respect to the observed surface changes.

**MON 18****Enhanced hydorstability and detailed characterization of carbon nanotubes filled with MOF-5 and Pd functionalized carbon nanotubes filled with MOF-5**

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Metal-organic frameworks (MOFs) are a rapidly growing class of microporous materials. Various MOFs with tailored nanoporosities have recently been developed as potential storage media for hydrogen. However, wider applications have been limited because even atmospheric moisture levels cause MOF instability, and unexpectedly low hydrogen storage capacity, at 298 K. To overcome these problems, we synthesized CNT filled with MOF-5 (MOF@CNT) (as a reference sample) and Pd nanoparticles functionalized acid-treated carbon nanotubes (Pd@CNT) being filled with MOF-5(MOF-Pd@CNT). In a successful synthesis, well-dispersed Pd@CNT

in dimethylformamide (DMF) were mixed with a DMF solution of zinc nitrate tetrahydrate and terephthalic acid. The MOF@CNT and MOF-Pd@CNT had the same crystal structure and morphology as those of virgin MOF-5, but exhibited and much improved hydrostability in the presence of ambient moisture. Next step is concentrated on the H<sub>2</sub> storage capability investigation of the samples.

## MON 19

### A systematic study of optical and Raman spectra of peapod-based DWNTs

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We followed the preparation of DWNTs from fullerene peapods by optical and Raman spectroscopy in a systematic way. 1.4 nm average diameter nanotubes were opened by oxidation in air, and filled by sublimation with C<sub>60</sub>. The peapods were converted to DWNTs by annealing at 1250 C. As a reference, a control sample was also prepared, where the same sequence of treatments was applied but no C<sub>60</sub> was added. We monitored each preparation step from pristine nanotubes to DWNTs by Raman and wide range FIR-UV transmission spectroscopy.

In the Raman spectra of peapods, the radial breathing modes of the nanotubes show clear changes. Beside the shifts that were reported earlier, the linewidths of the components become smaller. When the tubes are converted to DWNTs, the RBMs of the host tubes recover their original shape.

In the optical spectra, interband transitions of DWNTs show less structure than SWNTs, probably because of broadening of the components. We do not see either significant increase or broadening of the Drude peak, indicating that there is little charge transfer between the outer and the inner tube.

## MON 20

### Investigation of fullerene encapsulation in carbon nanotubes using a complex approach based on vibrational spectroscopy

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For carbon nanotubes filled with fullerenes (“peapods”), it is a key issue to find an analytical method that distinguishes the molecules inside the nanotube from those adsorbed on its surface. High-resolution transmission electron microscopy (HRTEM) detects both encapsulated and adsorbed molecules which are large enough

(e.g. fullerenes), but being a local method, it cannot be applied to large amounts of sample. In Raman spectroscopy, the empirical rules for line shifts and splitting are nanotube-type dependent and often ambiguous. We prepared C<sub>60</sub> peapods by nano-extraction using supercritical CO<sub>2</sub> as a solvent, and subsequently removed the adsorbed fullerene molecules by washing the sample with toluene. We analyzed the samples by the combination of HRTEM, Raman and infrared ATR spectroscopy. Although the TEM images proved that the nanotubes were filled with fullerenes, we did not observe any shift in the C<sub>60</sub>'s A<sub>g</sub>(2) Raman mode at 1463 cm<sup>-1</sup> compared to C<sub>60</sub> crystals, or change on washing. ATR spectra, on the other hand, were found to detect only the adsorbed molecules. The explanation lies probably in the surface sensitivity of the latter method.

**MON 21****Microphotoluminescence and photoconductivity of multi-wall and single-wall Boron-Nitride nanotubes**

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Boron-Nitride (BN) nanotubes (NT) present a large potential for the development of UV light sources, thanks to strong emission bands between 200 nm and 380 nm under an excitation at 193 nm. Very few studies exist on the optical properties of BNNT, because of the paucity of the samples and the specific equipment required for experiments in this spectral range. Previous studies have already related the photoluminescence properties of multi-wall(MW) BNNT, as well as hBN and have demonstrated the importance of the excitonic effects in these phenomena. However the study of single-wall(SW) BNNT is more delicate and has required the specific development of a microphotoluminescence (mPL) experimental set up for which a special care has been taken to increase the spatial resolution and the signal-to-noise ratio of the detection. By this way, recent advances corresponding to the mPL of MWBNNT and SWBNNT are presented. Complementary to these mPL experiments, an original method to study the photoconductivity of SWBNNT, MWBNNT and hBN is proposed, in order to measure their band gap energy and eventually to highlight a "fine structure" in the band gap, which can be correlated to the mPL results.

**MON 22****Polarised Raman measurements of carotene in photosystem II and  $\beta$ -carotene encapsulated in SWNTs**

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Oxygenic photosynthesis, one of the most important mechanisms for dissipation of energy in plants and some bacteria, takes place in photosystem I and II and begins with the conversion of sunlight into a separation of charge. In photosystem II, two types of pigment molecules are located in different orientations: chlorophyll and  $\beta$ -carotene.

Here we present polarised Raman measurements of  $\beta$ -carotene encapsulated in SWNTs [1]. For the carotene inside the tubes, we can assume that their orientation is along the tube axis. We compare these measurements, where the molecules have well defined orientation, with the  $\beta$ -carotene spectra in crystals of photosystem II, where several carotene molecules with different orientation contribute to the Raman signal [2]. We discuss the results with respect to the interaction of the carotene molecules with their different environments.

[1] K. Yanagi, Y. Miyata and H. Kataura, *Adv. Mater.*, **18**, 437 – 441 (2006)

[2] K. Brose et al., *Phys. Status Solidi B*, **246**, 2813 – 2816 (2009)

**MON 23****Spin coherence times of metallofullerenes**

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The electron spin associated with atomic nitrogen encapsulated in fullerenes (N@C<sub>60</sub>) has been shown to possess coherence times up to several hundred microseconds [1]. In contrast, metal ions encased in a similar way, termed metallofullerenes, have not shown particularly long coherence times ( $< 1.5 \mu\text{s}$ ) [2,3], attributed to the much greater spin density on the fullerene cage. Here, we report spin relaxation ( $T_{1e}$ ) and

coherence times ( $T_{2e}$ ) of Y, Sc and La@C<sub>82</sub> in various solvents using pulsed electron paramagnetic resonance (EPR). The temperature dependence of these times indicates several different contributions to spin relaxation: arising from vibrational modes of the metal atoms in the C<sub>82</sub> cage, and nuclear spins in the solvent environment. In a deuterated o-terphenyl solvent, we report  $T_{2e}$  times greater than 200  $\mu$ s for all metallofullerenes at 10K, making metallofullerenes of increasing interest for areas such as spin labelling, spintronics and quantum computing.

- [1] Morton et al., Phys. Rev. B, 2007, 76, 85418
- [2] Knorr et al., Appl. Phys. A, 1998, 66, 257-264
- [3] Okabe et al., Chem. Phys. Lett., 1995, 235, 564-569

#### MON 24

##### **Development of graphene from graphite fluoride C<sub>2</sub>F and investigation its sensor performance**

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Graphite fluoride with a composition close to C<sub>2</sub>F has been synthesized by fluorination of highly oriented pyrolytic graphite using a gaseous mixture of BrF<sub>3</sub> and Br<sub>2</sub> at room temperature. Electronic structure of graphite fluoride was probed using near edge x-ray absorption fine structure (NEXAFS) spectroscopy. The spectra measured near the C K- and F K-edges showed retention of delocalized  $\pi^*$ -system in graphite fluoride C<sub>2</sub>F. The probable distribution of fluorine atoms on the graphite surface was determined from quantum-chemical modeling of the NEXAFS spectra. The fluorine atoms were found to be easily detached from the C<sub>2</sub>F surface under electron beam irradiation in a high vacuum. The electronic state of the restored surface is similar to that of the graphitic one. The conductivity of the graphene-like layer developed on the C<sub>2</sub>F substrate is dependent on the nature of adsorbing gas (NH<sub>3</sub>, NO<sub>2</sub>, Cl<sub>2</sub>). Thus, the graphite fluoride with the restored surface can be used as a gas sensor.

**MON 25****Non-Equilibrium Phonons and Negative Differential Resistance in Individual, Suspended, Single-Walled Carbon Nanotube FETs**

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I will present Raman spectra and electrical transport data from pristine single-walled carbon nanotube field effect transistors observed under applied gate and bias voltages. By applying a gate voltage, the high-bias conductance can be switched dramatically between linear (Ohmic) behavior and non-linear NDR behavior [1]. Phonon populations are observed to be in thermal equilibrium under Ohmic conditions, but switch to non-equilibrium under NDR conditions. A typical Landauer transport model assuming zero band gap is found to be inadequate to describe the experimental data. A mechanism and model describing the experimental data is presented, which explains the observed phenomena. This constitutes a method for dynamically controlling the phonon populations and differential resistance in carbon nanotubes under high bias, which has important implications for circuit interconnect design using carbon nanotubes.

1. A.W. Bushmaker, V.V. Deshpande, S. Hsieh, M.W. Bockrath, and S.B. Cronin, "Gate Voltage Controlled Non-Equilibrium and Non-Ohmic Behavior in Suspended Carbon Nanotubes." Nano Letters, 9, 2862 (2009).

**MON 26****Atomically precise bottom-up fabrication of porous graphene and graphene nanoribbons**

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The promising prospects for graphene-based devices derive from several remarkable properties that make graphene attractive for use in nanoscale devices. However, graphene is semimetallic and thus not directly suitable for most electronic or optoelectronic devices, which require a semiconductor. This can be overcome by structuring graphene via lithographic techniques or chemical treatment experi-

mentally on the nanometer scale with the possibility to create specific and tunable bandgaps suitable for room-temperature applications, but both methods are limited with respect to their ultimate resolution and precision. Here, we demonstrate the bottom-up fabrication of surface-supported porous graphene and graphene nanoribbons with atomic accuracy, following a simple and straightforward surface-chemical route. Described as porous graphene, a sp<sup>2</sup>-hybridized 2D polymer with a controlled pore structure was assembled by the two-dimensional polymerization of a halogen-functionalized macrocycle. Based on a significant extension of this approach, we further present the synthesis of graphene nanoribbons with atomically defined edge periphery, width and topology.

**MON 27****Wedging Transfer: A New Technique for Transferring Graphene and Nanostructures**

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We demonstrate a versatile one-step method for transferring hydrophobic patterns or nanostructures onto surfaces of various shapes and compositions. The transfer occurs through water intercalation between a hydrophilic substrate and a hydrophobic thin polymeric coating, molded around an object of interest (think of graphene, CNT's, quantum dots). Since water wets hydrophilic surfaces, a thin layer of water intercalates underneath the hydrophobic polymer coating and progressively invades until the whole film is lifted-off (i.e. wedged). At that stage the object has been transferred to the hydrophobic polymeric film, the latter being stretched flat by the surface tension of the air-water interface. This setup allows the polymeric film to be precisely handled and aligned and to be further transferred onto a target substrate by removal of the water. The versatility of this transfer technique goes beyond so far existing transfer methods. We show that graphene and patterned metallic nanostructures can be precisely aligned even on top of curved objects such as microspheres ( $\sim 10$   $\mu$ m). The method is simple to use, fast, and does not require specific skills or equipment.

**MON 28****Giant inelastic tunneling in epitaxial graphene mediated by localized states**

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Epitaxial graphene on SiC is a very promising material for electronic applications. Despite of technological promises of this material, charge carrier mobility of epitaxial graphene on Si(0001) is orders of magnitude smaller than the best mobility



observed in mechanically exfoliated graphene. This striking difference is most probably caused by unknown interaction with the underlying graphene/SiC interface layer.

Here we present a detailed study of local electronic structures of nanometer-sized patches of epitaxial graphene and its interface layer with SiC(0001) by atomically resolved scanning tunneling microscopy and spectroscopy. Localized states belonging to the interface layer of a graphene/SiC system have been found to essentially influence the electronic structure of graphene. Giant enhancement of inelastic tunneling, reaching 50% of the total tunneling current, has been observed at the localized states on a nanometer-sized graphene monolayer surrounded by defects. Giant local asymmetric inelastic phonon signatures of graphene are explained on the base of an inelastic electron tunneling model using nonequilibrium Green's function formalism.

## MON 29

### Universal mechanical response in radially compressed single-wall carbon nanotubes

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Interesting phenomena, such as metal-insulator transitions, may arise when SWNT are radially compressed by a tip of an AFM[1]. In the present work, we report [2] the observation of a universal-type behavior of the mechanical response of SWNTs to radial compression. Specifically, we find that the quantity  $Fd^{3/2}(2R)^{-1/2}$ , where  $F$  is the force applied by an AFM tip (with radius  $R$ ) and  $d$  is the SWNT diameter, is a universal function of the compressive strain. Such universality is reproduced analytically in a model where the graphene bending modulus is the only fitting parameter. The application of the same model to the radial Young modulus  $E_r$  leads to a further universal-type behavior that explains the large variations of the SWNTs  $E_r$  reported in the literature. Finally, the implications of such universal-type behavior to nanometrology are briefly discussed.

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[2] A. P. M. Barboza, H. Chacham and B.R.A. Neves, Phys. Rev. Lett. 102, 025501 (2009).

**MON 30****Optical absorption and photoluminescence of narrow diameter fractions of single-wall carbon nanotubes**Alexander Chernov<sup>1</sup> Elena Obraztsova<sup>1</sup><sup>1</sup>GPI RAS, Moscow

Last years a few promising techniques for separation of single-wall carbon nanotubes (SWNTs) onto fractions with a narrow diameter distribution (including semiconducting and metallic fractions) have been developed. A high purity ( > 97 weight % for metallic SWNTs and > 95% for semiconducting SWNTs) separation can be achieved [1,2]. The pure semiconducting nanotubes are very promising for nanotube-based transistors. The pure metallic tubes are used for ITO replacement. In this work a density gradient centrifugation (DGU) has been used for separation of SWNTs. Variation of DGU parameters resulted in extraction of metallic and semiconducting SWNT fractions with different diameter distributions. The obtained fractions have been used for preparation of SWNT films deposited on quartz substrates. The liquid fractions and films have been investigated by UV-VIS-NIR optical absorption spectroscopy and photoluminescence.

The work was supported by RFBR-09-02-01051 and RFBR-09-02-91076 projects.

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[2] A.I. Chernov, E.D. Obraztsova, PSSB 246 (2009), 2477-2481.

**MON 31****Single-walled Carbon Nanotube Growth in a Wide Temperature Range**Shohei Chiashi<sup>1</sup> Taiki Inoue<sup>1</sup> Hiroto Okabe<sup>1</sup> Junichiro Shiomi<sup>1</sup> Shigeo Maruyama<sup>1</sup><sup>1</sup>The University of Tokyo, Tokyo

It is important to understand the growth mechanism of single-walled carbon nanotubes (SWNTs) and control their structure in their growth stage. Especially, the growth at low temperature is inevitable for the device applications of SWNTs. In the present study, we performed SWNT growth by a catalytic CVD method in a wide temperature range. Ethanol and dimethyl ether (DME) were used as the carbon source and Co/Mo metal particles deposited on silicon substrates were used as the catalyst. The CVD temperature ranged from 400 to 900 degree C. The optimum ethanol gas pressure was strongly depended on the CVD temperature. When the CVD temperature decreased, the optimum ethanol pressure decreased. Moreover, at low ethanol gas pressure (0.01 Pa), SWNTs were synthesized only at low CVD temperature (500 C). It indicated that the balance between the growth rate of SWNTs and the injection speed of carbon atoms to the catalyst was important. On the other hand, the gas pressure and temperature ranges were quite narrow in the case of DME. DME thermally decomposed more efficiently than ethanol during CVD process, which was one of the reasons why the growth conditions were limited.

**MON 32****Size dependence of the magnetic response of graphene flakes – an electron spin resonance study**

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There have been many theoretical proposals for the magnetic behavior of graphene, like the one where ferromagnetism could originate from the interaction of localized spins along the edges of the sample, but systematic experimental studies are missing. We have investigated series of samples of graphene obtained from chemical reduction of graphene oxide sheets with different ‘edge contributions’. Each batch had a different size distribution of graphene flakes due to the changes in the oxidation/reduction parameters. Electron Spin Resonance (ESR) experiments in a broad temperature range (4-300 K) show that the magnetic response varies with the size of the graphene flakes. These results show that the magnetic behavior of graphene can be tailored which might be of interest in future electronic applications.

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**MON 33****Electric field-tunable bandgap and giant infrared phonon resonance in bilayer graphene**

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Infrared spectroscopy is a powerful technique to study the effect of electrostatic gating on the band structure and lattice dynamics of stacked graphene layers. We measured infrared reflectivity spectra of bottom-gated exfoliated bilayer graphene. One of the most striking features that we observed is a giant anomalous growth and softening of the  $E_u$  in-plane mode (0.2 eV) as a function of gate voltage. The phonon peak features a pronounced Fano-like asymmetry, which is a signature of a strong coupling of this mode to a continuum of interband transitions [1]. This effect opens up a new window to studying electron-phonon interaction in graphene-like

materials. Another important result of our study is the extraction of the gate voltage dependent bandgap and determination of the parameters of the tight-binding Slonzewski-Weiss- McClure model [2]. We demonstrate an important influence of electrostatic self-screening on the value of the bandgap.

[1] A. B. Kuzmenko *et al.*, Phys. Rev. Lett. **103** 116804 (2009).

[2] A. B. Kuzmenko *et al.*, Phys. Rev. B **80** 165406 (2009).

### MON 34

#### Cooper pair splitter realized in a two-quantum-dot Y-junction

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An important step towards the realization of solid state based quantum computer is the demonstration of entangled spatially separated electrons. Cooper-pairs of superconductors are a natural source of spin entangled electrons, the separation of these electron pairs is the underlying concept of several theoretical proposals.

In this work [1] we present the first experimental realization of a tunable Cooper Pair Splitter. The device contains a superconducting electrode coupled to two quantum dots, which is fabricated based on InAs Nanowire. In a superconducting beam splitter configuration two basic processes can happen with a Cooper-pair: the two electrons either split up into the two arms of the beam splitter or they leave the device in the same arm. The charging energy strongly suppresses to put two electrons on the same quantum dot, therefore implementing quantum dots into the arms of the beam splitter serves as a filter for the desired splitting process. Performing non-local transport measurements on such devices, we have demonstrated the Cooper-pair splitting process.

[1] L. Hofstetter, S. Csonka *et. al.*, Nature **461**, 960 (2009).

**MON 35****Symmetry of zinc-oxide nanostructures**Milan Damnjanovic<sup>1</sup> Ivanka Milosevic<sup>1</sup><sup>1</sup>NanoLab, Faculty of Physics, University of Belgrade, Belgrade

Nanostructured ZnO crystals took a great attention due to their electro-optical and mechanical properties, which have potentially wide applicability as these materials are both bio-safe and bio-compatible. Therefore, a number of growth techniques is developed, resulting in a variety of nanostructures, most of them being quasi one-dimensional (nanorods, nanotubes and nanosprings). Recently, classification of all theoretically possible conformations of this type is performed with help of their line group symmetry.

Symmetry groups of these nanowires enable to reduce the number of independent degrees of freedom, which is essential for efficient density functional (or density functional tight-binding) relaxation necessary to single out stable ones. After this, their properties could be examined. It turns out that all the mentioned structures are semiconducting, but the gap varies a lot. Also, piezoelectric properties depend strongly on the type of structure, as well as Raman and optical spectra.

**MON 36****Optical Properties and Electronic Structure of (6,5)/(6,4) Single Wall Carbon Nanotubes**Katrien De-Blauwe<sup>1</sup> Paola Ayala<sup>1</sup> Christian Kramberger<sup>1</sup> Ferenc Simon<sup>1</sup> Hans Kuzmany<sup>1</sup> Thomas Pichler<sup>1</sup> Hide Shiozawa<sup>2</sup> P. Hoffmann<sup>3</sup> Yasumitsu Miyata<sup>4</sup> Hiromichi Kataura<sup>5</sup><sup>1</sup>Dept. of Physics, University of Vienna, Wien<sup>2</sup>Surrey University, UK<sup>3</sup>Bessy II, Germany<sup>4</sup>Nagoya University, Japan<sup>5</sup>AIST, Japan

Due to the growing number of applications of small diameter Single Wall Carbon Nanotubes (SWCNTs) in opto-electronics and biological imaging, there is a strong need for better understanding their electronic properties. This presentation reports on detailed analysis of electronic structure of (6,5)/(6,4) nanotubes. First distribution and relative fraction of the two constituents are elucidated using optical, luminescence and resonance Raman spectroscopy. Details of resonance will be compared to complementary Raman response of (6,5),(6,4) inner tubes in DWCNT grown from C60 and ferrocene precursors with special emphasis to influence of different Van der Waals interactions. Secondly we will present detailed valence and conduction band response of these narrow diameter tubes using x-ray absorption and photoemission as probes. For thick diameter tubes results of these measurements allow direct comparison to tight binding and ab-initio calculations.

For narrow diameter tubes these calculations are influenced by curvature effects giving rise to modified band structure and excitation spectrum. We compare observed electronic structure and optical properties to recent ab-initio calculations

**MON 37****n-Type Doping Effect of Single Walled Carbon Nanotubes with Aromatic Amines.**

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We investigated the chemical doping of SWNTs networks by a treatment with aromatic amines. Adsorption and intercalation of amine molecules in bundled SWNTs leads to the typical n-type doping observed already for alkali metals. The electron donation to SWNTs is demonstrated by the XPS spectra, where the carbon C 1s peak observed at 284.4 eV for the sp<sup>2</sup> carbon in pristine sample is shifted by 0.4 eV to higher binding energy upon chemical treatment. The development of a Breit-Wigner-Fano (BWF) component on the lower energy side of the G- mode in the Raman spectrum as well as the shift of the G+ to lower frequency provides an evidence of the charge accumulation in the nanotube network and the Fermi level shift. The spectroscopic changes are accompanied by the modification of the SWNTs electrical properties. Reduction of electrical conductivity is an indication for the electron transfer to the naturally p-type doped semiconducting tubes. From the two selected n-type dopants, the tetramethyl-p-phenylene-diamine, shows stronger changes in the XPS and the Raman spectrum than the tetramethylpyrazine, where the two nitrogen atoms are involved in the electron delocalized pi system.

**MON 38****Study of Diamond-like Nanostructures on the Surface of Carbon Fiber by Combined Spectroscopy**

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<sup>1</sup>Dora Texas Corp, Rice university, houston

New nano structures were grown on the surface of carbon fiber (CF) using two methods CO<sub>2</sub>-laser radiation and direct thermal heat in carbon-content gas environment. A correlation was estimated between the size of these particles and the temperature of growing process. Both regular and high resolution Raman spectroscopy was used to determine the nature of the new nano structures. New combination scattering line was discovered after laser radiation of the surface of CF. The new line around 1330cm<sup>-1</sup> can be responsible of the creation of the new diamond-like nano structure. The size of the new nano structures were estimated and found to be in the range of 10 nm. The new diamond-like nano particles can provide better heat transfer and higher strength of composite materials on base of CF .

**MON 39****Growth at the Rim of a Carbon Nanotube - Influencing the Chirality**Heiko Dumlich<sup>1</sup> Stephanie Reich<sup>1</sup><sup>1</sup>Fachbereich Physik, Freie Universität Berlin, 14195 Berlin, Germany

The control of chirality in the carbon nanotube growth was predicted to depend on the nucleation phase of the cap of the carbon nanotube by Reich et al.[1]. Ding et al.[2] suggested that not only the nucleation phase contains a chirality dependence, but it is inhabited in the growth process as well. Following this idea we developed notations to study the rim of carbon nanotubes. With the help of these notations a detailed study of the addition of  $C_2$  at the rim of carbon nanotubes was conducted. We show that an influence on the growth speed can be derived. Also an influence on the chirality distribution can be observed. Our notations and ideas can also be applied to graphene nanoribbons.

[1] S. Reich, L. Li, and J. Robertson, Phys. Rev. B 72, 165423 (2005).

[2] F. Ding, A.R. Harutyunyan, and B. I. Yakobson, PNAS 106, 2506 (2009).

**MON 40****Multi-walled carbon nanotubes with ppm level impurities**Vladimir L Kuznetsov<sup>1</sup> Karina V Elumeeva<sup>1</sup> Arcady V Ischenko<sup>2</sup> Natalya Yu.-Beylina<sup>3</sup> Andrey A Stepashkin<sup>3</sup> Sergey I Moseenkov<sup>1</sup> Anatoly I Romanenko<sup>4</sup> Olga B Anikeeva<sup>4</sup> Eugene N Tkachev<sup>5</sup><sup>1</sup>Boreskov Institute of Catalysis SB RAS, Lavrentiev ave. 5, 630090, Novosibirsk, Russia<sup>2</sup>Novosibirsk State University, Pirogova ave. 2, 630090, Novosibirsk<sup>3</sup>FGUP "NII Graphite", Electrodnaya 2, 111141, Moscow, Russia<sup>4</sup>Nikolaev Institute of Inorganic Chemistry, Lavrentiev ave. 3, 630090, Novosibirsk, Russia<sup>5</sup>Novosibirsk State Technical University, K. Marx ave. 20, 630092, Novosibirsk, Russia

High temperature treatments are traditionally used to produce high quality graphite and graphite based materials. Several groups have investigated purification and structural annealing of multiwalled carbon nanotubes (MWNT) at graphitization temperatures (1500-3000°C) with production of 99.9 percent purity products. Here MWNT of different average diameters with ppm level purity were produced by a low temperature  $C_2H_4$  pyrolysis on Fe-Co type catalysts combined with forthcoming graphitization at 2200-2800°C in argon flow. Annealed nanotubes were characterized with X-ray fluorescent analysis, BET surface measurements, HR TEM, XRD, DTA analysis, Raman spectroscopy and measurements of temperature and magnetic field dependences of conductivity. The graphitization of MWNT results in removal of residual metal catalyst and impurities, reduce the wall defects, enhance the NT graphitization and closure of NT tips. Mention that extent of these effects

depends on MWNT diameters. The mechanism of MWNT graphitization is discussed. The graphitization is initiated by a significant thermal displacement and diffusion of carbon atoms at temperatures higher the Debye temperature.

**MON 41****One Pot Exfoliation and Chemical Functionalization Sequence Yielding Covalently Derivatized Graphene**

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Graphene has been attracting great interest throughout the communities of physicists, chemists and material sciences since 2004. Commonly these sheets composed of a single layer of hexagonally arranged carbon atoms (SLG) are produced by micromechanical cleavage of graphite, epitaxial growth, harsh oxidation or ultrasound assisted surfactant solution processing. We developed a solution based reaction sequence which does not require destructive oxidative treatment using in situ generated intercalated and thus activated graphite. The formation of the graphite intercalation compound (GIC) reduces the van der Waals interaction between the individual graphene sheets facilitating the exfoliation by chemical treatment with highly reactive aryl diazonium salts. The entropy gain and formation of aryl radicals gives rise to functionalized SLG. Characterization of the intermediate and the product were carried out by AFM, optical microscopy and micro Raman spectroscopy. Results from Raman spectroscopy prove the presence of the GIC by characteristic G-band splitting, functionalization by increasing D-band intensity and monolayer character of the product by the 2D-band lineshape and intensity.

**MON 42****Growth of vertically aligned carbon nanotubes by using oxidising catalyst pre-treatments**

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We report the use of oxidising pre-treatments to grow vertically-aligned carbon nanotubes (VACNTs) on Ni-, Co-, or Fe-coated silica. X-ray photoemission spectroscopy reveals that, during catalyst formation, oxygen induces a solid-solid reaction at the catalyst-support interface to form metal silicates. These compounds reflect strong catalyst-support interactions since promote metal restructuring into small, high-density nanoparticles of reduced mobility, which nucleate VACNTs. We explain in detail how the catalyst is formed and its influence on CNT growth. Fur-



ther, we observe a switch from tip to base growth as the interactions strengthen, which we discuss in terms of nucleation density and growth conditions. This work demonstrates that engineering the catalyst-support interaction at the interface is vital for controlling surface growth CNTs or other nanostructures.

**MON 43****STRUCTURAL MODIFICATION OF INITIAL AND FLUORINATED SINGLE-WALL CARBON NANOTUBES UNDER ARGON ION IRRADIATION**

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The effect of argon ion irradiation on the initial and fluorinated SWCNTs have been studied using TEM, Raman spectroscopy and in situ XPS and XANES measurements. SWCNTs were synthesized by catalytic chemical vapor deposition method and fluorination was performed by gaseous BrF<sub>3</sub> at room temperature. The samples of initial and fluorinated SWCNTs were placed in vacuum chamber and exposure to radiation of argon ions with 1 keV kinetic energy. TEM images indicated that the Ar ion irradiation did not destroy tubular structure of initial and fluorinated SWCNTs but shortened them and creates new structural defects. XPS data showed that argon ion irradiation led to defluorination of fluorinated SWCNTs and initiation of defect sates into nanotube's cages. The nature and quantity of post-irradiation defects in the fluorinated SWCNTs were similar to defects in the initial nanotubes. Raman spectroscopy confirmed this conclusion and pointed to slight differences in the radial-breathing mode region. Information about density of unoccupied electron states before and after argon ion irradiation of fluorinated SWCNTs were received from the XANES spectra.

**MON 44****Catalytic synthesis of coiled carbon nanotubes over asymmetric particles**

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Coiled carbon nanotubes would on one hand have a toughness resembling the toughness of nanotubes more than of carbon fibers, and that on the other hand, if used in composites, they would be better anchored in their embedding matrix than straight nanotubes. Coiled carbon nanotubes can also be used as pressure or tactile sensors, electromagnetic absorbers, and nano-velcro for anchoring different component parts to each other, which might achieve a major role in nanotechnology. The object of our experiments was the production of spiral carbon nanotubes selectively. The influence of asymmetric catalytic particles prepared by various methods

was investigated on the growth of spiral carbon nanotubes under CVD conditions. Asymmetric particles were prepared by either /wet/milling or crystallization from oversaturated solution onto the surface of catalyst support or catalyst impregnation at pH 8-9. As-prepared catalysts were tested in the decomposition of acetylene at 720C. For qualitative characterization of carbon deposit on the surface, products were imaged by transmission and scanning electron microscopy (TEM,SEM). The activity of each catalyst sample was characterized by carbon yield.

**MON 45****Electron Spin Resonance of differently obtained Carbon Nantubes**

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We studied by electron spin resonance (ESR) several kinds of single wall carbon nanotubes synthesized by different methods. We have observed that ESR is a sensitive probe which allows to observe important differences between the samples of carbon nanotubes, related to their proportion of magnetic catalysts, impurities or defects. We analyzed the ESR spectra of carbon nanotubes as usual by three overlapping lines, and implemented a function to fit these, the fitting allows as to obtain the intensity, linewidth and factor g of each component line. The narrowest and asymmetric line, assigned to the conduction electrons is narrower for samples with higher purity, as expected. From the temperature evolution of ESR spectra in the range 160 K – 300 K we observe that for the asymmetric line, the signal amplitudes increases with increasing temperature following an Arrhenius law. We find the activation energy of 47 meV for CVD and laser ablation samples, whereas for the carbon nanotubes produced with a nonmagnetic Pt/Rh catalyst the amplitude thermal dependence does not follow an exponential law. The double integral of the ESR line due to itinerant spins must be proportional to the spin susceptibility. We have calculated it for the different samples, and compared with data obtained

**MON 46****Analysis of carbon nanotube chiralities obtained from a bimetallic Co-Mo catalyst**

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Single-walled carbon nanotubes (SWNTs) have potential applications in semiconductor technology since each one has an unique band gap, depending on the chiral index (n,m). However, all growth methods usually result in a wide distribution of

chiral indices (n,m). Bimetallic catalysts can narrow this distribution [1,2]. Here we grow SWNTs by a Co-Mo catalyst and measure the different chiral distributions for an array of growth parameters. A CoMo-acetate solution from Maruyama et al.[2] was used to prepare the catalyst and dip coated on a standard Si-wafer. After calcination the catalyst was heated in hydrogen to growth temperature at which growth was done for acetylene and ethanol. The temperature range was 450-750 C and the pressure range  $3 \times 10^{-3}$  to 5 mbar for both carbon sources. The grown SWNTs were characterized by multi-wavelength resonant Raman spectroscopy on the radial breathing mode with laser energies from 1.91 to 2.66 eV and the chiral indices (n,m) are assigned by a Katauraplot [3].

[1] G. Lolli et al., J. Phys. Chem. B 110, 2108 (2006).

[2] Y. H. Miyauchi et al., Chem. Phys. Lett. 387, 198 (2004).

[3] J. Maultzsch et al., Phys. Rev. B, 72, 205438 (2005)

#### MON 47

##### **Investigation of the Jahn-Teller effect in $C_{60}^-$ monoanion under high pressure by infrared spectroscopy**

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$(Ph_4P)_2IC_{60}$  is a monoanionic salt, where the  $C_{60}^-$  is well separated and provides the possibility to investigate a nearly isolated  $C_{60}^-$  ion in a very symmetrical environment. Since  $C_{60}^-$  has incompletely filled degenerate molecular orbitals in the ground and the excited electronic states, it is prone to symmetry lowering by static and dynamic distortions according to the Jahn-Teller (JT) theorem. JT distortion of the ground  $^2T_{1u}$  and excited  $^2T_{1g}$  states of  $C_{60}^-$  leads to symmetry lowering to  $D_{5d}$  or  $D_{3d}$ , resulting in a rich vibrational structure in the infrared spectrum. We present the synthesis of  $(Ph_4P)_2IC_{60}$  by electrochemical crystallization technique and first high-pressure investigations using infrared spectroscopy. At ambient conditions the dynamic JT effect is manifested in the IR spectrum and at higher pressure the static distortion stabilizes by low-symmetry perturbations. Furthermore, activation of silent odd modes owing to symmetry lowering and the even modes due to electron-phonon coupling and orientational disorder in fulleride salt are observed. We will discuss the JT dynamics of  $C_{60}^-$  monoanions under high pressure.

**MON 48****Compression Behavior of Single-layer Graphene**

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A detailed study of stress uptake and compression buckling strain in single graphene flakes of different geometries using a cantilever beam[1] is presented for the first time. The mechanical response is monitored by in-situ Raman measurements through the shift of G and 2D phonons of graphene. The sensitivities of the individual G sub-bands are higher under tension, comparable to [2], and follow linear trends in the strain range  $<1\%$ . However, the behavior under compression is governed by the critical buckling strain, which is in turn reflected in a gradual decrease of the G and 2D shift rates and substantial band broadening. The graphene flakes embedded in plastic beams exhibit remarkably high critical buckling strain values in spite of their infinitely small thicknesses. For length(l)-to-width(w) ratios  $>0.2$  the buckling strain is of the order of  $-0.5\%$  to  $-0.6\%$ . However, for  $l/w < 0.2$  no failure is observed for strains even higher than  $-0.7\%$ . Post-mortem examination of flakes failed in compression indicates the presence of permanent wrinkling.

[1] G. Tsoukleri et al. Small 5, 2397 (2009).

[2] T.M.G. Mohiuddin et al. Physical Review B 79, 205433 (2009).

**MON 49****Superconductivity enhanced conductance fluctuations in graphene nanoribbons**

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We investigate the mesoscopic disorder induced rms conductance variance  $\delta G$  in graphene nanoribbons (GNR) contacted by two superconducting (S) Ti/Al contacts. By sweeping the back-gate voltage, we observe pronounced conductance fluctuations superimposed on a linear background of the two terminal conductance  $G$ . The fluctuations  $\delta G$  depend on temperature  $T$  and source-drain voltage  $V_{sd}$ .  $\delta G$  increases with decreasing  $T$  and  $|V_{sd}|$ . When lowering  $|V_{sd}|$ , a pronounced cross-over at a voltage corresponding to the superconducting energy gap  $\Delta$  is observed. For  $|V_{sd}| < \Delta$  the fluctuations are markedly enhanced. Expressed in the conductance variance  $G_{GS}$  of one graphene-superconductor (G-S) interface, values of  $0.58e^2/h$  are obtained at the base temperature of 230 mK. The conductance variance in the sub-gap region are larger by up to a factor of 1.4-1.8 compared to the normal state. The observed strong enhancement is due to phase coherent charge transfer caused by Andreev reflection at the nanoribbon-superconductor interface.

**MON 50****Site-selective deposition of single-wall carbon nanotube film using patterned self-assembled monolayer for fabricating thin-film transistors**Shunjiro Fujii<sup>1</sup> Takeshi Tanaka<sup>1</sup> Takeo Minari<sup>2</sup> Kazuhito Tsukagoshi<sup>2</sup> Hiromichi Kataura<sup>1</sup><sup>1</sup>National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan<sup>2</sup>International Center for Materials Nanoarchitectonics, NIMS, Tsukuba, Ibaraki, Japan

Thin-film transistors (TFTs) using single-wall carbon nanotubes (SWCNTs) have attracted an attention for their possible use in flexible, high-speed, and high-current electronics. Recently, we achieved performance enhancement of solution-processed TFTs by using semiconductor-enriched SWCNTs (s-SWCNTs) separated by agarose gel. However, for a realization of integrated circuits by solution processes, appropriate fabrication technique for patterning SWCNT films in designed geometry is required. In this study, we performed a site-selective deposition of SWCNT film by patterning self-assembled monolayers (SAMs) of octadecyltrichlorosilane (OTS) on SiO<sub>2</sub>/Si surface. The OTS-SAM was patterned by UV light and then partly replaced by the SAM of 3-aminopropyltriethoxysilane (APTES). Due to the different affinity with each SAM, drop-cast s-SWCNT solution was selectively placed onto the area covered with APTES, resulting in a selectively adsorption of SWCNTs on the channel region. TFTs were fabricated

from the patterned s-SWCNT films with top-contact and back-gate geometry. Stable transfer characteristics were observed with low hysteresis. On/off current ratios were typically higher than  $10^4$ .

**MON 51****MoSI nanowires: from a one-dimensional quantum fluid to self-organised critical self-assembled networks**

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Individual transition metal chalcogenide molecular wires have extremely low coupling to the environment and to each other, which leads to extreme one-dimensional quantum electronic transport behaviour. Flexible MoS<sub>2</sub> nanowires with different diameters reveal systematic power-law dependence of the conductivity on temperature and voltage. This behaviour can be most convincingly described by tunneling through Tomonaga-Luttinger liquid segments of MoSI wire, which is in some cases modified by environmental Coulomb blockade from deformations or imperfections of the MoSI wires. Scale-free self-organized critical networks such as the human brain show resistance to failure, fast signal processing, and are of particular interest for nanoelectronics. Hybrid networks of MoSI wires and gold nanoparticles self-assemble in solution. While the length distribution of individual nanowires is log-normal, the lengths of the edges in the network deposited on a substrate show a strong power-law tail indicating scale invariance. This shows that the self-organized critical behaviour is not a property of the nanowire synthesis, but of their self-assembly into networks.

**MON 52****Alteration of the Raman G mode of single-walled carbon nanotubes under pressure**

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We have used Raman spectroscopy to probe the mechanical changes in single-walled carbon nanotubes under pressure. We expect increased pressure coefficients for the frequency of the Raman modes under pressure. The tangential Raman mode (GM) is well studied. We observed a blue shift for the frequency of this mode upon immersion in different solvents. Intermediate plateaus and different rates of shift under pressure are also observed with different solvents. We attributed these changes to the difference in the resonance conditions and their changes with pressure.

**MON 53****Screened-exchange approach for bandstructure calculations of graphene and graphene nanoribbons**Roland Gillen<sup>1</sup> John Robertson<sup>1</sup><sup>1</sup>Department of Engineering, University of Cambridge, 9 JJ Thomson Ave., Cambridge CB3 0FA, United Kingdom

Graphene-based materials are of considerable interest due to their outstanding electronic properties, such as high mobility and unique band structure. So far, density functional theory (DFT) calculations of these properties have been performed mainly within the local (spin) density approximation (L(S)DA) for the exchange and correlation interaction of electrons. However, the calculated Fermi velocity considerably differs from that obtained from photoemission experiments [1]. Similarly, the peculiar spin-localized edge state in zigzag graphene nanoribbons is described incorrectly within L(S)DA [2]. Additional GW calculations can be used to account for the weaknesses of DFT-LDA [2], but those quasi-particle corrections come with significant calculational effort. We show that use of the screened-exchange (SX) approximation for the electron exchange interaction yields results comparable to GW calculations, while being computationally less expensive.

[1] A. Bostwick, T. Ohta, T. Seyller, K. Horn, and E. Rotenberg, *Nature Physics* 3, 36 (2007)

[2] L. Yang, C-H Park, Y-W. Son, M. Cohen, and S. Louie, *Phys. Rev. Lett.* 99, 186801 (2007)

**MON 54****Topgated bilayer graphene devices for quantum confinement measurements**A.M. Goossens<sup>1</sup> K. Bolotin<sup>2</sup> F. Ghahari<sup>3</sup> L.M.K. Vandersypen<sup>1</sup><sup>1</sup>TNW / Quantum Transport, TU Delft, Delft, NL<sup>2</sup>Physics Department, Vanderbilt University, Nashville, Tennessee 37212, USA<sup>3</sup>Department of Physics, Columbia University, New York, New York 10027, USA

In our group we want to study quantum confinement in graphene nanostructures. We are especially interested in the effect of the unusual properties of graphene such as the valley degeneracy and the predicted long spin coherence lifetime. Our approach is to confine carriers by electrostatic gating, as this gives the greatest level of control and tunability. To confine carriers by electrostatic gating a bandgap is required. Unfortunately graphene does not have a bandgap intrinsically, but in bilayer graphene, a finite bandgap can be induced by a perpendicular electric field. In our experiments, the electric field was provided by two external gates. We have used this technique to test split gate devices and observe that the conductance can be suppressed in the channel between the split gates. Up to now those measurements did not show quantum confinement effects as the mean free path was shorter than the device dimensions ( $\sim 50\text{nm}$ ). Fabrication and measurement on suspended graphene devices, where mean free paths up to a  $\mu\text{m}$  have been reported, are underway.









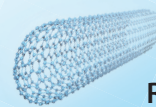
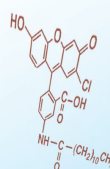
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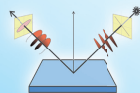


## Molekular- und Mikroanalyse



Raman  
Fluoreszenz  
Photolumineszenz  
Mikro-Röntgenfluoreszenz  
Oberflächen-Plasmonenresonanz (SPRi)

## Schichtmesstechnik



Spektroskopische Ellipsometrie  
Metrologie  
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$$\rho = r_p / r_s = \tan \psi e^{i\Delta}$$



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**HORIBA**

Tuesday, March 9

**Carbon nanotube spectroscopy; noncarbon nanowires**

- 8:30 – 9:30     **S. K. Doorn, US**  
*Raman Spectroscopy of Chirality-Enriched Single Walled Carbon Nanotubes*
- 9:30 – 10:00   **J. Sauvajol, FR**  
*Indexing of individual single-walled carbon nanotubes from Raman spectroscopy*
- 10:00 – 10:30   **Coffee break**
- 10:30 – 11:00   **W. Plank, AT**  
*Electronic structure of carbon nanotubes with ultrahigh curvature*
- 11:00 – 11:30   **P. Ayala, AT**  
*A high-energy spectroscopy viewpoint to access the electronic properties of metallicity selected functionalized SWCNT*
- 11:30 – 12:00   **K. Suenaga, JP**  
*Electron microscopy and spectroscopy of low-dimensional materials*
- 12:00 – 17:00   **Mini Workshops**
- 17:00 – 18:30   **Dinner**
- 18:30 – 19:00   **S. Hwang, KR**  
*Electronic properties of single crystalline aluminium nanowires*
- 19:00 – 19:30   **R. Kitaura, JP**  
*Fabrication of novel low-dimensional nanomaterials using carbon nanotube nanoreactors*
- 19:30 – 20:00   **B. A. Korgel, US**  
*Semiconductor Nanowires: Growth, Mechanical and Optical Properties, and a Bendable Ceramic Fabric*

Tuesday, March 9

**8:30****Raman Spectroscopy of Chirality-Enriched Single Walled Carbon Nanotubes**Stephen K. Doorn<sup>1</sup> Juan Duque<sup>1</sup> Erik Haroz<sup>2</sup> Jun Kono<sup>2</sup> Hang Chen<sup>3</sup> Anna Swan<sup>3</sup>Xiaomin Tu<sup>4</sup> Ming Zheng<sup>4</sup><sup>1</sup>Los Alamos National Laboratory<sup>2</sup>Rice University<sup>3</sup>Boston University<sup>4</sup>NIST

Recent advances in carbon nanotube separations are providing samples highly enriched by metallicity and in single chiralities. We present Raman measurements on such samples that reveal new behaviors that would be difficult to probe at the single-tube level and may be masked in mixed-chirality ensembles. Density gradient ultracentrifugation of nanotubes suspended in cosurfactant systems provide fractions enriched in armchair metallic chiralities. We present Raman characterization of the enrichment process. G-band data for spectroscopically isolated armchair chiralities show that the low frequency LO mode is absent for these structures, in contrast with recent theoretical results. We also present resonance window behavior of G-band spectra for single chirality semiconducting species. The Raman excitation profiles allow testing of different models for the Raman scattering process and reveal new evidence for the importance of non-Condon effects in the Raman response. Investigations into the behavior of the highly dispersive G-prime mode and Raman interference effects will also be presented.

**9:30****Indexing of individual single-walled carbon nanotubes from Raman spectroscopy**

Jean-Louis Sauvajol<sup>1</sup> Matthieu Paillet<sup>1</sup> Thierry Michel<sup>1</sup> Denise Nakabayashi<sup>1</sup> Vincent Jourdain<sup>1</sup> Ahmed Zahab<sup>1</sup> Janik Meyer<sup>2</sup>

<sup>1</sup>LCVN, Université Montpellier 2, Montpellier, France

<sup>2</sup>University of Ulm, Ulm, Germany

From combined Raman spectroscopy and electron diffraction studies on several freestanding single-walled carbon nanotubes (SWNT), we define Raman criteria which correlate the main features of the Raman spectrum (Radial Breathing Mode and G-modes) and the optical transitions with the structure of the SWNT under investigation. On this basis, we discuss the possibilities to determine the (n,m) indices of an individual SWNT from a single wavelength Raman experiment. We show the efficiency of this metrological approach in assigning the (n,m) structure of different individual nanotubes including all types of achiral SWNTs. Finally, the limits and the accuracy of the method are discussed.



**10:30****Electronic structure of carbon nanotubes with ultrahigh curvature**

Wolfgang Plank<sup>1</sup> Rudolf Pfeiffer<sup>1</sup> Christoph Schaman<sup>1</sup> Hans Kuzmany<sup>1</sup> Matteo Calvaresi<sup>2</sup> Francesco Zerbetto<sup>2</sup> Jannik Meyer<sup>3</sup> Ludger Wirtz<sup>4</sup>

<sup>1</sup>Faculty of Physics, University of Vienna

<sup>2</sup>Institute of Inorganic Chemistry, University of Bologna

<sup>3</sup>Electron Microscopy Group of Materials Science, University of Ulm

<sup>4</sup>Institute for electronics, Microelectronics, and Nanotechnology (CNRS UMR 8520), Lille

The electronic and the vibrational structure of carbon nanotubes with ultrahigh curvature were systematically studied by resonance Raman scattering, high resolution transmission electron microscopy (HRTEM), molecular dynamics and *ab initio* DFT calculations. The tubes were grown from ferrocene filled into commercial HiPco tubes. TEM showed partial filling of the outer tubes with inner tubes and mobility of the latter in the electron beam, and examples of fractional transformation to ultrahigh curvature tubes. The smallest analyzed tube was of chirality (5,0) and had a DFT determined diameter of 0.406 nm and a radial breathing mode frequency of 570 cm<sup>-1</sup>. For all inner tubes which had transitions in the visible spectral range transition energies and RBM frequencies were determined with a resonance width of only 45 meV. Experimentally determined transition energies revealed dramatic deviations up to several eV compared to tight-binding calculations but were in agreement with many-electron contribution corrected extended tight-binding results and with results from DFT calculations.

**11:00****A high-energy spectroscopy viewpoint to access the electronic properties of metallicity selected functionalized SWCNT**Paola Ayala<sup>1</sup> Yasumitsu Miyata<sup>2</sup> Katrien De Blauwe<sup>1</sup> Hidetsugu Shiozawa<sup>3</sup> Christian Kramberger<sup>1</sup> Philip Hoffmann<sup>4</sup> Hiromichi Kataura<sup>5</sup> Thomas Pichler<sup>1</sup><sup>1</sup>Fakultät für Physik, Universität Wien, Wien<sup>2</sup>University of Nagoya, Japan<sup>3</sup>University of Surrey, UK<sup>4</sup>BESSY II, Berlin, Germany<sup>5</sup>AIST, Japan

Accessing the unique electronic and optical properties of SWCNTs, their semiconducting or metallic behaviour and wall modifications is of great interest for further applications. Whether we are dealing with the inevitable interactions of nanotubes in a bundle or single doping defects, the energies of charge carriers and lattice vibrations are modified. For this reason, photoemission and x-ray absorption spectroscopy effectively allow analysing the details in modifications of the underlying basic correlation effects in the bonding environment. I will show our recent progress on how metallicity-sorting combined with high energy spectroscopy techniques can nicely disentangle the characteristic density of states of SWCNTs unambiguously. The various functionalization routes that allow modifying the electronic properties of SWCNT will also be discussed, providing a solid basis for a further insight into the influence of doping, chemical interactions on the electronic ground state and the transport properties of SWCNTs. We will analyze the changes in the site selective electronic structure within various types of metallicity pure SWCNTs (metallicity-sorted and functionalized).

**11:30**

**Electron microscopy and spectroscopy of low-dimensional materials**

Kazu Suenaga

Nanotube Research Center, AIST, Tsukuba

Interrupted periodicity plays a most crucial role in physical properties of low dimensional material. Electron microscopy and spectroscopy can be used to image the atomic structures and clarify the chemical states of low-dimensional materials such as defects, dopants or edge configurations. We show here how TEM based techniques can be applied to characterize the structures of low-dimensional materials such as nanotubes, nano-sheets and nanowires. The work presented here was done in collaboration with C. Jin, Z. Liu, Y. Sato, M. Koshino and K. Kobayashi. Supported by JST-CREST and Kakenhi.

**18:30****Electronic properties of single crystalline aluminium nanowires**Sungwoo Hwang<sup>1</sup> Dongmok Whang<sup>2</sup> Siegmur Roth<sup>3</sup><sup>1</sup>School of Electrical Engineering, Korea University, Seoul<sup>2</sup>SKKU Advanced Institute of Nanotechnology and School of Advanced Materials Science & Engineering, Sungkyunkwan University, Suwon<sup>3</sup>Max Planck Institute for Solid State Research, Stuttgart and School of Electrical Engineering, Korea University, Seoul

It is very difficult to fabricate metal nano-structures which are free of grain boundaries. The main effect grain boundaries have on nano-structures is the size effect on electron scattering, which increases the resistivity. Here, we present the electronic properties of bottom-up synthesized aluminium nanowires with almost perfect crystallinity. The resistivity found in these nanowires is comparable to the lowest bulk value of aluminium, and thus unprecedentedly smaller than the ones observed in similar size metal nano-structures. As an application of the ultralow resistivity, we demonstrate the microwave transmission through a single suspended nanowire with a cutoff frequency of up to 140 GHz. Finally, our single crystal nanowire shows a clear 1-dimensional superconducting transition and the coherence length is several times larger than the values of previous 1D aluminium superconductors. This is the first observation of superconductivity in a single crystal aluminium nanostructure.

**19:00****Fabrication of novel low-dimensional nanomaterials using carbon nanotube nanoreactors**Ryo Kitaura<sup>1</sup> Hisanori Shinohara<sup>1</sup><sup>1</sup>Nagoya University, Nagoya

Substantial research efforts have been devoted to fabricate metallic or semiconducting low-dimensional materials, such as nanowires, because of their fundamental interest on optical, electrical and magnetic properties, which are qualitatively different from those at larger dimensions, as well as of versatile and promising applications towards nanoelectronic and nanospintronic devices. Chemically and thermally stable one-dimensional nanospace of carbon nanotubes (CNTs) can be used as an ideal nano-sized reaction-space, therefore, we can use carbon nanotubes as nanoreactors for fabrication of novel nanomaterials. In this presentation, we focus on high-yield fabrication of atomically thin metal, metal-complexes and carbon nanowires using CNTs template and their characterization using high-resolution transmission electron microscope (HRTEM), Raman spectroscopy, photoluminescence spectroscopy and SQUID magnetometry.

Tuesday, March 9

Carbon nanotube spectroscopy; noncarbon nanowires

**19:30**

**Semiconductor Nanowires: Growth, Mechanical and Optical Properties, and a Bendable Ceramic Fabric**

Brian A Korgel

Department of Chemical Engineering, University of Texas at Austin, Austin

For the past several years, we have been developing the supercritical fluid-liquid-solid (SFSL) approach to the synthesis of semiconductor nanowires. By this method, large quantities of crystalline nanowires can be made, such as a gram of silicon or germanium nanowires in a single reaction. With these large amounts of nanowires, applications like functional non-woven fabrics, paper, absorbents and membranes, can be explored. Examples of Ge and Si nanowire paper will be presented, along with their properties, including solvent absorption properties, conductivity and photoconductivity. The mechanical properties of individual germanium nanowires and the optical properties collections of germanium nanowires dispersed in solvents or in polymers will also be presented.

**TUE 1****Competing transport channels of quantum dots within a carbon nanotube rope**

Karin Goß<sup>1</sup> Carola Meyer<sup>1</sup> Maarten R. Wegewijs<sup>2</sup> Sebastian Smerat<sup>3</sup> Claus M. Schneider<sup>1</sup>

<sup>1</sup>Institute of Solid State Research, IFF-9, Research Centre Jülich & JARA Jülich Aachen Research Alliance, Wilhelm-Johnen-Straße, 52428 Jülich, Germany

<sup>2</sup>Institute of Solid State Research, IFF-3, Research Centre Jülich & JARA Jülich Aachen Research Alliance, Wilhelm-Johnen-Straße, 52428 Jülich, Germany

<sup>3</sup>Physics Department, Arnold Sommerfeld Center for Theoretical Physics and Center for NanoScience, Ludwig-Maximilians-Universität München, 80333 München, Germany

We report quantum transport measurements on a carbon nanotube (CNT) quantum dot in the single electron tunneling regime. In addition to the standard pattern of diamonds, the stability diagram shows resonances in the Coulomb blockade regime. These resonances, however, are not caused by inelastic cotunneling processes through a single CNT. The finite slope and anomalous anti-crossings with the diamond edges suggest a different mechanism. In fact, atomic force microscopy images reveal a rather large diameter  $\sim 7$  nm, suggesting the contacted device to consist of a rope of nanotubes. In a constant interaction picture the observed transport phenomena can be understood on the basis of two nanotubes acting as coupled quantum dots. The anti-crossings of the additional resonances with the diamond edges indicate a hybridization of the states of the two dots. The difference of both the asymmetry of the tunneling and the screening properties between the two dots allows this hybridization to be probed. Additionally, the evolution of the resonances belonging to two dots can be examined by changing the magnetic field.

**TUE 2****Electron-beam irradiation induced metal-insulator transitions in carbon nanotubes**

Felix M. Haas<sup>1</sup> Christoph W. Marquardt<sup>1</sup> Simone Dehm<sup>1</sup> Frank Hennrich<sup>1</sup> Hilbert v. Löhneysen<sup>2</sup> Manfred M. Kappes<sup>3</sup> Ralph Krupke<sup>1</sup>

<sup>1</sup>Institut für Nanotechnologie, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany

<sup>2</sup>Institut für Festkörperphysik, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany

<sup>3</sup>Institut für Physikalische Chemie, Karlsruhe Institute of Technology, 76128 Karlsruhe, Germany

Recently we have reported on local electron-beam irradiation induced reversible metal-insulator transitions in metallic single-walled carbon nanotubes [1]. We have

studied now in detail the influence of the substrate thickness and the electron beam energy on the conductance suppression. We have studied the retention time of an insulating state under exposure to nitrogen and air, and fabricated samples with air-stable insulating states. On such samples, with one and two insulating segments, we have measured the temperature dependence of the conductance to test the validity of the previously proposed hopping transport model.

[1] C.W. Marquardt et al., Nano Lett. 8 (2008) 2767.

### TUE 3

#### **Targeted growth of single walled carbon nanotubes for applications in nanosensor devices**

Lukas Durrer<sup>1</sup> Matthias Muoth<sup>1</sup> Moritz Mattmann<sup>1</sup> Thomas Helbling<sup>1</sup> Kiran Chikkadi<sup>1</sup> Tobias Suss<sup>1</sup> Miro Haluska<sup>1</sup> Christofer Hierold<sup>1</sup>

<sup>1</sup>Micro and Nanosystems, D-MAVT ETH, Tannenstrasse 3, 8092 Zurich, Switzerland

Field-effect transistors utilizing individual SWNTs as conducting channels are promising functional structures for nanoelectronic systems. The production of nanotubes possessing preferential characteristics and grown directly on predefined sites of a substrate is requested for their use in pressure and gas sensors. SWNTs with a work function allowing the formation of a low Schottky barrier on the metal-nanotube interface should be grown. For this reason, the CVD growth of SWNTs from diameter selected catalyst particles is used. The catalysts are prepared by a loading of apoferritin with iron ions, followed by gradient ultracentrifugation of the ferritin solution. The SWNTs are grown at 850 C in 230 mbar CH<sub>4</sub>/H<sub>2</sub> [1]. Selected nanotubes are contacted by metal leads and the chips are further processed prior to their use in the applications. The devices are characterized by AFM, electrical measurements and SEM. By this process, ultra-small, highly sensitive, sensors, with long term stability, are prepared [2, 3].

[1] L. Durrer et al.: Nanotech. 20 (2009) 355601.

[2] M. Mattmann et al.: Appl. Phys. Lett., 94 (2009) 183502.

[3] T. Helbling et al.: Nanotech. 20 (2009) 434010.

### TUE 4

#### **Large Scale Exfoliation and Sorting of Graphene**

Tawfique Hasan<sup>1</sup> Giulia Privitera<sup>1</sup> Felice Torrisi<sup>1</sup> Francesco Bonaccorso<sup>1</sup> Andrea C. Ferrari<sup>1</sup>

<sup>1</sup>Department of Engineering, University of Cambridge, Cambridge CB3 0FA, UK

Large-scale liquid-phase exfoliation of graphite is emerging as a preferred means for mass production single and multi layer graphene flakes [1]. Here we demonstrate high yield production of graphene based on a long mild-sonication of graphite in



Sodium Deoxycholate (SDC) followed by a sedimentation based-separation in a centrifugal field [2]. Transmission Electron Microscopy (TEM) measurements show that 66% of the exfoliated flakes are monolayer. We then apply density gradient ultracentrifugation (DGU) [3] to sort the flakes by number of layers. The surfactant minimizes the repulsion between the hydrophobic surface of graphene and water, providing a variation of buoyant density dependent on flake thickness. We then show that the separation process is strongly affected by the coverage and clustering of the surfactant molecules. Finally we use these flakes to prepare transparent conducting electrodes for polymer dispersed liquid crystal (PDLC) devices. A smart window prototype will be demonstrated.

#### References

1. Y. Hernandez, et al. Nat. Nano. 3,563(2008)
2. F. Bonaccorso et al. submitted(2010)
3. Green, A. A., Hersam, A. M. Nanoletters 2009 doi 10.1021/nl902200b

#### TUE 5

##### **Photoluminescence on single-walled carbon nanotubes: A recipe to relative signal intensities**

Sebastian Heeg<sup>1</sup> Joel T. Abrahamson<sup>2</sup> Michael Strano<sup>2</sup> Stephanie Reich<sup>1</sup>

<sup>1</sup>Fachbereich Physik, Freie Universitaet Berlin, Berlin, Germany

<sup>2</sup>Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, USA

Photoluminescence excitation (PLE) is a reliable and well established spectroscopic characterization tool in carbon nanotube (CNT) research. It reveals the presence, species [2] and optical transition energies of semiconducting single-walled-CNTs in the lower diameter regime ( $d \approx 1$  nm). To study the chirality specific solubilisation efficiency of surfactants/molecules or to estimate the relative abundance of different species in a given sample, a reliable determination of the relative signal intensities is necessary. We propose a volume generated by the FWHM of PL, PLE and their mutual peak height as the appropriate measure. Besides chirality specific PL properties, this is supported by a technical analysis focussing on PL spectrometers which use an incoherent light source for excitation. In addition, we deliver a straight forward recipe to obtain the relative signal intensities as proposed above.

[1] S.M. Bachilo et al., Science, 2002

**TUE 6****Dispersion of Single Walled Carbon Nanotubes using Carbazole and Fluorene based Polymers**

Frank Hennrich<sup>1</sup> Fabien Lemasson<sup>1</sup> Timo Strunk<sup>1</sup> Sergei Lebedkin<sup>1</sup> Marcel Mayor<sup>2</sup>  
Wolfgang Wenzel<sup>1</sup> Manfred M. Kappes<sup>3</sup>

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<sup>3</sup>Institut für Physikalische Chemie, Universität Karlsruhe, D-76128 Karlsruhe, Germany

Separation techniques for single walled carbon nanotubes (SWNTs) have become an important research field over the last several years, because present synthesis methods do not allow the growth of nanotubes of one length, diameter, chirality, electronic type (metallic or semiconducting) and free of byproducts. In this current work, a variety of conjugated polymers based on carbazole and fluorene units has been synthesized and used to obtain dispersions of SWNTs in organic media after ultrasonic treatment. Moreover, these suspensions were subjected to density gradient centrifugation to obtain an enrichment of (n,m) species depending on the polymers. Evidence is provided by optical absorbance and photoluminescence excitation spectra. In addition we performed MD simulations to further confirm our experimental findings.

## References

N. Stürzl, F. Hennrich, S. Lebedkin, M. M. Kappes, J. Phys. Chem. C 113 (2009), 14628.

**TUE 7****Toxicity Study of Graphene Materials**

Lenke Horvath<sup>1</sup> Arnaud Magrez<sup>2</sup> Beat Schwaller<sup>1</sup>

<sup>1</sup>Unit of Anatomy, Department of Medicine, University of Fribourg, Switzerland

<sup>2</sup>Institute of Physics of Complex Matter, Ecole Polytechnique Fédérale de Lausanne, Switzerland

Recent advances in nanotechnology led to the development of various nanostructures especially that of carbon-based nanomaterials (CBNs) for industrial and biomedical uses. Among these, the use of graphene is foreseen in large scale applications as composite material or transparent electrodes. The forecast expansion in production of graphene-based materials makes it likely that human exposure will increase in coming years. Thus, it is primordial to also know the associated health hazards. We performed cell viability studies on different types of cultured cells exposed to graphene-oxide (GO) and its reduced form (RGO). Compared to other CBNs [1], Graphene shows low to intermediate toxicity which depends on cell type as well. Further experiments are aimed at elucidating the mechanisms of toxicity.

The work is performed in collaboration with R. S. Sundaram, M. Burghard and K. Kern. The project is supported by the Swiss National Foundation.

[1] A. Magrez, et al Nano Letters 6, 2006, 1121

## TUE 8

### **Novel Carbon Nanotubes Based Composite Materials for Solar Cells and Battery Applications**

Endre Horváth<sup>1</sup> Stephane Bungener<sup>1</sup> Arnaud Magrez<sup>1</sup>

<sup>1</sup>Institute of Physics of Complex Mater, Ecole Polytechnique Fédérale de Lausanne, Lausanne

One opportunity to improve the performances of Dye Sensitized Solar Cells (DSCs) and Lithium ion batteries is to enhance the electron transport rate within the functional materials (for instance TiO<sub>2</sub> or Li intercalation materials) of the device. Thanks to their exceptional electrical properties, the application of CNTs in such devices is the subject of intensive research. However, substantial improvement of the device performances has not yet been obtained. The preparation of high quality CNTs-functional materials composite with enhanced electrical properties is a major issue. Here, two preparation processes developed recently will be reported. First, self-standing and flexible membranes are prepared by mixing functional materials with millimeter long CNTs. Second, the preparation process involves the CNTs growth, by the equimolar C<sub>2</sub>H<sub>2</sub>-CO<sub>2</sub> reaction,[1] directly on the functional materials previously coated with metallic nanoparticles. Structural and electrical properties of these novel composite materials will be presented as well as the performances of the devices based on these composites.

[1] A.Magrez et al. Angew. Chem. Int. Ed. 46 2007 441-444.

## TUE 9

### **Decomposition of ethanol and dimethyl-ether during CVD synthesis of single-walled carbon nanotubes**

Bo Hou<sup>1</sup> Rong Xiang<sup>1</sup> Erik Einarsson<sup>1</sup> Junichiro Shiomi<sup>1</sup> Akira Miyoshi<sup>2</sup> Shigeo Maruyama<sup>1</sup>

<sup>1</sup>Department of Mechanical Engineering, The University of Tokyo, Tokyo 113-8656, Japan

<sup>2</sup>Department of Chemical System Engineering, The University of Tokyo, Tokyo 113-8656, Japan

In this study, the effect of carbon feedstock decomposition conditions on CVD (chemical vapor deposition) synthesis of SWNTs (single-walled carbon nanotubes) was investigated. Gas-phase thermal decomposition of ethanol and DME (dimethyl ether) at typical SWNT growth conditions were simulated using the chemical kinetic model. FT-IR (Fourier transform infra-red) spectroscopy was used to analyze the species resulting from ethanol and DME decomposition, confirming expected

reaction trends and primary byproducts. The molar fraction was correlated against residence time in the reactor by adjusting the flow rate, and concentration profiles of reaction species were compared to the predicted decomposition mechanism. Peak intensities were obtained and compared for C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub>, CO and H<sub>2</sub>O in the case of ethanol decomposition, and CH<sub>4</sub>, CO and CH<sub>3</sub>OH in the case of DME decomposition. In addition, synthesis of aligned SWNT arrays from various isotopes of ethanol was studied by resonance Raman spectroscopy. The results clearly show the dependence on the decomposition condition of the feedstock in CVD for synthesis of SWNTs, which is helpful in clarifying the SWNT growth mechanism.

## TUE 10

### Al-ion doped ZnO nanothin films: synthesis and characterization

A. Huczko<sup>1</sup> D.K. Madhup<sup>2</sup> D.K. Madhup<sup>3</sup> D.P. Subedi<sup>2</sup> S.P. Chimouriya<sup>2</sup>

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<sup>2</sup>Department of Physics, Kathmandu University, Dhulikhel, Nepal

<sup>3</sup>College of Biomedical Engineering and Applied Sciences, Hadigaun, Kathmandu, Nepal

The versatility of doped and un-doped ZnO in a variety of optoelectronic materials has prompted the extensive research of its morphology-selective synthesis because its properties strongly depend on its microstructure. Al-doped and un-doped ZnO nanothin films on quartz substrate were produced by ultrasonic spray pyrolysis of respected salt solutions (mole concentration of Al within 0-10 per cent). The films were characterized by SEM, XRD, AFM and UV to study its morphology and optical properties. The morphology studies (SEM) showed that ZnO thin films have uniform nanostructural character (size of crystallites well below 100 nm) with the islands of Al-related compounds the surface concentration of which steadily increases with the starting Al content. XRD measurements confirmed ZnO presence on quartz surface. The optical studies revealed that the increase in Al inside ZnO thin layer increases its band gap energy. The obtained value of band gap energy is very close to the determined oscillation energy. However, the dispersion energy is nearly half of band gap energy value. Acknowledgement. This research was partly financed by European Regional Development Fund within the framework of Operational Program Innovative Economy 2007-2013 (No. UDA-POIG.01.03.01-14-071/08-00).

**TUE 11****Influence of ion irradiation on the electronic system of SWNTs**

Martin Hulman<sup>1</sup> Viera Skakalova<sup>2</sup> Arkady V. Krasheninnikov<sup>3</sup>

<sup>1</sup>International Laser Centre, Bratislava

<sup>2</sup>Max-Planck Institut für Festkörperphysik, Stuttgart, Germany

<sup>3</sup>Material Physics Division, University of Helsinki, Finland

We irradiated single-wall carbon nanotubes by low-energy  $N^+$  and  $C^+$  ions. Besides the increase of the intensity of the D mode in Raman spectra due to defect creation, we also observed change in the shape of the G band of metallic nanotubes. This might point to a reduced metallicity of the latter after the irradiation. There are at least two reasons for this effect. Either the tubes are doped during the irradiation or a gap opens at the Fermi level. With a help of other experimental techniques, both scenarios are discussed.

**TUE 12****Contacting clean suspended single-wall carbon nanotube resonators**

Daniel Schmid<sup>1</sup> Dominik Preusche<sup>1</sup> Christoph Strunk<sup>1</sup> Andreas K. Hüttel<sup>1</sup>

<sup>1</sup>Institute for Experimental and Applied Physics, University of Regensburg, 93047 Regensburg, Germany

By first lithographically fabricating contact electrodes and then as last step CVD-growing nanotubes across the ready-made chip, many potential contamination mechanisms for nanotube devices can be avoided. Combining this with pre-defined trenches on the chip, such that the nanotubes are freely suspended above the substrate, enables the formation of highly regular electronic systems [1-3]. In addition, such suspended ultra-clean nanotubes provide excellent high-frequency and low-dissipation mechanical resonators [2,3], displaying strong interaction between electronic tunneling and mechanical motion in Coulomb blockade [3].

Up to now, in the corresponding devices platinum thin films were predominantly used as electrodes. We present results on the suitability of different contact materials for on-electrode growth of ultra-clean nanotubes. Our experiments aim towards integrating such devices into more complex low temperature electronic circuits.

[1] J. Cao et al, Nature Materials **4**, 745 (2005)

[2] A. K. Hüttel et al, Nano Letters **9**, 2547 (2009)

[3] G. A. Steele, A. K. Hüttel, et al, Science **325**, 1103 (2009)

**TUE 13****Vacancy migration in carbon nanotubes and graphene at high temperatures studied by in situ TEM**Chuanhong Jin<sup>1</sup> Kazu Suenaga<sup>1</sup> Sumio Iijima<sup>1</sup><sup>1</sup>Nanotube Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan

Vacancy defects play an important role on determining the physical and chemical properties of carbon nanostructures. As reported earlier, a single vacancy could dramatically modify the mechanical and electronic properties of carbon nanotubes. Therefore, to understand the formation and migration of vacancy in carbon nanotubes, as well as graphenes, is indispensable for tailoring their mechanical and electrical properties. In this talk, we will present our recent in situ high-resolution transmission electron microscopy (HR-TEM) studies results on the formation, migration and coalescence of large vacancies (or vacancy-holes) in carbon nanotubes and graphene at high temperatures. We observed the formation, migration and aggregation of large vacancies in all the samples (SWNTs, DWNTs, MWNTs and graphenes) used in this study, which were heated to very high temperatures through joule heating. However, depending on the system, different kinds of reconstruction behaviors were also found: (1) SWNT could largely heal the large vacancies by shrinking its diameter locally; (2) while such kind of reconstruction hardly happened on the outer shells of DWNTs and MWNTs, due to the presence of inner shells; (3) for graphenes, the large vacancies could migrate towards their open edges, which could a

**TUE 14****Studying disorder in graphene with Raman spectroscopy and other microscopy techniques**Ado Jorio<sup>1</sup> Erlon H Ferreira<sup>2</sup> Marcia M Lucchese<sup>2</sup> Fernando Stavale<sup>2</sup> Carlos A Achete<sup>2</sup> Braulio S Archanjo<sup>2</sup> Marcus V O Moutinho<sup>3</sup> Rodrigo B Capaz<sup>3</sup><sup>1</sup>Dept. Fisica, UFMG, Belo Horizonte<sup>2</sup>INMETRO, Rio de Janeiro<sup>3</sup>Inst. Fisica, UFRJ, Rio de Janeiro

In this work we use Raman spectroscopy, atomic force microscopy, scanning tunneling microscopy and scanning electron microscopy to study disorder in graphene, induced by ion bombardment. Both focused ion beam and disordered bombardment are applied. We analyze the evolution of the Raman peak frequencies, linewidths, intensities and integrated areas as a function of the disorder morphology. The evolutions are modeled thus providing physical insights about the disorder effects, as well as other information about the Raman scattering event, such as the Raman relaxation length. The study is developed for mono-, bi-, tri- and many-layer graphene samples, and correlated with bulk highly oriented pyrolytic graphite (HOPG) and carbon nanotubes.

**TUE 15****Effect of C60 encapsulation on Radial Breathing Mode of Metallic and Semiconducting Single-Wall Carbon Nanotubes**Soon-Kil Joung<sup>1</sup> Toshiya Okazaki<sup>1</sup> Susumu Okada<sup>2</sup> Sumio Iijima<sup>1</sup><sup>1</sup>National Institute of Advanced Industrial Science and Technology (AIST)<sup>2</sup>CREST, Japan Science and Technology Agency (JST)

We have investigated the effects of C60 encapsulation on the radial breathing mode (RBM) frequencies of metallic and semiconducting Single-Wall Carbon Nanotubes (SWCNTs). Metallic and semiconducting SWCNTs having different absorption region were irradiated with corresponding excitation energy as following, 1.46 eV-1.77 eV and 1.16 eV-1.46 eV, respectively. The 2D intensity contour maps of resonance Raman spectra in RBM phonon region for both metallic and semiconducting nanotubes have revealed that the interaction between SWCNTs and C60 is different for metallic and semiconducting nanotubes. The present results provide important insights into the difference in the intrinsic properties between metallic and semiconducting nanotubes.

**TUE 16****Mesoscopic Resistance Fluctuations in Graphene**Alan B. Kaiser<sup>1</sup> Keoni Mahelona<sup>1</sup> Viera Skákalová<sup>2</sup><sup>1</sup>MacDiarmid Institute for Advanced Materials and Nanotechnology, Victoria University of Wellington, PO Box 600, Wellington 6140, New Zealand<sup>2</sup>Max Planck Institute for Solid State Research, 70569 Stuttgart, Germany

Reproducible mesoscopic resistance fluctuations (MRFs), first observed in narrow 2D semiconductor channels, are also seen in graphene, but extend to much higher temperatures. The decay of the MRFs in graphene in samples of graphene of micron size follows an exponential decay with increasing temperature (1) rather than inverse power laws as expected theoretically. To investigate further the MRFs in these graphene samples, we determine the autocorrelation functions and power spectra for the MRFs, finding fluctuations of higher frequency (as a function of gate voltage) near the neutrality point, and some evidence for characteristic fluctuations.

(1) V. Skákalová, A.B. Kaiser, J.S. Yoo, D. Obergfell and S. Roth, Phys. Rev. B 74, 153404 (2009).

**TUE 17****The role of doping in evaluation of defects concentration in SWCNT**Martin Kalbac<sup>1</sup> Ladislav Kavan<sup>1</sup><sup>1</sup>J. Heyrovsky Institute of Physical Chemistry, ASCR, J. Heyrovsky Institute of Physical Chemistry, ASCR, Prague

One of the major issues in carbon nanotubes science and technology is their purity and quality. For the evaluation of the defects is the Raman spectroscopy frequently used, since the intensity of the D band in the Raman spectra of SWCNT is related to the concentration of defects. However, the dependence of the D band on charge-transfer doping is generally ignored, despite the studied samples are often naturally doped. We studied the intensity of the D band, the ratio of the intensities of the D band and TG band (ID/ITG) and the ratio of the intensities of the D and G' band (ID/IG') in the Raman spectra of the SWCNT in dependence on a doping level. It is shown that the D band intensity is significantly attenuated in doped carbon nanotubes sample for both semiconducting and metallic tubes. Furthermore we found that the ID/ITG ratio is weakly dependent on doping for semiconducting tubes but for metallic tubes the ID/ITG ratio exhibits dramatic dependence on doping. The ID/IG' ratio, which is most frequently used for quantification of the defects, is changed only weakly at low doping levels but at high doping levels the ID/IG' ratio exhibits significant dependence on charging.

**TUE 18****Cell adhesion on oxygen/hydrogen terminated carbon nanotubes**Marie Kalbacova<sup>1</sup> Antonin Broz<sup>1</sup> Martin Kalbac<sup>2</sup> Marina Davydova<sup>3</sup> Alexander Kromka<sup>3</sup><sup>1</sup>Institute of Inherited Metabolic Disorders, 1st Faculty of Medicine, Charles University, Prague, Czech Republic<sup>2</sup>J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of Czech Republic, Prague, Czech Republic<sup>3</sup>Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic

One of the emerging application fields for carbon nanostructures is tissue engineering where these materials play either passive role (i.e. as a substrate for controlled cell cultivation) or active role (i.e. they penetrate into the cell for further monitoring and/or stimulation of biochemical processes). However, pristine carbon nanotubes do not exhibit ideal cell adhesion properties. This can be improved by a post-treatment procedure. One of the promising procedures is an oxygen plasma treatment of carbon nanotubes, which enhances their hydrophilic character. Here we studied the interaction of human osteoblasts with different carbon nanotube types used as the artificial substrates and they were: 1) as grown and O-treated vertically aligned MWCNTs, 2) as grown and O-treated angled MWCNTs, 3) as



grown and O-treated SWCNTs and 4) appropriate controls. On these substrates human osteoblasts were plated and after different times their adhesion patterns as well as their growth were studied, compared and discussed in this report.

**TUE 19****The effect of doping on transmission and conductivity of transparent conducting nanotube films**

Katalin Kamarás<sup>1</sup> Áron Pekker<sup>1</sup> Bea Botka<sup>1</sup>

<sup>1</sup>Research Institute for Solid State Physics and Optics, Budapest

Transparent conducting coatings made of carbon nanotubes have to be optimized in two respects: high dc conductivity and high transmission in the visible range. Wide-range optical spectroscopy is an ideal tool to determine both quantities from one type of measurement, and the requirements translate in this case to high absorbance in the far infrared and low in the visible. We have found that doping is beneficial in both respects, and present a systematic study of hole doping by acids on different nanotube types, on both self-supporting thicker and substrate-supported thinner layers. Our spectroscopic data unambiguously prove that the changes in conductivity are intrinsic, and not just a result of improving the contact between nanotubes. For self-supporting films, the dc conductivity of the networks is close to that extrapolated from the low-frequency optical conductivity. We also studied the time evolution of the doping process. While doping occurs on the scale of minutes, and there is significant initial dedoping, we find that the improvement remains over several weeks.

**TUE 20****Energy distributions of field emitted electrons from carbon nanosheets: manifestation of the quantum size effect**

V. L. Katkov

Joint Institute for Nuclear Research (JINR), Bogoliubov Laboratory of Theoretical Physics, Dubna

The field emission from few-layer graphene films is studied within the method of independent channels. The crucial influence of the band structure on the energy distribution of field emitted electrons is established. In addition to the main peak we found characteristic sub-peaks in the energy distribution. Their positions strongly depend on the number of layers and the inter-layer interaction. The discovery of these peaks in field emission experiments from carbon nanosheets would be a clear manifestation of the quantum size effect in few-layer graphene.

**TUE 21****Temperature-dependent Raman Scattering of Silicon Nanowires**S. Khachadorian<sup>1</sup> H. Scheel<sup>1</sup> A. Colli<sup>2</sup> A. Vierck<sup>1</sup> A. C. Ferrari<sup>2</sup> C. Thomsen<sup>1</sup><sup>1</sup>Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstrasse 36, 10623 Berlin, Germany<sup>2</sup>Department of Engineering, University of Cambridge, Cambridge CB3 0FA, UK

Silicon nanowires were grown on Au-coated Si substrates by vapor transport and the first and second-order Raman spectra of the silicon nanowires studied in the temperature range from 77 to 900 K. The first-order and second-order Raman peaks were found to shift and broaden differently with increasing temperature. We believe this to be due to differences in the temperature dependence of the optical phonons at the  $\Gamma$  point and the X point. Moreover, the temperature dependence of the phonon branches of silicon nanowires differs from their bulk counterpart. The broadening of the second-order Raman peak of silicon nanowires reflects the changed phonon density of states. Our measurements also show that with increasing temperature the intensity of second-order Raman peak increases relative to the first-order Raman peak.

**TUE 22****Graphene Schottky Barrier Diode**Hye-Young Kim<sup>1</sup> Kangho Lee<sup>1</sup> Shishir Kumar<sup>2</sup> Tarek Lutz<sup>2</sup> G. T. Kim<sup>1</sup> G. S. Duesberg<sup>2</sup><sup>1</sup>School of Electrical Engineering, Korea University, Seoul, South Korea<sup>2</sup>School of Chemistry and CRANN, Trinity College Dublin, Dublin

Schottky barrier which has rectifying characteristics at a metal-semiconductor junction is a considerable phenomenon in electronics. Graphene has ambipolar characteristics and is adjustable as p- and n-type semiconducting behaviour by applying adequate gate voltage. In this presentation, we suggest a Schottky diode made from graphene with these natures. A graphene layer is synthesised by chemical vapour deposition (CVD) growth and metal contacts are prepared after e-beam lithography. This graphene Schottky diode has two different metal contacts, which have higher and lower work function than graphene. Applying gate voltage determine p- or n-type characteristics of graphene, due to gate voltage tunes a graphene work function. Therefore one of metal contacts occur Schottky barrier with semiconducting graphene.

**TUE 23****Raman Spectroscopy of Graphene in Different Dielectric Environments**Philipp Klar<sup>1</sup> Cinzia Casiraghi<sup>1</sup><sup>1</sup>Fachbereich Physik, Freie Universität Berlin, Berlin

The high carrier mobility of graphene makes it a promising candidate for future electronic devices. However, large variations in the transport features have been observed and attributed to charged impurities [1,2]. Here we investigate the charged impurities in graphene by increasing the dielectric constant of the surrounding environment: the effect of the charged impurities is expected to be minimized by dielectric screening. We performed Raman Spectroscopy of graphene deposited on a silicon/silicon oxide substrate and immersed in water, ethanol and chloroform. We observed changes in the doping level and amount of disorder, depending on the dielectric, but no direct dependence on the dielectric constant has been observed [3,4]. Raman Spectroscopy also shows that it is possible to minimize the effect of the charge impurities by depositing graphene on an un-conventional substrate, such as Calcium Fluoride [4]. This shows that the charged impurities are strongly related to the silicon/silicon oxide substrate.

[1]Y.W. Tan et al., PRL 99, 246803(2007)

[2]P. Blake et al., Sol. State Comm. 149, 1068(2009)

[3]C.Casiraghi, PSS RRL 3, 175(2009)

[4]Ph. Klar and Casiraghi, submitted

**TUE 24****A Comparative Study of Field Emission from Arrays of Nanobuds, Graphene Flakes and Pure or N-doped Single-Wall Carbon Nanotubes**V.I. Kleshch<sup>1</sup> T. Susi<sup>2</sup> E.D. Obraztsova<sup>1</sup> A.N. Obraztsov<sup>3</sup> E.I. Kauppinen<sup>2</sup><sup>1</sup>A.M. Prokhorov General Physics Institute, Moscow<sup>2</sup>Helsinki University of Technology, Helsinki<sup>3</sup>M.V. Lomonosov Moscow State University, Moscow

Field emission characteristics of multi-emitter arrays of N-doped single-wall carbon nanotubes (SWNTs), NanoBuds and a few-layer graphene flakes have been examined. The cathodes based on these materials demonstrated a low field electron emission with the “turn-on” fields of few Volts per micron, which may be ascribed to a high aspect ratio of nanocarbons. The films of NanoBuds and graphene flakes possess an excellent emission pattern homogeneity contrary to the conventional SWNT films. We believe that the high density of emission sites strongly depends on mechanical properties of the nanostructures. In particular, a high flexibility of carbon nanotubes negatively influences on the emission pattern uniformity increasing the field screening effect. Properties of N-doped and pure SWNT arrays have been compared. The role of N-doping has been established. The materials examined are of great interest due to their unique characteristics being promising

for development of new types of field emission devices. The work was supported by FP6-033350 and RFBR-07-02-91033 projects.

**TUE 25****Transmission signatures of peapod-grown double walled carbon nanotubes**

János Koltai<sup>1</sup> Viktor Zólyomi<sup>2</sup> László Oroszlány<sup>1</sup> Jenő Kürti<sup>1</sup>

<sup>1</sup>Eötvös University Budapest, Budapest

<sup>2</sup>Lancaster University, Lancaster

Single walled carbon nanotubes can be used as nanoscale reaction chambers for producing smaller nanotubes within the host tube from encapsulated fullerenes by annealing. The diameter of the host outer tube restricts the diameter of the inner tube due to van der Waals interactions, but not chirality; however, only a few chiralities are allowed for any given outer tube diameter. It is possible that inner tubes with different chiralities start to grow at different places at the same time. A straight junction occurs at the connection of these two tubes.

The ballistic transport of double walled nanotubes with such junctions on the inner wall are studied using the Landauer-Büttiker formalism and compared to the case of a pristine inner tube. The junctions produce well defined signature structures in the transmission making it possible to identify the presence of such junctions on the inner tube by measuring the transmission of the outer tube.

**TUE 26****Low-temperature synthesis of few-layer and multi-layer graphene on a substrate by chemical vapor deposition**

Daiyu Kondo<sup>1</sup> Shintaro Sato<sup>1</sup> Katsunori Yagi<sup>1</sup> Naoki Yokoyama<sup>1</sup>

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Graphene has been attracting much attention as a candidate for a novel material used in future electronics due to their excellent physical properties. Synthesis of graphene directly on a desired substrate at low temperature is important to apply it to electronics in order to reduce thermal damages to devices during the synthesis process. However, there have not been many reports regarding low-temperature synthesis of graphene. In this study, we demonstrate synthesis of few-layer and multi-layer graphene at temperatures lower than 650C, and propose a new method to fabricate graphene field-effect transistors directly on a substrate without using graphene-transfer processes. Graphene was synthesized by chemical vapor deposition with acetylene as the carbon source. As catalyst, iron films with thicknesses of 5-500 nm were deposited on a substrate. Analyzing the results, we have found that thicknesses of multi-layer graphene are dependent on the catalyst thickness and the substrate temperature. By optimizing the synthesis conditions, we have also found that, by optimizing the synthesis conditions, few-layer and multi-layer graphene can be synthesized at temperatures below 600C.

**TUE 27****Towards imaging atomic resolved single molecular reactions: an example of fullerene fusion**

Masanori Koshino<sup>1</sup> Yoshiko Niimi<sup>2</sup> Eiichi Nakamura<sup>3</sup> Hiromichi Kataura<sup>1</sup> Toshiya Okazaki<sup>1</sup> Kazutomo Suenaga<sup>1</sup> Sumio Iijima<sup>1</sup>

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<sup>2</sup>ERATO, Japan Science and Technology Agency

<sup>3</sup>University of Tokyo

Some reactions of a molecule start from an encounter with other molecules accelerated by phonons, photons or electrons. Classic approaches to characterize such behaviours are based on the analysis of thermodynamics, spectroscopy, or microscopy that dealt with enormous amounts or assembly of molecules. Scientists have dreamed of capturing the very moment of reactions when the molecules change their structures. Recently it has been demonstrated that the motional behaviours of single molecules can be characterized by transmission electron microscopy (TEM). The motional analysis at atomic-level has a great potential to witness various chemical reactions. Here we report a study on bimolecular reactions of fullerene and metallo-fullerene molecules inside carbon nanotubes as a function of electron dose. Pictures of how the fullerenes move during the dimerisation process reveal the specific orientations in which the two molecules interact, as well as how bond reorganization occurs after their initial contact. Studies on the concentration, specimen temperature, effect of metals and accelerating voltage indicate that the reactions can be imaged under a variety of conditions.

**TUE 28****Graphene preparation by dispersing and exfoliating graphite in the liquid phase**

Nina V. Kozhemyakina<sup>1</sup> Frank Hauke<sup>1</sup> Andreas Hirsch<sup>1</sup>

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Graphene, being the last up to now known member of the family of carbon allotropes, has attracted much attention right after its discovery [1]. The two dimensional structure of a single graphitic monolayer leads to such phenomena as free charge carriers and the Hall effect [2,3], tempting to expect prospective applications, e.g. in field-effect transistors [4] and transparent electrodes [5]. For the large-scale production of graphene, dispersing of graphite in water and organic solvents seems to be the most promising method. This work is focused on the production and characterization of few- and monolayer graphene in water and organic solvents, with and without the use of non-covalently binding agents. The main characterization methods are Raman spectroscopy, atomic force microscopy, UV/Vis and fluorescence spectroscopy. As an important factor, the sample preparation history

is considered.

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- [2] Y. Zhang, Y.-W. Tan, et al., Nature, 2005, 438, 201.
- [3] A.K. Geim, K.S. Novoselov, Nat. Mater., 2007, 6, 183.
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## TUE 29

### **Comparative study of plasma excitations in single-walled carbon nanotubes and graphite by inelastic x-ray and electron scattering**

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The dynamical structure factor  $S(q, \omega)$  in both graphite and freestanding thin-bundled single-walled carbon nanotubes (SWNTs) is probed by means of inelastic x-ray and electron scattering. We utilize the equivalency and complementarity of the two techniques in our combined approach. The plasmon dispersions provide direct insight into the imprints of macroscopic screening and low-dimensional confinement on excitonic inter-band transitions in SWNTs.

## TUE 30

### **Pressure-induced phenomena in single-walled carbon nanotubes probed by infrared spectroscopy: Role of pressure transmitting medium**

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The study of single-walled carbon nanotubes (SWCNTs) under high pressure has attracted much interest recently as the application of pressure induces radial deformation and collapse of nanotubes. Numerous high-pressure Raman and x-ray diffraction experiments were carried out on bundled SWCNTs using various pressure transmitting media. Despite the theoretical predictions for a circular-to-oval structural phase transition, these experiments found contradictory results, which were attributed to the pressure transmitting medium and its possible intercalation. Furthermore, the role of nanotube bundling for the pressure-induced phenomena is not clear.

We studied the effect of pressure on the electronic properties of bundled nanotubes by infrared transmission measurements on unoriented SWCNT films. Different pressure transmitting media were employed to verify their influence on the observed pressure dependence. A redshift of the optical absorption bands is observed under pressure. Irrespective of the pressure transmitting medium, the pressure-induced frequency shifts of the optical transitions show an anomaly at a critical pressure  $P_c=2-3$  GPa, which can be attributed to the predicted circular-to-oval structural phase transition.

**TUE 31****Direct imaging of nitrogen doped graphene**

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We imaged nitrogen doped graphene by ultra high resolution TEM and were able to identify single atom substitutions where one carbon atom was replaced by a nitrogen atom.

According to conventional TEM simulation this should not be possible because the contrast difference between carbon and nitrogen atoms is too small. The traditional simulation technique neglects all kinds of inter atomic interactions inside the specimen.

We included chemical bonding into the TEM simulation by calculating the electrostatic specimen potential by density functional theory (DFT). From a charge analysis we found significant changes in the electron distribution on the neighbouring carbon atoms, rather than the nitrogen atom itself, enabling the detection of the substitution atom.

We show that chemical bonding has a detectable effect on TEM images. Hence, in combination with image simulations, a TEM can be utilized to obtain information about the electronic configuration of the specimen (not only structural information). This opens a way to discern electronic arrangements in point defects or other non-periodic objects that can not be analyzed in an electron or X-ray diffraction experiment.

**TUE 32****Preparation and properties of a conducting composite of the C<sub>60</sub> polymer and single-wall carbon nanotubes**

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A mechanism of the C<sub>60</sub> electropolymerization, induced by the superoxide anion radical (O<sub>2</sub><sup>·-</sup>) was refined using simultaneous cyclic voltammetry (CV) and vis-NIR spectroelectrochemistry. Products of both the first (C<sub>60</sub>/C<sub>60</sub><sup>·-</sup>) and second (C<sub>60</sub><sup>·-</sup>/C<sub>60</sub><sup>2-</sup>) reduction of C<sub>60</sub> in the presence of O<sub>2</sub> were identified by MS MALDI TOF. Most likely, the oxygen atom was built into the dimerized C<sub>60</sub> molecules in the initial stage of the electropolymerization. The deposited C<sub>60</sub> polymer (C<sub>60</sub>-O) film was investigated by Raman spectroscopy and imaged by AFM both at the early and advanced stage of the electropolymerization. An electrophoretically deposited film of the non-covalently surface modified with 1-pyrenebutyric acid HiPCO single-wall carbon nanotubes (pyr-SWCNTs) was coated by electropolymerization with the C<sub>60</sub>-O film under potentiodynamic conditions to result in a polymer-CNTs composite material. Specific capacitance of the electrode coated with this material was 184 F g<sup>-1</sup>, a value comparable to those for other SWNT composite film electrodes suggesting its plausible application for electrodes of supercapacitors.

**TUE 33****Low temperature ESR from PtRhRe-catalyst grown and fully separated metallic and semiconducting SWCNT**

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<sup>3</sup>Department of Physics, Tokyo Metropolitan University, Tokyo, J

<sup>4</sup>Department of Chemistry, Nagoya University, Nagoya, J

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While the ESR response from localized spins in SWCNTs has been frequently observed the response from free carriers has been questioned due to the Tomonaga-



Luttinger Liquid character of electrons in these tubes. The situation changed when sample material became available with separated semiconducting and metallic tubes grown from a non-magnetic catalyst. We report on ESR experiments in the temperature range between 1.5 and 300 K. The semiconducting samples exhibit a narrow, 3.5 G broad, resonance line of weak Dysonian shape and typical  $1/T$  temperature dependence. The metallic samples exhibit a well expressed Dysonian line shape and a nearly temperature independent intensity at high temperatures as expected for free electrons. At 3 K a sharp transition to a new state is observed where the phase factor of the Dysonian line decreases abruptly and the intensity of the absorption increases dramatically within a fraction of a degree. The results for the metallic tubes will be discussed in the frame of a Coulomb correlation gap and from the point of view of a mobility gap originating from disorder in the 3D bundles of the tubes.

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## TUE 34

### Electrocorrosion properties of multiwall carbon nanotubes

Alexander Simonov<sup>1</sup> Vladimir L. Kuznetsov<sup>2</sup> Olga Sherstyuk<sup>1</sup> Ilya Mazov<sup>3</sup> Karina Elumeeva<sup>2</sup> Arcady Ischenko<sup>4</sup>

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Carbon nanotubes are perspective functional materials for developing of a number electrochemical applications (batteries, supercapacitors, sensors, catalyst supports for the proton-exchange membrane of fuel cells etc). The electrochemical stability is supposed to be one of the most important issues to be addressed before their commercialization. In this paper we have performed comparative study of electrochemical stability of multi walled carbon nanotubes (MWNT) of different average diameters (7-20 nm with corresponding surface area 420-100 m<sup>2</sup>/g) and others traditional carbon supports (Vulcan XC-72). The initial cyclic voltammograms (CV) curves of both MWCNT and Vulcan XC-72 exhibit no distinguishable peaks evidencing of the absence of the reasonable amount of the surface oxides. After the anodic treatment, the redox peaks of the hydroquinone/quinone couples are clearly observed for all of the samples tested. The amount of the surface oxides formed on the MWCNT samples linearly depends on the surface area of the carbon materials and were much less than that of Vulcan XC-72. Thus MWNTs demonstrate higher corrosion resistance of the surface in comparison with other carbon materials.

**TUE 35****Pressure induced phase transition in carbon nanotube bundles**

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The effects of pressure on a bundle of single walled carbon nanotubes is studied theoretically and experimentally. Unoriented films are placed under hydrostatic pressure of up to 8 GPa in an anvil cell and studied with optical spectroscopy. Anomalies in the pressure dependence of the optical properties suggest that a phase transition occurs at around 2 GPa. Calculations at the local density approximation level of density functional theory are performed to model the experiments. The phase transition is found theoretically as well, albeit at a different critical pressure. The possible reasons for this discrepancy are discussed in detail.

**TUE 36****Au nanoparticle formation in diblock copolymers and hydrogels**

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We apply surface- and tip-enhanced Raman scattering to investigate the formation of Au nanoparticles in diblock copolymer micelles and the interaction of Au nanoparticles with another class of polymers, poly-N-isopropylacrylamide (PNIPAm) microparticles. The growth of gold nanoparticles from organometallic precursors within the amphiphilic diblock copolymer chains is governed by the specific functional groups of the polymer. In-situ Raman measurements at different steps of the growth process allow the identification of these groups and the explanation of the growth. PNIPAm hydrogel composites with Au nanoparticles demonstrate light-changeable structural properties. Spatially resolved Raman measurements from a combined AFM-Raman set-up allow the investigation of the impact of the gold particles on the switching and the role of the other components like acids.

**TUE 37****Mechanism study of aerosol CVD synthesis for N-doped SWCNTs**

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Spin-polarized periodic density functional theory has been employed to study the formation mechanisms of N-doped SWCNTs, which are easily synthesized through an aerosol assisted method using a floating catalyst reactor that allows directly depositing as-grown material from the gas phase via simple continuous process using a hot wire/CO/ammonia system [1]. In detail, the bonding and chemistry of CO, NH<sub>3</sub> and their fragment on a Fe<sub>55</sub> icosahedral cluster, has been considered. A possible dissociation path for NH<sub>3</sub> to atomic nitrogen and hydrogen was identified. The calculated lowest reaction barrier for the overall process is comparable to an experimentally determined value [1]. For CO molecule, the lowest dissociation barrier found (0.77 eV) is lower than on most of the studied Fe surfaces [2]. Possible secondary reactions, producing HCN, has been investigated with thermodynamics studies and first principle calculations. The identified formation path presents a reaction barrier of 1.65 eV, in good agreement with a thermodynamically determined value (1.51 eV).

[1] T. Susi et al., manuscript in preparation.

[2] G. Lanzani et al., Journal of Physical Chemistry C, 113 (2009) 12939.

**TUE 38****Raman spectroscopy of carbon nanotubes with electrostatically attached cytochrome c**

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Enzymes are highly effective and specialized in the chemical conversion of substances. A special subgroup are the redox enzymes, which need an electron supply for the conversion. For technical usage it is desirable to couple the enzymes directly to an electron donor.

Here we study single-walled carbon nanotubes (SWCNTs) coupled to cytochrome *c*. Oxidized SWCNTs were used to create an electrostatic linkage between the nanotubes and cytochrome *c*. By Raman spectroscopy we study the interaction between the nanotube and the protein with respect to structural changes and possible charge transfer between the constituents.

**TUE 39****Chemical sensors made from CVD growth graphene**

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Graphene is one of promising building blocks to fabricate next generation electronic devices and quantum device architectures, even chemical and molecular sensors. Unlike the primary method for isolating graphene, micromechanical exfoliation of graphite, epitaxial growth of graphene makes easier to scale up for applications. For sensing graphene produced by chemical vapour deposition (CVD) is employed. Results on the graphene synthesis are presented. After purification steps single flake of micron size are obtained. Ni/Au contacts were deposited after e-beam lithography. To decline substrate-induced carrier inhomogeneity from graphene-silicon dioxide interface, we prepare suspended configuration. Further, additional structure, such like heater for sensitivity recovery, is normally required. We suggest a simple way to improve the properties of graphene sensors by pulse heating. Absorbed molecules will be removed by applying a moderate electrical pulse. Electrical pulse shots exclusively to pass source and drain electrodes each other, occurs Joule heating through the graphene and it's helpful to dissociate molecules on the graphene.

**TUE 40****Shear-induced nanotube networks in epoxy resins: an anisotropic conductivity study**

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Unreacted thermoset matrices as well as thermoplastic polymer melts filled with multi-wall carbon nanotubes (MWNT) are of scientific interest as systems undergoing jamming transition under applied shear. The formation of networks from attractively interacting MWNT subjected to a shear flow is of great practical interest. Application of a specific shear flow can result in formation of strongly anisotropic MWNT network structures and lead to substantial anisotropy of composite properties. In this study we concentrate on the evolution of the conductive MWNT networks in epoxy resins under applied steady shear flows of confined

quasi-2D geometry. For the anisotropic electric conductivity measurements in two directions (parallel and perpendicular to shear flow) a special rheo-dielectric setup equipped with finger electrodes was constructed. Electric conductivity associated with the evolution of the MWNT network under shear was monitored in two orthogonal directions for various shear rates and geometries, different shear durations and temperatures. The anisotropic conductivity study was related to the MWNT network micro-structures observed in a rheo-microscope at similar flow conditions.

**TUE 41****The line shape analysis of electron spectra for identification of Csp<sup>2</sup>/sp<sup>3</sup> bonds in oxidized MWCNTs**

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Multiwall carbon nanotubes functionalized by the oxidation reaction (ox-MWCNTs) and their temperature modification are studied by XAES, EPES REELS and the line shape analysis. The k-nearest neighbor (kNN) rule using different similarity criteria between two spectra was applied. One of measures, i.e. Euclidean distance function, is used in the standard version of the kNN rule. For the second similarity measure, the Pearson correlation coefficient was applied. The methods consider the spectra represented as n-dimensional vector points in n-dimensional Euclidean space and deal with statistic of distances between vector points. The spectra are identified on the basis of a reference set containing the spectra recorded from graphite and diamond of well defined C sp<sup>2</sup>. The results of classification based on the reference set indicated identification of graphite and diamond as containing C sp<sup>2</sup> and C sp<sup>3</sup> hybridizations, respectively. The identification of surface C hybridization content at ox-MWCNTs submitted to annealing indicated mainly C sp<sup>2</sup> bonds. The results of application of the kNN rule, obtained for both above mentioned similarity criteria between two spectra, were consistent.

**TUE 42****Separation of single-walled carbon nanotubes by gel**Huaping Liu<sup>1</sup> Ye Feng<sup>2</sup> Takeshi Tanaka<sup>3</sup> Hiromichi Kataura<sup>1</sup><sup>1</sup>NRI, AIST and Japan Science and Technology Agency (JST), CREST, Japan<sup>2</sup>NRI, AIST, and JST-CREST and Institute of Materials Science, University of Tsukuba, Japan<sup>3</sup>Nanotechnology Research Institute (NRI), National Institute of advanced industrial science and Technology (AIST), Japan

Metallic (M) and semiconducting (S) single-walled carbon nanotubes (SWCNTs) are usually grown together in a mixture of different structure types, which will result in low on-off ratios, low effective field-effect mobility. We have to obtain SWCNTs with well-defined structures and electronic properties before their application. Recently, our research group developed novel and simple methods to large-scale separate MS SWCNTs by agarose gel [1, 2]. Especially, continuous MS separation of SWCNTs has been realized by gel filter. In these works, the successful MS separation of SWCNTs is ascribed to the selective adsorption of the surfactants on MS SWCNTs. Here we have done some additional experiments and confirmed the selective adsorption of S-SWCNT on the agarose gel. Further, we found that the surfactants have selectivity in the adsorption not only on the electronic states but also on the structural difference. In this presentation, we will show recent progress of the separation of SWCNTs by gel filter. References [1] T. Tanaka, et al., Nano Lett. 2009, 9, 1497. [2] T. Tanaka, et al., Appl. Phys. Exp. 2009, 2, 125002.

**TUE 43****Silver Nanowire Networks as Flexible, Transparent, Conducting Films: Extremely High DC to Optical Conductivity Ratios**Philip E. Lyons<sup>1</sup> Sukanta De<sup>1</sup> Thomas M. Higgins<sup>2</sup> Evelyn M. Doherty<sup>1</sup> Peter N. Nirmalraj<sup>3</sup> Werner J. Blau<sup>1</sup> John J. Boland<sup>3</sup> Jonathan N. Coleman<sup>1</sup><sup>1</sup>School of Physics, Trinity College Dublin, Dublin 2, Ireland and Centre for Research on Adaptive Nanostructures and Nanodevices, Trinity College Dublin, Dublin 2, Ireland.<sup>2</sup>School of Chemistry, University of Wollongong, Wollongong NSW 2522 Australia<sup>3</sup>School of Chemistry, Trinity College Dublin, Dublin 2, Ireland and Centre for Research on Adaptive Nanostructures and Nanodevices, Trinity College Dublin, Dublin 2, Ireland.

Aqueous dispersions of silver nanowires (Length  $\sim 6.5\mu\text{m}$  & diameter  $\sim 85\text{nm}$ ) were used to prepare flexible, transparent, conducting, thin films. At low thickness, the films consist of networks but appear to become bulk-like for mean film thicknesses above  $\sim 160\text{nm}$ . These films display good optical transmittance (550nm), reaching as high as 92% for low thickness and decreasing with increasing thickness. The sheet resistance decreases with increasing thickness, to  $< 1\Omega/\text{Sq}$  for thicknesses

> 300nm. This results in a DC conductivity increase of  $2 \times 10^5$  S/m for very thin films up to  $5 \times 10^6$  S/m for thicker films. The ratio of DC to optical conductivity increases with increasing thickness from 25 for the thinnest films, saturating at  $\sim 500$  for thicknesses above  $\sim 160$ nm. We believe this is the highest conductivity ratio ever observed for nanostructured films and is matched only by doped metal oxide films. We have prepared films with optical transmittance and sheet resistance of 85% and  $13\Omega/\text{Sq}$  respectively. Such results make these films possible replacements for ITO as transparent electrodes.

#### TUE 44

##### Linear scaling between momentum and spin scattering in graphene

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Spin transport in graphene carries the potential of a long spin-diffusion length at room temperature. However, extrinsic relaxation processes limit the current experimental values to 1–2  $\mu\text{m}$ . We present Hanle spin precession measurements in gated lateral spin valve devices in the low to high (up to  $10^{13}\text{cm}^{-2}$ ) carrier density range of graphene. A linear scaling between the spin-diffusion length and the diffusion coefficient is observed. We measure nearly identical spin- and charge diffusion coefficients indicating that electron-electron interactions are relatively weak and transport is limited by impurity potential scattering. When extrapolated to the maximum carrier mobilities of  $2 \cdot 10^5\text{cm}^2/\text{Vs}$ , our results predict that a considerable increase in the spin-diffusion length should be possible.

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#### TUE 45

##### Study of top-gated graphene devices by Raman spectroscopy

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Raman scattering has been a successful experimental tool to study single- and few-layer graphene samples. In this work, a study of top-gated bilayer graphene by Raman spectroscopy is presented. Top gating was achieved by using a polymer electrolyte consisting of  $NaClO_4$  and polyethylene glycol and the gate voltage was applied between a gold electrode in contact with the graphene layer and a platinum wire electrode inserted in the electrolyte. Graphene samples were produced by micro-mechanical cleavage of graphite and deposited on Si covered with 300nm of  $SiO_2$ . The contacts were made by optical lithography. In the case of bilayer graphene devices, we have observed that the application of a gate voltage breaks the inversion symmetry and the Raman G band splits into two components associated with the symmetric and anti-symmetric vibrational modes. The study of the positions, bandwidths and relative intensity of the two Raman peaks as a function of the electron concentration will be presented and compared with theoretical calculations.

**TUE 46****Growth of Carbon Nanotubes by CVD over oxide nanoparticles**

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It is generally believed that the growth of carbon nanotubes (CNTs) by Chemical Vapour Deposition (CVD) requires the use of supported metal nanoparticles over which the carbon source molecules decompose, and from which the growth of carbon nanotubes stems subsequently. However, the presence of metal nanoparticles has detrimental effect for electronic devices, for filtration applications by clogging CNTs as well as for biological applications because of the high toxicity of metal nanoparticles. Recently, the development of new CVD process, based on the addition of oxygen containing species to the carbon source [1, 2], yielded to highly efficient CNTs growth such as replacing the metal nanoparticles by oxide nanoparticles is foreseen. In this paper, we will report on the synthesis of CNTs by CVD process based on the oxidative dehydrogenation of acetylene which reaction kinetics is fast such as large quantity of CNTs can be grown directly on numerous oxide nanoparticles (including  $Al_2O_3$ ,  $CaCO_3$ ,  $TiO_2$ , to name but a few).

[1] K. Hata et al, Science (2004)

[2] A. Magrez et al, Angew. Chem. Int. Ed. (2007)



**TUE 47****Magnetism induced by irradiation of hydrogen or helium ions – a comparative study**

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To identify the origin of defect-induced magnetism in ion-irradiated graphite, a comparative study of samples of graphite irradiated with hydrogen H<sup>+</sup> and helium He<sup>+</sup> ion is performed. It has been found that the irradiated samples show an anisotropic nonlinear magnetic response with the saturation magnetization larger for the external magnetic field oriented perpendicular to the graphite planes. The observed magnetic anisotropy can be understood as due to correlations of the lattice defects – like vacancies and interstitial carbon atoms – created along the ion tracks. Compared to the case of the hydrogen ion irradiation, the optimal helium irradiation dose is an order of magnitude lower. From this we conclude that the hydrogen chemistry is essentially irrelevant, and the ferromagnetic-like response of the irradiated graphite is due to structural defects regardless of their origin.

**TUE 48****Functionalized carbon nanotubes as substrates for molecular switches**

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Since carbon nanotubes (CNT) show a high-sensitivity to changes in the surrounding medium, they are optimal substrates for functionalization with molecules. In particular, photochrome spiropyran molecules are promising candidates for engineering molecular switches. Spiropyranes can be reversibly switched between two metastable conformations, which are characterized by a large difference in the dipole moment. As a result, the attached molecule has a different influence on the CNT transition energy and the oscillator strength depending on its conformation.

We perform microscopic investigations on the optical properties of pristine and non-covalently functionalized carbon nanotubes. Our approach is based on a combination between the density matrix formalism (CNT dynamics) and quantum-chemical DFT calculations (molecule geometry). We find considerable red-shifts of CNT transitions ( $\sim 100$  meV), when a molecule is attached. Depending on the dipole moment and its orientation even a peak splitting can be observed.

**TUE 49****Electroluminescence from SWNT-Molecule-SWNT Junctions**

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The reliable fabrication of metallic single-wall carbon nanotube (mSWNT) electrode pairs with sub-10nm spacing allows us to contact organic molecules (M) via dielectrophoresis and to form mSWNT-M-mSWNT junctions. For this purpose we used specific designed molecules which have an appropriate length to bridge the SWNTElectrode gap, and a sufficient polarizability to allow the molecule deposition between the SWNTElectrodes via DC-dielectrophoresis. The molecules comprise a fluorescent chromophore subunit. During transport measurements several mSWNT-M-mSWNT junctions showed light emission at voltages  $\geq 4V$ . The electroluminescence spectrum from the junction is very similar to the photoluminescence signal of the molecules on HOPG-surfaces. This result together with control experiments indicates that light is emitted from the chromophore core of the mSWNT contacted molecule.

**TUE 50****Evidence for excitons in metallic carbon nanotubes by temperature dependent Raman scattering**

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We present resonant Raman measurements of the optical transition energy  $E_{ii}$  in metallic and semiconducting nanotubes at different temperatures. In semiconducting nanotubes, the transition energy decreases at high temperatures, whereas in metallic nanotubes  $E_{ii}$  first decreases and then increases again. We discuss this different behaviour of semiconducting and metallic nanotubes and suggest an interpretation in terms of excitons in metallic nanotubes. We suggest that the excitons in metallic nanotubes, due to their small binding energy, dissociate into free electron-hole pairs at temperatures related to the exciton binding energy.

**TUE 51****Raman study of inhomogeneities in carbon nanotube distribution in CNT-PMMA composites**

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A recent attempt to synthesize a PMMA composite material with enhanced mechanical properties based on functionalized single wall carbon nanotubes (SWCNTs) was unsuccessful due to the presence of CNT aggregates despite a high degree of nanotube dispersion [1]. The current work is aimed at characterization of the CNT distribution inhomogeneity in the composites by high-resolution Raman spectroscopy. In particular, we focus on study of the boundary regions between the CNT aggregates and the surrounding areas where the CNTs are well dispersed in the PMMA matrix. Different laser excitation energies (1.96 and 2.33 eV) were used to preferentially probe metallic and semi-conducting SWCNTs respectively. At both photon energies, spectral line scans across the boundary regions revealed fairly narrow (4-6nm) interface areas exhibiting a substantial drop in intensity of G+ CNT Raman mode and an increase of D/G+ intensity ratio. The latter testifies to a preferential dispersion of functionalized CNTs in the PMMA matrix. Certain inhomogeneities were observed even in the areas with well dispersed CNTs.

[1] Vigolo B., et al. J. Phys. Chem. C 2009, 113, 17648

**TUE 52****Low-frequency phonon coupling in an individual multi-walled carbon nanotube**

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Carbon nanotubes (CNTs) have generated a lot of interest as material for nanoelectromechanical devices. In multi-walled CNTs (MWCNTs), the coupling strength between the shells has a direct impact on the vibrational properties [1]. The Raman spectrum of CNTs changes with the number of shells as previously shown for double-walled CNTs [2]. Raman spectroscopy is thus a versatile tool to study the

coupling between nanotube shells. We study a selected individual MWCNT. The information about the low-frequency Raman spectrum is correlated with the diameter of the nanotube shells obtained in high-resolution TEM measurements. We confirm the coupling of the low-frequency modes to breathing-like modes (BLMs) as predicted in [3]. These BLMs show a strong deviation from the well established  $1/d$  dependence of RBMs for single-walled CNTs for the embedded shells (ca. 20%). The coupling between the shells is lower than the coupling between the layers in bulk graphite.

[1] Q. Zheng et al., Phys. Rev. Lett. 88, 045503(2002)

[2] F. Villalpando-Paez et al., Nano Lett. 8, 3879(2008)

[3] V. N. Popov et al., Phys. Rev. B 65, 235415(2002); E. Dobardžić et al., pssb 237, R7(2002)

## TUE 53

### EPR spectra of MoS<sub>2</sub>/C<sub>60</sub>

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MoS<sub>2</sub>/C<sub>60</sub>, discovered by M. Remskar, has turned out to be an extremely good lubricant not only at room temperature but also at low temperatures and vacuum conditions. It may be important for aerospace applications. The structure consists of layers of opened MoS<sub>2</sub> nanotubes separated by layers of unpolimerized C<sub>60</sub>. The two layers are incommensurate to each other allowing for easy layer sliding. We have measured the temperature dependence of the X-band EPR spectra of the charged C<sub>60</sub> ions and found that between room temperature and 100 K the g factor is about 2.3. Below 100 K a strong g shift takes place and the g factor diminishes to about 2.1. The EPR spectra are relatively broad and their intensity decreases with decreasing temperature. The relation between the EPR spectra and the sliding of the layers which is related to the lubrication properties is investigated

## TUE 54

### Pentaheptite carbon nanotubes: stability and conduction properties

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Most of the theoretical investigations of carbon nanotubes (CNTs) are using model of perfect, defect free CNTs, where their high symmetry makes the symmetry arguments extraordinary powerful. Still, CNTs may have structural defects, one of which is the Stone-Wales bond rotation. Such a defect deforms the ornament of four adjacent hexagons into 57-ornament with two pentagons and two heptagons. Although it is primarily a random defect known in graphite, the numerical results

show the stability of the graphene allotropes, called pentaheptites, with regular tiling of 57-ornaments.

Numerical calculations of stability and conducting properties of pentaheptite carbon nanotubes (57NTs) are performed. Pathway of synthesis of 57NTs from the conventional CNTs which have firstly been mechanically deformed in a way which maximally reduces the height of the kinetic barrier is proposed.

## TUE 55

### Electrical Properties of SU8-CNTs Composites

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Electrical Properties of SU8-CNTs Composites

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SU8 is a negative and inexpensive epoxy photoresist which can be easily processed in high aspect ratio structures with standard photolithography. Therefore, it has a very broad range of applications (fluidics, MEMS...). However, SU8 is an insulating and brittle polymer. Carbon nanotubes exhibit outstanding electrical, mechanical and thermal properties, and are considered as the best candidate for the reinforcement of polymers [1, 2]. Therefore, polymer properties can be enhanced by preparing SU8/CNTs composites. We will report on the preparation of the composites. Gamma Butyrolactone (GBL) is the solvent of commercially available SU8 materials. Therefore, we have studied the effect of numerous surfactants on the stability of CNTs in GBL. The characterisation of the electrical properties of homogeneous solid CNTs-SU8 composites will be presented as a function of CNTs content.

[1] P. Pöschke et al., Macromolecular Symposia 254 (1) 392, 2007 [2] M. Mioni<sup>2</sup> et al., Physica Status Solidi B 1-4, 2009

## TUE 56

### Computational Design of Chemical Nanosensors: Metal Doped Carbon Nanotubes

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<sup>2</sup>Center for Atomic-scale Materials Design, Department of Physics, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

We use computational screening to systematically investigate the use of transition metal doped carbon nanotubes for chemical gas sensing. For a set of relevant target molecules (CO, NH<sub>3</sub>, H<sub>2</sub>S) and the main components of air (N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O),

we calculate the binding energy and change in conductance upon adsorption on a metal atom occupying a vacancy of a (6,6) carbon nanotube. Based on these descriptors, we identify the most promising dopant candidates for detection of a given target molecule. From the fractional coverage of the metal sites in thermal equilibrium with air, we estimate the change in the nanotube resistance per doping site as a function of the target molecule concentration assuming charge transport in the diffusive regime. Our analysis points to Ni-doped nanotubes as candidates for CO sensors working under typical atmospheric conditions.



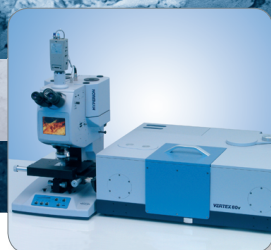






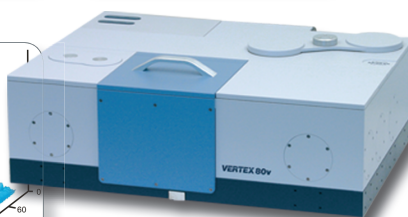
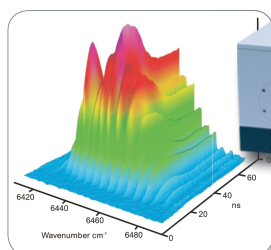


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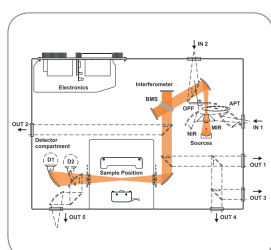
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Wednesday, March 10

## Graphene transport and mechanics

- 8:30 – 9:00     **K. Novoselov, UK**  
*Mobility and Resonant Scatterers in Graphene*
- 9:00 – 9:30     **E. Y. Andrei, US**  
*Electronic properties of graphene*
- 9:30 – 10:00    **N. Tombros, NL**  
*Electronic Spin Transport and Spin Precession in Single Graphene Layers*
- 10:00 – 10:30   **Coffee break**
- 10:30 – 11:00   **B. Dóra, HU**  
*Nuclear spin relaxation and Korringa relation for Dirac electrons in graphene*
- 11:00 – 11:30   **J. Hone, US**  
*Mechanics and Tribology of Graphene and Related Materials*
- 11:30 – 12:00   **A. Bachtold, ES**  
*ElectroMechanical Resonators based on Nanotube and Graphene*
- 12:00 – 17:00   **Mini Workshops**
- 17:00 – 18:30   **Dinner**
- 18:30 – 19:00   **A. M. van der Zande, US**  
*Nano-electro-mechanical systems from arrays of graphene membranes*
- 19:00 – 19:30   **H. S. van der Zant, NL**  
*Carbon nanotube mechanical resonators*
- 19:30 – 20:00   **G. Steele, NL**  
*Clean carbon nanotubes: Single-electron quantum dots and strong coupling to nanomechanical motion*
- 20:00 – 20:30   **A. N. Obraztsov, RU**  
*Production, properties and applications of graphite films of nanometer thickness*

Wednesday, March 10

**8:30****Mobility and Resonant Scatterers in Graphene**Kostya Novoselov

School of Physics &amp; Astronomy, University of Manchester, Manchester

High mobility of charge carriers in graphene makes this material a strong favorite to be used in future electronic devices. However, the typical mobility achieved for graphene devices at the moment, although impressive ( $20,000 \text{ cm}^2/\text{V}\cdot\text{s}$ ) is still one order of magnitude short from the predicted limit at room temperature. Thus, it is of ultimate importance to identify the source of scattering for quasiparticles in graphene. Here we demonstrate that scattering on the mid-gap states is likely to be the limiting mechanism. Getting rid of such scatterers allowed us to bring the mobility in our devices to  $1,000,000 \text{ cm}^2/\text{V}\cdot\text{s}$ . Fractional quantum Hall effect has been observed in such samples.

Wednesday, March 10

Graphene transport and mechanics

**9:00**

**Electronic properties of graphene.**

Eva Y Andrei

Rutgers University, Piscataway, NJ

Graphene, a one-atom thick membrane of crystalline carbon possesses extraordinary electronic properties which make it a prime candidate for novel nano-electronic devices, at the same time raising the prospect to observe phenomena hitherto unseen in bench top experiments. I will present scanning tunneling microscopy and transport experiments that provide access to the dynamics of the charge carriers in this material and give new insights their unique world. The findings include direct observation of the Landau level energy spectrum, observation of the fractional quantum Hall effect and a magnetically induced insulating phase.

**9:30****Electronic Spin Transport and Spin Precession in Single Graphene Layers**Nikolaos Tombros

University of Groningen, the Netherlands

I will give an overview of electron spin injection, spin transport, spin precession and spin manipulation in graphene. The focus will be on recent experiments on single graphene field effect devices with ferromagnetic contacts. I will show that: a) Spins can be transported through a graphene layer with a spin relaxation length of about 1.5 micrometer. By applying a perpendicular magnetic field Hanle spin precession can be studied and information about spin relaxation and the carrier diffusion can be obtained. b) By applying a large DC electric field the transport of spins between injector and detector can be manipulated (sped up or slowed down) using carrier drift. c) The spin relaxation is found to be slightly anisotropic, with spins directed perpendicular to the graphene plane relaxing faster than spins directed in the plane. d) We have observed a scaling between the spin relaxation times and lengths and the carrier mobility in graphene. I will discuss the possibility that in intrinsic graphene spin relaxation lengths of 100 micrometer in graphene at room temperature might be possible, and even longer ones at lower temperatures.

**10:30**

**Nuclear spin relaxation and Korringa relation for Dirac electrons in graphene**

Balázs Dóra<sup>1</sup> Ferenc Simon<sup>1</sup>

<sup>1</sup>Institute of Physics, Budapest University of Technology and Economics, Budapest

We present the theory of nuclear magnetic resonance (NMR) in graphene. The canonical form of hyperfine interaction is strongly modified by the linear electronic dispersion. The NMR shift and spin-lattice relaxation time are calculated as function of temperature, chemical potential, and magnetic field and three distinct regimes are identified: Fermi-, Dirac-gas, and extreme quantum limit behaviors. A critical spectrometer assessment shows that NMR is within reach for fully  $^{13}\text{C}$  enriched graphene of reasonable size.



**11:00**

**Mechanics and Tribology of Graphene and Related Materials**

James Hone

Columbia University, New York

Graphene's tremendous strength (130 GPa) makes it an ideal material for mechanical structures, and also allows the study of materials properties far beyond the equilibrium structure. This talk will describe measurements and theoretical analysis of the mechanics of graphene and related materials such as bilayers/trilayers and hydrogenated graphene (graphane), as well as studies of the Raman spectra (G, 2D, and 2D' modes) of graphene under strain. These properties also influence frictional behavior: monolayer materials display universally larger friction than multilayers.

**11:30****ElectroMechanical Resonators based on Nanotube and Graphene**Adrian Bachtold

CIN2(CSIC-ICN) Barcelona, Barcelona

Carbon nanotubes and graphene offer unique scientific and technological opportunities as nanoelectromechanical systems (NEMS). Namely, they have allowed the fabrication of mechanical resonators that can be operable at ultra-high frequencies and that can be employed as ultra-sensitive sensors of mass or charge. In addition, nanotubes and graphene have exceptional electron transport properties, including ballistic conduction over long distances. Coupling the mechanical motion to electron transport in these remarkable materials is thus highly appealing. In this talk, I will review some of our group's recent results on nanotube and graphene NEMSs, including initial mass sensing with nearly atomic resolution, imaging ultra-rapid mechanical oscillations of nanotube and graphene resonators with an atomic force microscope, and the control of the mechanical oscillation using individual electrons tunneling onto and out of the nanotube.

**18:30****Nano-electro-mechanical systems from arrays of graphene membranes**

Arend M van der Zande<sup>1</sup> Shriram Shivaraman<sup>1</sup> Rob A. Barton<sup>1</sup> Jonathan S. Alden<sup>1</sup>  
Xun Yu<sup>1</sup> Lihong Herman<sup>1</sup> MVS Chandrasekhar<sup>1</sup> Jiwoong Park<sup>1</sup> Jeevak M. Parpia<sup>1</sup>  
Harold G. Craighead<sup>1</sup> Michael G. Spencer<sup>1</sup> Paul L. McEuen<sup>1</sup>

<sup>1</sup>Cornell Center for Materials Research (CCMR), Cornell University, Ithaca

We study the mechanical properties of arrays of electrically contacted, gated, suspended, single layer graphene membranes. The graphene is produced using chemical vapor deposition or epitaxial growth on silicon carbide and then suspended, with yields of 80 % for lengths and widths between 300 nm and 3 microns. We measure the resonance frequency and quality factor using laser interferometry or electrical mixing. We find membrane resonance frequencies range from 1-300 MHz with quality factors of 30-300 at room temperature. Resonator frequency depends strongly on both the intrinsic tension and the static deformation of the graphene sheet. At low temperatures, the frequencies increase slightly and the quality factors rise dramatically, comparable to previous results on exfoliated graphene. These arrays of high-quality suspended graphene devices open the door to both fundamental studies and applications for these remarkable atomically-thin membranes.

**19:00****Carbon nanotube mechanical resonators**Herre S.J. van der Zant

Kavli Institute of Nanoscience, Delft University of Technology, Delft

Nano-electromechanical systems (NEMS) make use of electrically induced mechanical motion and vice versa. Carbon nanotubes are ideal building blocks of NEMS because of their unique (mechanical) properties and their low mass. This puts them in an unexplored regime of motion which approaches the fundamental detection limit set by quantum mechanics. At room temperature, we use mixing techniques to probe the bending-mode vibration of a suspended carbon nanotube -the gate voltage strains the carbon nanotube and thereby tunes its frequency. At low temperatures, mechanical vibrations are actuated by a nearby antenna and a record high Q-value of 150000 at a resonance frequency of a few hundred MHz is achieved. Electron tunneling and mechanical motion are strongly coupled resulting in single-electron tuning oscillations of the mechanical frequency and in energy transfer to the electrons causing mechanical damping. Furthermore, the nanotubes are easily driven into the non-linear regime, showing a complicated response to the external drive. Recent progress includes the observation of GHz resonance frequencies in shorter nanotubes.

**19:30****Clean carbon nanotubes: Single-electron quantum dots and strong coupling to nanomechanical motion**Gary Steele<sup>1</sup> G. Gotz<sup>1</sup> A. K. Hüttel<sup>1</sup> B. Witkamp<sup>1</sup> M. Poot<sup>1</sup> H. B. Meerwaldt<sup>1</sup> H. S. J. van der Zant<sup>1</sup> L. P. Kouwenhoven<sup>1</sup><sup>1</sup>Kavli Institute of Nanotechnology, TU-Delft, Delft, The Netherlands

In conventional nanotube devices, nanotubes are first deposited on the surface of a substrate and subsequently patterned to make nanoscale devices. While this process is very flexible, it has the disadvantage that the nanotube can become contaminated and damaged by chemical and electron beam processing. Here, we present results from a new type of clean nanotube device that avoids all possible damage to the nanotube by growing it in the last step of fabrication. By eliminating disorder, we achieve a new level of control over single electrons in a carbon nanotube, tuning continuously from a single quantum dot (“artificial atom”) to a double dot (“artificial molecule”) for a single electron or hole confined in the nanotube. Studying this tunability, we observe a curious type of tunneling that is analogous to Klein tunneling in relativistic quantum mechanics. Clean carbon nanotubes also exhibit spectacular mechanical properties as nanomechanical resonators with quality factors exceeding  $10^5$ . Here, we study the coupling of this motion a quantum dot embedded in the nanotube. We find that this coupling is remarkably strong, dominating the dynamics of the mechanical motion.

**20:00****PRODUCTION, PROPERTIES AND APPLICATIONS OF GRAPHITE FILMS OF NANOMETER THICKNESS**Alexander N Obraztsov<sup>1 2</sup><sup>1</sup>Department of Physics, Moscow State University, Moscow, Russia<sup>2</sup>Department of Physics and Mathematics, University of Eastern Finland, Joensuu, Finland

One of the major problems hampering exploitation of the unique properties of graphene and multi-graphene layers relates to production of this material with large-area and high-quality. Recently, we have developed a technique for fabrication of graphite films of nanometer thickness by using chemical vapor deposition method. Structural peculiarities of the graphite films consisting of few graphene layers were evaluated by electron microscopy and Raman techniques. The films exhibit quasi single-crystal structural characteristics with area of up to few centimeters square. Optical characteristics of the films were proved to be applicable in optoelectronic devices and for Terahertz generation. Electronic properties of the films allow fabrication of the field-effect transistors. We propose models and mechanisms explaining formation of the films and observed optical and electronic phenomena.



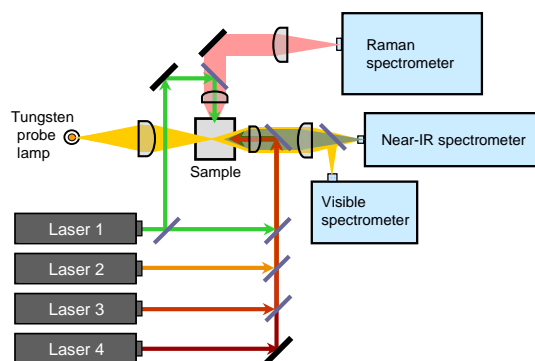
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Thursday, March 11

## Graphene transport, optics and theory

- 8:30 – 9:00     **W. Skakalova, DE**  
*Conduction in graphene: the low-temperature anomaly*
- 9:00 – 9:30     **F. Mauri, FR**  
*Transport in graphene at high bias: current saturation and Klein tunneling*
- 9:30 – 10:00    **K. Tsukagoshi, JP**  
*Gate-tunable band gap in bilayer graphene*
- 10:00 – 10:30   **Coffee break**
- 10:30 – 11:00   **F. Wang, US**  
*Bilayer graphene: tunable bandgap and electron-phonon Fano resonances*
- 11:00 – 11:30   **M. A. Pimenta, BR**  
*Dispersion of electrons and phonons, and electron-phonon interactions in bilayer graphene investigated by Resonance Raman scattering*
- 11:30 – 12:00   **J. Maultzsch, DE**  
*Vibrational properties of graphene nanoribbons*
- 12:00 – 17:00   **Mini Workshops**
- 17:00 – 18:30   **Dinner**
- 18:30 – 19:00   **E. Molinari, IT**  
*Illuminating graphene nanostructures*
- 19:00 – 19:30   **M. Mohr, DE**  
*Electronic and vibrational properties of graphene under strain*
- 19:30 – 20:00   **X. Blase, FR**  
*Conductance of doped or functionalized nanowires, nanotubes and graphene*

Thursday, March 11

**8:30****Conduction in graphene: the low-temperature anomaly**Viera Skakalova<sup>1</sup> Alan B. Kaiser<sup>2</sup> Jai Seung Yoo<sup>3</sup> Siegmund Roth<sup>1</sup><sup>1</sup>Max Planck Institute for Solid State Research, Stuttgart<sup>2</sup>MacDiarmid Institute for Advanced Materials and Nanotechnology, SCPS, Victoria University of Wellington, P O Box 600, Wellington, New Zealand<sup>3</sup>Department of Physics and Astronomy, Seoul National University, Seoul 151-747, Korea

The resistance  $R(T)$  of graphene often shows a monotonic increase or decrease as temperature increases from 4.2 K to around 70 K. We find this anomaly can change sign for even very small changes in gate voltage, indicating that it is not a systematic effect. Using the field effect transistor configuration, we have conclusively determined the cause of this anomaly as arising from the decay of mesoscopic resistance fluctuations (MRFs) due to progressive dephasing of the interfering scattered electron waves as  $T$  increases. Our measurements of  $R(T)$  at different constant gate voltages  $V_g$  tuned to different features of the MRFs observed in  $R(V_g)$  at constant temperature reveal some surprising features not well understood by current theory, for example the exponential rather than power law decay of MRFs with temperature, and the variation of MRF properties as  $V_g$  changes [1].

[1] V. Skákalová, A.B. Kaiser, J.S.Yoo, D. Oberfell and S. Roth, Phys. Rev. B 74, 153404 (2009).

**9:00****Transport in graphene at high bias: current saturation and Klein tunneling**Francesco Mauri<sup>1</sup> Amelia Barreiro<sup>2</sup> Niels Vandecastelle<sup>1</sup> Michele Lazzeri<sup>1</sup> Adrian Bachtold<sup>2</sup><sup>1</sup>IMPMC, Universite Pierre et Marie Curie - Paris 6, Paris<sup>2</sup>CIN2(CSIC-ICN), Campus UAB, E-08193 Barcelona, Spain

I will present a theoretical/experimental study of the high-current transport properties of graphene as a function of the doping. In doped samples, ( $|V_{gate}| > 6$  Volt with a standard SiO<sub>2</sub> bottom gate) the current tends to saturate as the voltage across graphene is increased but never reaches the complete saturation as in metallic nanotubes. Measurements are compared to a model, which includes electron-scattering processes due to charged and neutral impurities, graphene optical phonons, and electron-electron repulsion. The saturation is incomplete because of the competition between disorder and optical phonon scattering. Finally, in undoped samples, we identify the signature of interband Klein tunneling.

**9:30****Gate-tunable band gap in bilayer graphene**Kazuhito Tsukagoshi<sup>1</sup> Hisao Miyazaki<sup>1</sup> Songlin Li<sup>1</sup> Akinobu Kanda<sup>2</sup><sup>1</sup>MANA, NIMS, Tsukuba<sup>2</sup>University of Tsukuba, Tsukuba

A band gap formation in graphene is one of the most interesting challenges for graphene switching device. We introduce our experimental trial to induce a band gap in bilayer graphene under a high electric field. An ambipolar resistance peak in the graphene was enhanced as the high electric field between the dual gates was increased. In a conductance plot of the ambipolar behavior, when the resistance was enhanced in the electric field, the conductance closely approached zero conduction. Voltage difference extracted from the threshold of the p-type and the n-type region in the top-gate voltage scan was typically 0.5 V at the gate electric field of 1.4 V/nm, and strongly depended on the applied electric field. As a further experiment, temperature dependence of the ambipolar resistance peak was carried out. The conductance extracted from the peak resistance was well fitted by thermal activations with two conduction components. One of them was based on the conduction due to the variable range hopping conduction via localized states. Another component was caused with the larger activation energy over 0.1 eV, suggesting the existence of the band gap in the order of hundreds of meV.

**10:30**

**Bilayer graphene: tunable bandgap and electron-phonon Fano resonances**

Feng Wang

University of California, Berkeley, Berkeley

Graphene, a single layer of carbon atoms, exhibits novel two-dimensional electronic behavior. With an extra layer, bilayer graphene gives rise to even richer behavior. In this talk, I will describe how we can use electrical gating to control the electronic bandgap in bilayer graphene and probe the induced bandgap using infrared spectroscopy. I will also discuss a new elementary excitation composed of coupled phonon and exciton in bilayer graphene. This hybrid phonon-exciton excitation shows striking Fano interference behavior, which can be tuned by varying the bilayer bandgap.

**11:00****Dispersion of electrons and phonons, and electron-phonon interactions in bilayer graphene investigated by Resonance Raman scattering**Marcos A Pimenta<sup>1</sup> Leandro M Malard<sup>1</sup> Daniela L Mafra<sup>1</sup> Daniel C Elias<sup>1</sup> Juliana C Brant<sup>1</sup> Flavio Plentz<sup>1</sup> Elmo S Alves<sup>1</sup><sup>1</sup>Departamento de Física, Universidade Federal de Minas Gerais, Belo Horizonte, Brasil

Raman spectroscopy is a very useful tool to study graphene samples, since it furnishes important information about the graphene structure, presence of disorder, defects, charges, strain, etc. However, important information about electrons can be also obtained in a Resonance Raman investigation, where the energy of the laser excitation can be tuned. We will present experimental results of the dispersion of electrons and phonons in bilayer graphene obtained from a resonant Raman study using different laser energies in the visible and NIR range. The electronic structure will be discussed within the tight-binding approximation. We will show that the Kohn anomaly of the phonon branches near the K point is different for the symmetric and anti-symmetric branches, and results evidence the importance of considering electron-phonon and electron-electron interactions. We will also present results in gated graphene devices where the position of the Fermi level can be changed by applying a gate voltage, which splits the Raman G band. The dependence of the position, linewidth and intensity of these components on the charge concentration will be presented and compared to theoretical predictions.

**11:30****Vibrational properties of graphene nanoribbons**Janina Maultzsch<sup>1</sup> Marcel Mohr<sup>1</sup> Christian Thomsen<sup>1</sup> Roland Gillen<sup>1</sup><sup>1</sup>Institut für Festkörperphysik, Technische Universität Berlin, Germany

Graphene nanoribbons, narrow stripes from graphene, allow in principle tailoring a band gap. The size of the gap depends critically on the width of the ribbons and the crystallographic orientation of the ribbon axis. Vibrational spectroscopy has proven a valuable tool for the determination of structural and electronic properties of carbon nanomaterials. Here we present the vibrational properties of graphene nanoribbons obtained by ab-initio calculations. We show the specific properties of armchair- and zigzag-edged ribbons and discuss how their vibrational signature can be determined in experimental spectra. We predict a width-dependent breathing-like mode, which can be useful for nanoribbon characterization. Furthermore, we determine by group theory the Raman and IR active modes and give selection rules for Raman scattering geometries. We discuss the similarities and differences to carbon nanotubes, such as zone-folding approach, splitting of the graphene optical phonon, and degeneracy of modes.



**18:30**

**Illuminating graphene nanostructures**

Elisa Molinari

S3 Istituto di Nanoscienze CNR, and Physics Dept, Modena, Modena

I will introduce the electronic properties and excitations of graphene ribbons [1] and quantum dots [2], and illustrate the effects of electron interactions by comparing graphene nanostructures with nanotubes and with related C-based semiconducting nanosystems. By discussing the fundamental underlying mechanisms I will also introduce strategies [3] for designing systems with novel and relevant optical and excitation spectra.

1. D. Prezzi, D. Varsano, A. Ruini, A. Marini, E. Molinari, Phys. Rev. B77, 041404 (2008).
2. D. Prezzi, D. Varsano, A. Ruini, E. Molinari, to be published.
3. C. Cocchi, M.J. Caldas, D. Prezzi, A. Ruini, E. Molinari, to be published.

**19:00****Electronic and vibrational properties of graphene under strain**Marcel Mohr<sup>1</sup> Konstantinos Papagelis<sup>2</sup> Janina Maultzsch<sup>1</sup> Christian Thomsen<sup>1</sup><sup>1</sup>Institut für Festkörperphysik, Technische Universität Berlin, Germany<sup>2</sup>Materials Science Department, University of Patras, 26504 Rio, Patras, Greece

Strain effects are important in epitaxially grown graphene or in graphene monolayers transferred onto flexible substrates. Understanding the changes of the electronic and vibrational properties under compressive and tensile strain helps to interpret recent experimental data. We apply ab-initio calculations to investigate changes of the electronic and vibrational spectrum by biaxial and uniaxial strain in arbitrary directions. Under small strain graphene remains semimetallic. The Dirac cones move away from the high-symmetry K-points. Raman spectroscopy has proven a valuable tool to detect and quantify strain fields in graphene samples. Polarized Raman measurements of uniaxially strained graphene sheets allow to determine the crystallographic orientation. However, the full phonon dispersions are needed, in order to understand strain-induced changes of the double-resonant D and 2D mode, which involve phonons from the Brillouin zone edge. Therefore, we calculate the vibrational spectrum in the whole Brillouin zone for different strain levels and analyze double resonant Raman scattering.

**19:30****Conductance of doped or functionalized nanowires, nanotubes and graphene**Xavier Blase<sup>1</sup> A. Lopez-Bezanilla<sup>2</sup> B. Biel<sup>2</sup> M.-V. Fernandez-Serra<sup>3</sup> P. Margine<sup>4</sup> S. Roche<sup>2</sup><sup>1</sup>CNRS/UJF, Institut Néel, Grenoble<sup>2</sup>CEA-INAC, Grenoble, France.<sup>3</sup>Dpt. Physics and Astronomy, Stony Brook University, NY<sup>4</sup>Department of Materials, Oxford University, UK

We will review in this presentation recent theoretical work aiming at understanding the impact of doping or functionalization on the transport properties of silicon nanowires [1], nanotubes [2] and graphene [4,5]. Based on ab initio calculations (DFT-Landauer formalism) we show that while in general the random modification of the conducting channel destroys quickly the conductance in 1D systems, strategies can be found to limitate, or exploit, the negative impact of random doping and functionalization. We show further that ab initio calculations can address the problem of the conductance of micrometer long tubes with hundreds of grafted molecules, bridging thus the gap between ab initio calculations and mesoscopic physics.

[1] X. Blase and M.-V. Fernández-Serra, Phys. Rev. Lett. **100**, 046802 (2008).

[2] A. Lopez-Bezanilla, F. Triozon, S. Latil, X. Blase, S. Roche, Nano Letters **9**, pp 940944 (2009).

[3] B. Biel, X. Blase, F. Triozon and S. Roche, Phys. Rev. Lett. **102**, 096803 (2009).

[4] A. Lherbier, X. Blase, Y.-M. Niquet, F. Triozon, S. Roche, Phys. Rev. Lett. **101**, 036808 (2008).



**THU 1****Encapsulation of electrical contacts for suspended SWNTs by atomic layer deposition**

Matthias Muoth<sup>1</sup> Kiran Chikkadi<sup>1</sup> Moritz Mattmann<sup>1</sup> Thomas Helbling<sup>1</sup> Christofer Hierold<sup>1</sup>

<sup>1</sup>Micro and Nanosystems, Department of Mechanical and Process Engineering, ETH Zurich, Zurich, Switzerland

We show encapsulation of suspended electrical contacts to single-walled carbon nanotubes (SWNTs) by selective nucleation of Al<sub>2</sub>O<sub>3</sub> from atomic layer deposition (ALD). Integration of suspended SWNTs instead of surface-bound nanotubes for electrical-transport-based devices minimizes influences from the supporting substrate. However, applicability of resist-based patterning to process suspended SWNTs is limited as freestanding structures are fragile. Passivating electrical contacts is often required to prevent degradation of devices [1] and for chemical sensing it separates sensing mechanisms either dedicated to metal contact regions or SWNT channels [2]. Typically, encapsulation of contacts was achieved before suspending SWNTs by etching a window into the protection layer. As ALD is known not to grow on clean SWNTs [3] it is applied here selectively on suspended contacts. TEM imaging on micromachined structures [4] enables to investigate the mask-less fabricated encapsulation.

1. Helbling T., Nanotechnology 20, 434010 (2009).
2. Mattmann M., Appl. Phys. Lett. 94, 183502 (2009).
3. Farmer D. B., Electrochem. Solid State Lett. 8, G89 (2005).
4. Muoth M., Proc. Chem. 1, 601 (2009).

**THU 2****Resonant Raman Scattering on Carbon Nanotubes Covalently Functionalized with Lithium Decyne**

Matthias Müller<sup>1</sup> J. Maultzsch<sup>1</sup> B. Gebhardt<sup>2</sup> Z. Syrgiannis<sup>2</sup> F. Hauke<sup>2</sup> A. Hirsch<sup>3</sup> C. Thomsen<sup>1</sup>

<sup>1</sup>Institut für Festkörperphysik, TU Berlin, Berlin

<sup>2</sup>Zentralinstitut für Neue Materialien und Prozesstechnik, Universität Erlangen-Nürnberg, Fürth

<sup>3</sup>Institut für Organische Chemie, Universität Erlangen-Nürnberg, Erlangen

We present Raman measurements on single carbon nanotubes (SWCNTs) covalently functionalized with lithium decyne. The reaction sequence is performed with two different decyne concentrations (5 and 50 equivalents related to mol carbon) yielding derivatives with different degree of functionalization. We study the influence of the moieties on the optical transitions of the nanotubes. From the extracted resonance profiles of the radial breathing modes (RBMs) the chiral indices of the

corresponding tubes are assigned [1]. We observe slight red shifts of the optical transitions, which implies only a little charge transfer due to the chemical reaction. The reaction shows a pronounced diameter dependence as previously observed for comparable reactions with different addends [2]. Additionally we discuss the present results in the context of the equilibrium conditions in the nucleophilic addition sequence. The performed defunctionalization procedure, including the interception of the addend molecules, yields CNT derivatives with a highly decreased amount of alkyne functionalities. [1] J. Maultzsch et al., Phys. Rev. B 72, 205438 (2005). [2] M. Müller et al., ChemPhysChem (2009), submitted

### THU 3

#### **Double resonant Raman spectra in graphene and graphite: a two-dimensional explanation of the Raman amplitude**

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We report calculated Raman spectra of the D and 2D modes in graphene and graphite. Evaluating the Raman amplitude in the two-dimensional Brillouin zone, we reproduce the splitting of the modes when going from single-layer graphene to graphite. The energy dependence of the D mode in graphene is 24%–32% smaller than in graphite. We discuss the intensity of the D line and show that the double resonant phonons originate from the low-symmetry parts of the Brillouin zone. A comparison with recent experiments performed by us in both graphene and graphite is presented and their results discussed in light of our calculations.

### THU 4

#### **Controllable synthesis of homogeneous titania/MWCNT composite materials**

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CNTs have been receiving much attention over the past years due to their properties. CNTs as well as their composites have wide potential applications, such as reinforced materials and nanoscale electronic devices. However, before CNTs are used as reinforcing additives in composites, there are two major obstacles such as the dispersibility of CNTs in the matrix and undesirable interface reaction between CNTs and matrix at high temperature. Preparation of homogeneous and stable inorganic coatings on the surface of multi-wall carbon nanotubes (CNTs) was the most efficient method to overcome these problems and was realized in this work.

Precursor compounds such as  $\text{TiBr}_4$ ,  $\text{TiCl}_4$ ,  $\text{Ti}(\text{OPri})_4$  and  $\text{Ti}(\text{OEt})_4$  were used to cover the surface of CNTs under either solvent-free or solution conditions. Using the solvent method, organic compounds of various polarities have been tested. By varying the speed of hydrolysis we proved that the most homogeneous composite material can be prepared by slow hydrolysis. As-prepared titania layers were characterized by TEM, SEM, and X-ray diffraction techniques. Results revealed that homogenous coverage can be achieved in a controllable way.

#### THU 5

##### **Infrared and Raman spectra of hydrogenated HiPCo nanotubes**

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We applied two different synthetic routes to hydrogenated HiPCo single-walled carbon nanotubes. Both synthetic methods were reductive. In the first one, the reductive agent was melted potassium which doped and exfoliated the nanotube bundles, so before hydrogenation all of the tubes had become metallic. In the second one, reduction occurs just before hydrogenation by naphthalenide radical anions. We characterized the products by wide-range infrared (30–12000  $\text{cm}^{-1}$ ) and Raman spectroscopy, with special emphasis on selectivity of the two methods. Our measurements show that while the second method is diameter-selective (smaller diameter tubes react more readily due to higher curvature and more strained structure), in the first case the bandgap selectivity dominates (small bandgap tubes have a higher reactivity, because initial doping is easier in their case).

#### THU 6

##### **Infrared light sensing using silicon/fullerene heterojunctions**

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Silicon/fullerene heterojunctions as a novel light sensing scheme that allows the detection of near to mid IR light are discussed. The heterojunction consists of a boron doped p-Si wafer with a fullerene layer (spin-coated methanofullerene [6,6] phenyl C61 butyric acid methyl ester, PCBM). For device characterization, Al contacts are evaporated. To ensure an Ohmic contact of the Al to the p-Si wafer, the Al/p-Si contact is alloyed at 580°C in a nitrogen/hydrogen atmosphere. Under broadband light IR illumination from a tungsten lamp, spectrally restricted by a high energy cut off silicon filter, the IV characteristics resemble the features of a photovoltaic device. The photocurrent between 77K and 300K has been spectrally

resolved by Fourier transform infrared spectroscopy. At 77K an open circuit voltage of 0.5 V and a finite short circuit current of  $40 \text{ nA cm}^{-2}$  is measured. The observed current threshold and the spectral behaviour is explained by a in real space indirect absorption mechanism from the valence band of Si into the the LUMO of the fullerene. Possible applications by the realization of optoelectronic devices are shown.

#### THU 7

##### **Palladium as catalyst for the CVD growth of helical carbon nanotubes**

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Palladium in the form of nano particles has been used earlier for both the growth of Y-shaped and helical carbon nanotubes (CNT). Moreover, palladium in combination with CNTs has also other interesting characteristics. Pd nano particle decorated bambooish CNTs give for example the possibility of catalytic active materials in pH ranges where nano particles usually would be oxidized and inactivated. Also fuel cells rely on highly active catalysts. Again, Pd decorated CNTs show high potential in that field given by the ability of oxygen reduction and the reduced cost compared to platinum-based techniques. We combine Pd and CNTs directly in our approach to synthesize CNTs. We use fullerene supported nano Pd particles as catalyst. The catalyst particles are produced in a wet chemistry process and then applied to silicon substrates. The growth is conducted in a standard CVD setup using acetylene as precursor. Hereby we gain the possibility to produce all different kind of nano structures up to helical and decorated CNTs in one single step. We also demonstrate the activity of the catalyst with different precursors, additives and parameters. The samples are investigated mainly by TEM.

#### THU 8

##### **SATURABLE ABSORBERS for SOLID STATE LASERS in FORM of HOLEY FIBERS FILLED with SINGLE-WALL CARBON NANOTUBES**

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Saturable absorbers (SA) in form of different media (liquids, polymers) with embedded single-wall carbon nanotubes (SWNTs) already have shown their efficiency in formation of sub-picosecond pulses in solid state lasers [1-4]. One of the main limitations is a thermal degradation of such elements in a powerful laser beam. For fiber lasers the best solution could be to get a piece of fiber containing the distributed nanotubes in the core. Unfortunately the fiber preparation temperatures



(exceeding 1000 K) are destructive for SWNTs. In this work we demonstrate SA formed via a RT filling of the holey fiber with an aqueous SWNT suspension, followed by drying. The evanescent field of the light propagating in the fiber interacts with the thin SWNT films deposited onto the walls of holes. The number of holes can be varied. Thus, an all-fiber SWNT saturable absorber has been realized. It provided a mode locking regime with the sub-picosecond output pulses in the Er-fiber laser. Thanks for support to RFBR and RAS projects. 1. N.N. Il'ichev et al. Quantum Electronics 34,572(2004). 2. A.V. Tausenev et al. APL 92,171113(2008). 3. M.A. Solodyankin et al., Optics Letters 33, 1336 (2008).

#### THU 9

##### **Effect of matrix on ultrafast kinetics of photoexcitation in single wall carbon nanotubes**

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This work is devoted to investigation with different pump-probe energies of femtosecond kinetics of photoexcitation in single wall carbon nanotubes (SWNTs) embedded in different media (carboxymethylcellulose, water and air). As it has been reported before the typical pump-probe kinetics of SWNTs consists of two major parts corresponding to the intra- and inter-band excitations [1,2]. In this work we report on dependence of the characteristic decay times of these excitations on the matrix surrounding SWNTs in the samples studied. We have found that the matrix removal leads to a substantial shortening of the exciton lifetimes. We assume that this effect can be attributed to the SWNT arrangement and to a possible difference in bundling degree in the samples. The work was supported by BIMORE FP6 Marie Curie network, RFBR and RAS projects. 1. L. Luer et al., PRL 102, 127401 (2009). 2. J. Wang et al., arXiv: 0911.2283v1.

**THU 10****Scanning Tunneling Spectroscopy on the Local Electronic Structure of Gd@C<sub>82</sub> Peapods**Kazunori Ohashi<sup>1</sup> Naoki Imazu<sup>1</sup> Ryo Kitaura<sup>1</sup> Hisanori Shinohara<sup>1</sup><sup>1</sup>Nagoya University, Nagoya

Metallofullerenes encapsulated in single-walled carbon nanotubes (SWCNTs) significantly modify the local electronic structure of SWCNTs [1,2]. In order to elucidate the origin of the encapsulation-induced electronic modification of SWCNTs, we performed STM/STS measurement on gadolinium metallofullerene (Gd@C<sub>82</sub>) nanopeapods. SWCNTs synthesized by arc-discharge method (Meijo Carbon, SWCNT SO type, diameter: 1.3-1.5 nm) were used to prepare the peapod. STM/STS measurements were performed with an Omicron VT-STM at RT.

We found that periodic spatial variations of the DOS at an interval of ca. 1 nm (equal to the intermolecular distance of neighboring Gd@C<sub>82</sub> molecules) were observed in STM/STS results even at RT. We also found that the periodic modifications depend on the bias voltage applied during STM observations, suggesting that charge transfer between metallofullerenes and SWCNT is a major factor in the periodic modulations.

[1] J. Lee et al., *Nature*, **415**, 1005 (2002).

[2] D. J. Hornbaker et al., *Science*, **295**, 828 (2002).

**THU 11****Growth of CdS nanoparticles on carbon nanotube arrays and electroluminescent properties of CdS/CNT hybrid material**Alexander V Okotrub<sup>1</sup> Yulia A Algaer<sup>1</sup> Artem V Guselnikov<sup>1</sup> Ursula O Kostas<sup>1</sup> Igor P Asanov<sup>1</sup> Lyubov G Bulusheva<sup>1</sup><sup>1</sup>Nikolaev Institute of Inorganic Chemistry SB RAS, Siberian Branch Russian Academy of Science, Novosibirsk

We developed a method for nucleation and growth of CdS nanoparticles on the surface and the ends of aligned multiwall carbon nanotubes (CNTs). Scanning electron microscopy (SEM) examination of the CNT arrays showed that changing the process of CdS deposition the nanoparticles with different shape and agglomerates of nanoparticles are obtaining. Depending on the synthesis conditions the size of the nanoparticles varies from 5 to 100 nm. The structure of the CdS nanoparticles was studied using high-resolution transmission electron microscopy. The electron diffraction carried out for different CdS nanoparticles showed the formation of hexagonal crystal lattice. Electronic state of elements in CdS/CNT hybrid material was examined using x-ray photoelectron spectroscopy. The shift of binding energy of Cd 3d<sub>5/2</sub> and S 2p<sub>3/2</sub> lines was detected compared to the bulk CdS. Electroluminescence properties of CdS nanoparticles deposited at the CNT tips were measured in the conditions of field electron emission from the CNT array.

**THU 12****Automated preparation of high-quality epitaxial graphene on 6H-SiC(0001)**Markus Ostler<sup>1</sup> Florian Speck<sup>1</sup> Markus Gick<sup>1</sup> Thomas Seyller<sup>1</sup><sup>1</sup>Lehrstuhl für Technische Physik, Universität Erlangen-Nürnberg, Erlangen

Thermal decomposition of silicon carbide is a viable route for preparing graphene films. In contrast to other methods it has the potential for upscaling graphene synthesis to a wafer scale and the advantage of providing an insulating substrate at the same time. In particular, graphenization of SiC(0001) surfaces in Ar atmosphere has been shown to yield graphene films superior to UHV-grown epitaxial graphene. In this contribution we present details on a recently installed hot-wall reactor for graphene growth on SiC in Ar. Both preparation steps, i.e. the preconditioning of the SiC substrate by hydrogen etching and the graphene growth are performed in this setup in a fully automated manner thus ensuring the preparation of high-quality graphene on an everyday basis. Samples were characterized by atomic force microscopy (AFM) and x-ray induced photoelectron spectroscopy (XPS). We present results on the optimization of the hydrogen etching procedure. The thickness distribution of graphene samples grown in the automated process is Gaussian with a mean value of 1.1 monolayers and a standard deviation of 0.15 monolayers. This indicates a highly controlled process.

**THU 13****Tip-enhanced Raman scattering on single-wall carbon nanotubes**Niculina Peica<sup>1</sup> Christian Thomsen<sup>1</sup> Janina Maultzsch<sup>1</sup><sup>1</sup>Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

The radial breathing mode (RBM) in the Raman spectrum of carbon nanotubes is one of the key spectroscopic signatures for both identification of single-wall carbon nanotubes (SWCNTs) and determination of the chiral indices (n,m). However, if the excitation wavelength is too far away from the resonance condition, it seems not possible to observe the RBM of individual tubes. Here we show by tip-enhanced Raman scattering (TERS) on small bundles that the RBMs are well-visible in near-field, even if they are not observable in far-field. Enhancement factors in TERS greater than  $10^4$ , depending on the thickness of the Au coating of the tip, the sharpness of the tip and the tube sensitivity under the incident excitation were observed. Furthermore, by comparing confocal Raman and TERS spectra, we discuss the local character of different Raman modes in SWCNTs and the strong dependence of the TERS signal on the distance between the tip and the sample.

**THU 14****A new figure of merit for nanotube based transparent conductors**Áron Pekker<sup>1</sup> Katalin Kamarás<sup>1</sup><sup>1</sup>Research Institute for Solid State Physics and Optics, Budapest

The most promising application of carbon nanotubes is that of transparent conductors. Owing to the variety in electrical and optical properties of different nanotube types, a figure of merit which uniquely characterizes each material is profoundly needed. In the general case of transparent conductors, this value is usually some combination of the transmission ( $T$ ) and the sheet resistivity ( $R_{sq}$ ) of the sample. Our figure of merit is based on the fact that the optical density ( $-\log T$ ) and the sheet conductivity ( $S_{sq}=1/R_{sq}$ ) both depend linearly on the sample thickness. The transmission and sheet conductance values of samples of the same material with different thickness fall on a line on a  $S_{sq}$  vs.  $-\log T$  plot. We propose the figure of merit to be the slope of this line, which has several advantages over previously used values: it is independent of thickness, easy to calculate, and the graphical representation of the data makes it simple to predict the way of optimization. We will present four point conductivity and transmission (from IR to UV) measurements on thin films of various modified and unmodified nanotubes to demonstrate the usefulness of our method.

**THU 15****The Physics Of Carbon Nanotube Interfaces**Marta Pelc<sup>1</sup> Włodzimierz Jaskolski<sup>1</sup> Leonor Chico<sup>2</sup> Hernan Santos<sup>2</sup> Andres Ayuela<sup>3</sup><sup>1</sup>Institute of Physics, Nicolaus Copernicus University, Torun<sup>2</sup>Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, 28049 Madrid, Spain<sup>3</sup>Centro de Física de Materiales de Madrid, CSIC-UVF/EHU, Departamento de Física de Materiales (Facultad de Químicas), and Donostia International Physics Center (DIPC), 20080 Donostia, Spain

Carbon nanotubes (CN) are currently regarded as one of the most promising materials to develop future nanoelectronics. Progress in this field towards real applications depends on the ability to form junctions between different tubes, as the controlled synthesis of CN's intramolecular junctions reported recently [1]. The subject of our study is the nature and origin of interface states in CN intramolecular junctions between tubes, relevant for electronic properties around Fermi level, such as transport properties. First we focus on achiral junctions between (n,n) and (2n,0) tubes. Our results show that these states, usually attributed to the presence of topological defects, are actually related to the graphene zigzag edge states, such as those appearing in graphene zigzag nanoribbons. Afterward, we have studied the effect of a constant external magnetic field on the energy spectrum of CN junctions [2]. Here we concentrate on the behavior of interface states when a magnetic field

is applied parallel to the nanotube axis.

[1] C. Jin, K. Suenaga, and S. Iijima, *Nature Nanotech.* 3, 17 (2008)

[2] H. Santos, A. Ayuela, W. Jaskólski, M. Pelc and L. Chico, *Phys. Rev. B* 80, 035436 (2009)

#### THU 16

##### **Nature of the metallic ground state in intercalated metallicity selected single wall carbon nanotubes**

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In this contribution we present recent results on the details of the electronic properties of intercalated metallicity selected single wall carbon nanotubes buckypaper samples using high energy spectroscopy as probe. The consequences of doping on the nature of the metallic ground state in metallic tubes as well as the semiconductor to metal transition in semiconducting tubes are elucidated in detail. Special emphasis will be given on the intercalation dependent change of the interaction between the metallic tubes in a bundle, yielding a transition of the 1D metallic Tomonaga-Luttinger liquid ground state to a normal 3D Fermi liquid. The impact of these results in accessing the maximum conductivity in carbon based conducting transparent electrodes will be discussed.

Work supported by the DFG projects PI 440 3/4/5 and FWF project P21333-N20.

#### THU 17

##### **Theoretical phonon dispersion of graphene and metallic carbon nanotubes beyond the adiabatic approximation**

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The dynamic corrections to the phonon dispersion of graphene and metallic carbon nanotubes are studied systematically within a non-orthogonal tight-binding model. We reproduce the results of previous estimations of the dynamic and doping effects on the G-modes of graphene and metallic carbon nanotubes. In addition, we present new results for these effects on the phonon dispersion of graphene and on the G-modes of a large number of metallic nanotubes.

**THU 18****Improved sorting of carbon nanotubes according to electronic structure using density gradient ultracentrifugation**

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So far as-produced carbon nanotubes constitute always a complex mixture of different chiralities which hinders their application in electronics, sensing and optics to a large extend. Recently, Arnold et al. reported on sorting of carbon nanotubes using density gradient ultracentrifugation (DGU) by enhancing the mass differences between the tubes by a non-covalent adsorption of surfactants that allows discriminating between different types of tubes. They and other groups were able to show that by using this method, sorting by bandgap, diameter, electronic type and even chirality is possible (1,2).

We report on an improved way of sorting according to the electronic type by applying a two-step procedure. In the first step, we sorted for semiconducting tubes. In the second step, the sorted fractions were reinserted and DGU was carried out under conditions which allow to winnow metallic carbon nanotubes to a high extend. Applying this procedure, the content of metallic carbon nanotubes could be reduced to 11 % starting from an original value of 38 %.

(1) M. Arnold et al. Nat. Nanotechnol. 1 (2006) 60

(2) R. Fleurier et al. Adv. Func. Mater. 19 (2009) 2219

**THU 19****Evolution of the Raman intensity and the transport properties of single-walled carbon nanotubes in various stages of electrochemical doping**

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We monitored the full sequence of electrochemical p-doping of a SWNT bundle sample in a KCl solution from double-layer charging to intercalation and functionalization with Raman spectroscopy, scanning electron microscopy and trans-

port measurements. The different doping dependences of the Raman intensity of metallic and semiconducting SWNTs are explained with the excitonic nature of the Raman effect in these nanotube species. Raman spectra of the second-order D\* mode as well as temperature dependent conductivity measurements indicate a decreasing metallicity of the sample with increasing doping level. We attribute this phenomenon to changes in the density of states of metallic SWNTs.

#### THU 20

##### **Catastrophe theory of caustics in single and bilayer Graphene: the fine structure of caustics**

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We study the scattering of electrons on a circular p-n junction in single and bilayer graphene in the semiclassical limit. Recent studies have shown that caustics appear in these systems due to a negative refractive index; the curves of the caustics can be calculated using differential geometry with the well-known Snell's law [1]. Caustics, which are envelopes of a family of rays at which the density of rays is singular, cannot be treated with geometrical optics, not even in the short wavelength limit. Here we present a method to calculate the caustics using the integral representation developed in catastrophe optics. We demonstrate that the wavefunction obtained by this approximate method is in excellent agreement with the exact wavefunction in the vicinity of the caustics, enabling the study of caustics even in systems where an analytical study is difficult or impossible. The results can be used for quantitative predictions, even in the case of divergent caustics. We also verify the universal scaling laws that govern the asymptotic behavior of the wave function in the limit where the wavenumber grows to infinity.

[1] Cs. Péterfalvi, A. Pályi and J. Cserti, Phys. Rev. B **80**, 075416 (2009).

#### THU 21

##### **Extended graphene flakes prepared by chemical vapor deposition**

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Graphene has already become one of the most famous nanomaterials for electronic applications [1]. The CVD technique for a large-scale graphene production from CH<sub>4</sub>/H<sub>2</sub> mixture has been proposed by the end of 2008 [2]. Here we present the modified CVD method of graphene growth. A very simple hand-made installation has been designed. The thin nickel and copper [3] foils (50 m and 25 m corre-

spondingly) were used as substrates. Different parameters of the process have been optimized to get a monolayer graphene of the best quality. One of the advantages of this method is an easy transfer of the graphene sheets onto any substrate. The graphene onto SiO<sub>2</sub>/Si substrate has shown the Raman picks positioned at 1582 cm<sup>-1</sup> and at 2682 cm<sup>-1</sup>. The glass and PDMS substrates were used for absorbance measurements of the graphene films. Taking into account the constant absorbance of each graphene layer of 2.3 percent we have estimated the layer number in different flakes.

Thanks for support RFBR 07-05-01505

[1] Rybin, etc. J. Nanoelectron. Optoelectron. 4, 239-242 (2009)

<http://www.aspbs.com/jno/>

[2] Yu, etc. APL, 93, 113103 (2008)

[3] Li, etc. Science, 324, 1312-1314 (2009)

## THU 22

### Interaction between carbon nanotubes and alkyl derivatives

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Among the various carbon allotropes, carbon nanotubes are incomparably versatile as, by passing from one tube to another, substantial change of their physical properties occurs: Depending upon the chirality, there are nanotubes that are metallic as well there are semiconducting ones. This big advantage acts also as a drawback as the synthesis process provides carbon nanotubes with different chiralities within the same batch. The selection of a single kind of nanotubes with the desired chirality is thus of big technological relevance. A possible way of achieving this purpose is exploiting the selective way some surfactants interact with some nanotubes belonging to a specific family. In the present work we consider the nanotubes interaction with an alkyl derivative that is able to isolate and solubilize nanotubes in water. Slight variations of the conformation of the compounds imply changes in the final product of the nanotubes suspensions. Optical analysis techniques, exploiting PLE and absorption spectroscopy, are performed in order to investigate and highlight the effects of the different compounds.



**THU 23****Catalyst and Diameter Dependent Growth of Carbon Nanotubes Determined Through Nano Test Tube Chemistry**

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Nano test tube chemistry uses the volumetric space inside single-walled carbon nanotubes to encapsulate atoms and molecules. This allows chemical reactions to be confined at the nanoscale such that individual chemistry processes can be traced at the molecular level. The inside of carbon nanotubes is free from contaminations and encapsulated precursor compounds provide elemental sources in a designer proportion. We use this unique method to study catalytic growth properties of carbon nanotubes. In our recent work two model metal catalysts, Fe and Pt, were prepared together with carbon feedstock via encapsulations of original single wall tubes with ferrocene and Pt(II) acetylacetonate, respectively. A combination of Raman spectroscopy and transmission electron microscopy allows precise and quantitative information of the growth properties to be obtained. Details of determined activation temperatures for specific chirality tubes and catalysts will be presented. Such information would be fundamental to possibly exercise control of chirality on the growth of carbon nanotubes on the bulk scale.

**THU 24****Metallicity selected Raman response for double-walled carbon nanotubes**

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Double-walled carbon nanotubes were prepared from SWCNTs separated according to their metallicity. The separation for the SWCNTs was performed with the density gradient ultracentrifugation method and DWCNTs were grown from from C<sub>60</sub> peapod precursors. The Raman spectra of the RBM range for inner tubes showed selectively the response from only different metallic or only different semiconducting outer tubes depending on whether the mother-tube system was metallic or semiconducting. A comprehensive resonant Raman study using a tunable laser system allows assignment of the inner tube RBM modes and their interaction with the outer tubes in detail. It provided characterization of the abundance of given inner/outer tube pairs selectively for the semiconducting and metallic outer tubes in the samples. Support from the Austrian science funds, FWF Nr. P21333-N20 is acknowledged.

**THU 25****Influence of the Surface Properties of the Alumina Support on the Growth of Millimeter Thick Carpet of Carbon Nanotubes**Rita Smajda<sup>1</sup> Arnaud Magrez<sup>2</sup> Klára Hernádi<sup>1</sup><sup>1</sup>Department of Applied and Environmental Chemistry, University of Szeged, Szeged<sup>2</sup>Institute of Physics of Complex Matter, Ecole Polytechnique Fédérale de Lausanne

Growth of millimeter thick carpet of CNTs has been achieved by introducing traces of water vapor together with the carbon source into the reactor.[1, 2] However, such a process is highly demanding and reproducible with difficulty. In particular, the compositional window of the reactor atmosphere (containing H<sub>2</sub>, Ar, C<sub>2</sub>H<sub>4</sub>, and H<sub>2</sub>O) is very narrow for efficiently enhancing the CNTs growth rate.[3] Here, we will present the effect of different chemical modifications of the alumina support surface on the thickness and growth rate of CNTs carpet. After suitable modification of Al<sub>2</sub>O<sub>3</sub> surface, the CNTs growth kinetics is much less dependent on the reactor atmosphere. The deposition of amorphous carbon beside CNTs is also drastically reduced as compared to the water assisted process.[4] The influence of numerous growth parameters such as the nature of metal catalyst, catalyst thickness will be presented as well as the characterization of the CNTs produced.

1.K. Hata, et al. Science, 306, 2004, 1362

2.R. Smajda, et al. Phys. Status Solidi B, 2009

3.K. Hasegawa, et al J. Nanoscience Nanotech 8, 2008, 6123

4.Y. Yasuda, et al Nano Letters 9, 2009,769

**THU 26****Study of tube-substrate interaction in carbon nanotube serpentines**Jaqueline S. Soares<sup>1</sup> A. P. M. Barboza<sup>1</sup> D. Nakabayashi<sup>1</sup> N. Shadmi<sup>2</sup> T. S. Yarden<sup>2</sup>A. Ismach<sup>2</sup> N. Geblinger<sup>2</sup> E. Joselevich<sup>2</sup> C. Vilani<sup>3</sup> L. G. Cançado<sup>1</sup> L. Novotny<sup>4</sup>G. Dresselhaus<sup>5</sup> M. S. Dresselhaus<sup>6</sup> B. R. A. Neves<sup>1</sup> M. S. C. Mazzoni<sup>1</sup> A. Jorio<sup>1</sup><sup>1</sup>Dept. Física, UFMG, Belo Horizonte<sup>2</sup>Dept. of Materials and Interfaces, Weizmann Institute of Science, Rehovot, 76100, Israel<sup>3</sup>Divisão de Metrologia de Materiais, INMETRO, Duque de Caxias, RJ, 25250-020, Brazil<sup>4</sup>Institute of Optics, U. of Rochester, Rochester, 14627, New York<sup>5</sup>Francis Bitter Magnet Laboratory, MIT, Cambridge, 02139, MA<sup>6</sup>Dept. of Physics and Dept. of Electrical Engineering and Computer Science, MIT, Cambridge, 02139, MA

Due to an unusually large surface-to-volume aspect ratio, single wall carbon nanotubes (SWNTs) are strongly affected by the environment. Recently, combined surface- and flow-directed growth enables the controlled formation of carbon nanotube serpentines (parallel tube flat segments connected by U-turns) on top of

crystalline quartz [1]. In this work we study these carbon nanotube serpentines, using Raman spectroscopy, to obtain information about tube-substrate interaction. Because of the sample morphology, i.e. the tube-substrate orientation varies along the U-turns, the effect of nanotube-substrate interaction is modulated and this modulation can be measured along the same physical nanotube. Important changes in the Raman spectra are observed, and these changes are clearly related to tube-substrate morphology and growth direction. The results are associated with doping, strain and growth dynamics, as discussed in our work. Scanning electron microscopy, electric force microscopy and density functional theory calculations are used to support our claims.

[1] N. Geblinger, A. Ismach and E Joselevich, *Nature Nanotechnology* 3, 195-200 (2008).

#### THU 27

##### **In-situ electrical conductivity and Raman study of C60 polymer under high pressures using designer diamond anvil cell**

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It was predicted that tetragonally polymerized C60 will transform from two-dimensional (2D) to three-dimensional (3D) polymer under uniaxial pressure of about 20 GPa. The new polymeric phase is expected to have metallic properties. Raman [2] and structural[3] experiments at high pressures confirmed formation of the new phase above 20 GPa although the question about it's electrical properties was still open. Here we report on the first simultaneous study of vibrational and electrical properties of 2D tetragonal C60 polymer at pressures up to 30 GPa. Anomalies were observed both in electrical conductivity and Raman spectra of the material at 15 and 25 GPa. The latter anomaly we tentatively associate with a phase transition into the conductive 3D polymeric C60. At high pressures the Raman spectra exhibit a high degree of disorder. Upon pressure release the order was partially restored although the initial 2D polymeric structure was not recovered.

[1] S. Okada, et al. *Phys. Rev. Lett.* 83, 1986 (1999). [2] K.P. Meletov, et al. *Phys. Rev. B* 63, 54106 (2001). [3] D.H. Chi, et al. *Phys. Rev. B* 68, 153402 (2003).

**THU 28****Temperature-independent current deficit due to induced nanowire vibrations**Gustav Sonne

Department of Physics, University of Gothenburg, Gothenburg, Sweden

Electronic transport through a suspended voltage-biased nanowire subject to a transverse magnetic field is considered. Extending on previously reported results (R. I. Shekther *et al.*, PRL **97**, 156801 (2006)) it is shown that the magnetic field — which acts to induce coupling between the tunneling electrons and the vibrational modes of the wire — not only affects the linear conductance as previously reported but also alters the current in novel ways. In particular it is found that at high bias voltage the system exhibits a temperature- and bias voltage independent current deficit as compared to the current at zero magnetic field. Furthermore, it is found that corrections to the current from the back-action of the vibrating wire decay exponentially in the high bias limit, a result which holds even if the nanowire vibrational modes have been driven out of thermal equilibrium.

**THU 29****Silver nanowire networks as flexible, transparent, conducting films: Linear variation of the DC conductivity with length and diameter**Sophie Sorel

Trinity College Dublin, Dublin

Thin transparent conducting films are critical for building many optoelectronic devices and components. Such films are usually made from doped metal oxides such as Indium Tin Oxide (ITO), which shows major drawbacks such as cost, brittleness and high temperature processing used in its production. We have prepared thin, flexible, transparent, conducting films from aqueous dispersions of silver nanowires(1). We obtained a sheet resistance of less than  $1\ \Omega/\square$  for a film with optical transmittance (550nm) of 92 %. Those results make silver nanowires a possible replacement for ITO. In order to fully exploit such applicable properties the factors controlling the film conductivity must be understood. These films exhibit a transition from network to bulk-like DC conductivities at thicknesses of  $160\text{nm}$ (1). By measuring the DC conductivity above this saturation point for a selection of nanowires with lengths,  $L$ , and diameters,  $D$ , varying from  $51\text{nm}$  to  $105\text{nm}$  and  $7.1\mu\text{m}$  to  $44\mu\text{m}$  respectively we expect to see the DC conductivity vary as  $LD^n$  where  $n \approx 4$ . (1)De et al. Silver nanowire networks as flexible, transparent, conducting films: extremely high DC to optical conductivity ratio. ACSNano

**THU 30****Raman spectroscopy on etched graphene nanoribbons**C. Stampfer<sup>1</sup> D. Bischoff<sup>2</sup> J. Güttinger<sup>2</sup> S. Dröscher<sup>2</sup> T. Ihn<sup>2</sup> K. Ensslin<sup>2</sup><sup>1</sup>JARA-FIT and II. Institute of Physics, RWTH Aachen, 52074 Aachen, Germany<sup>2</sup>Solid State Physics Laboratory, ETH Zurich, 8093 Zurich, Switzerland

We report on confocal Raman spectroscopy experiments on etched graphene nanoribbons with different widths ranging from 30 to 130 nm. We show (i) that the single-layer graphene character is still well preserved, (ii) that the absolute G-line and 2D-line intensities scale with the nanoribbon width, whereas (iii) the D-line intensity does not. Consequently we find that the D-line intensity depends only on the nanoribbon edge and its roughness, which can be further analyzed by performing polarization dependent measurements. Finally we observe that the positions of the G- and 2D-line shift towards smaller energies for decreasing ribbon width.

**THU 31****Multiwall carbon nanotubes purification and oxidation by nitric acid studied by the FTIR and electron spectroscopy methods**L. Stobinski<sup>1</sup> B. Lesiak<sup>2</sup> L. Kövér<sup>3</sup> J. Tóth<sup>3</sup> S. Biniak<sup>4</sup> G. Trykowski<sup>4</sup> J. Judek<sup>5</sup><sup>1</sup>Inst. Phys. Chem. PAS, Warsaw, Poland and Fac. Mat. Scien. and Eng., Warsaw Univ. Tech., Warsaw, Poland<sup>2</sup>Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland<sup>3</sup>Institute of Nuclear Research, Hungarian Academy of Sciences (ATOMKI), H-4001 Debrecen, P.O. Box 51, Hungary<sup>4</sup>Faculty of Chemistry, Nicolaus Copernicus University, Gagarina 7, 87-100 Toruń, Poland<sup>5</sup>Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warsaw, Poland

The process of wet chemical purification, oxidation and functionalization of multiwall carbon nanotubes (MWCNTs) is investigated. The aim of this work is to determine the structural and chemical changes in atomic bonding state under oxidation reaction in aqueous solution of concentrated HNO<sub>3</sub> at 120 °C. The as-prepared (denoted as MWCNTs) and oxidized (denoted as ox-MWCNTs) multiwall carbon nanotubes are studied using TEM, SEM, elemental analysis, mass spectrometry (ICP-MS), EDS, FTIR, Raman and electron spectroscopic methods, i.e. XPS, XAES, EPES, EELS and REELS. The proposed wet chemical purification and modification of MWCNTs, contaminated with amorphous carbon, catalyst supports and metallic catalysts results in the effective removal of all impurities coming from the catalytic reaction used to obtain the “as-received” MWCNTs. Additionally, the purified MWCNTs provide the standard material to be functionalized with different chemical groups, such as –COOH and –OH, changing their hydrophobic nature into a hydrophilic one.

**THU 32****Horizontally Aligned CVD Grown Single-Walled Carbon Nanotubes on Silicon - Stressed or Relaxed?**Ninette Stuerzl<sup>1</sup> Sharali Malik<sup>1</sup> Sergei Lebedkin<sup>1</sup> Yan Li<sup>2</sup> Manfred Kappes<sup>3</sup><sup>1</sup>Institut für Nanotechnologie (INT), Karlsruhe Institut für Technologie (KIT), Eggenstein-Leopoldshafen<sup>2</sup>Nanomaterials & Nanostructures Group, Peking University, Beijing<sup>3</sup>Institut für Physikalische Chemie Mikroskopischer Systeme, Karlsruhe Institut für Technologie (KIT), Karlsruhe

Horizontally aligned, individual single-walled carbon nanotubes (SWNTs) were grown on Si/SiO<sub>2</sub> substrates by applying chemical vapor deposition (CVD) at very low feeding gas flow rates at 970°C<sup>1</sup> and characterized by scanning electron (SEM), atomic force (AFM) and photoluminescence (PL) microscopy.<sup>2</sup>

In particular, strain effects on SWNTs were investigated in this work by means of PL microscopy. Strain in SWNTs results initially from an interplay between thermal compression of a tube and a substrate (by cooling down from the process to room temperature) as well as their interactions (adhesion of the tube to the substrate). Strain was also induced and relaxed in selected nanotube sites by their mechanical manipulation (bending, rupture) with an AFM tip. Furthermore, a focused ion beam (FIB) was applied as a well-defined cutting tool for SWNTs. Strain relaxation was observed for the FIB-cut ends of nanotubes.

1) Z. Jin et al., Nano Lett. 7, 2073 (2007) 2) O. Kiowski et al., Phys. Rev. B, 80, 075426 (2009)

**THU 33****Synthesis, characterization and applications of nitrogen-doped SWCNTs films**Toma Susi<sup>1</sup> Paola Ayala<sup>2</sup> Albert Nasibulin<sup>1</sup> Hong Lin<sup>3</sup> Raul Arenal<sup>4</sup> Jérôme Lagoute<sup>3</sup>Marina Zavodchikova<sup>1</sup> Dongming Sun<sup>5</sup> Cyrielle Roquelet<sup>6</sup> Yutaka Ohno<sup>6</sup> Jean-Sébastien Lauret<sup>6</sup> Annick Loiseau<sup>5</sup> Esko Kauppinen<sup>1</sup><sup>1</sup>NMG, Department of Applied Physics, Aalto University, Espoo, Finland<sup>2</sup>Fakultät für Physik, Universität Wien, Wien, Austria<sup>3</sup>MPQ, CNRS-U, Paris, France<sup>4</sup>LEM, ONERA-CNRS, Chatillon, France<sup>5</sup>Department of Quantum Engineering, Nagoya University, Nagoya, Japan<sup>6</sup>LPQM, ENS Cachan CNRS, Cachan, France

We have employed a method to synthesize N-doped single-walled CNTs using a gas phase floating catalyst reactor. The method practically allows depositing the as-grown material directly on various substrates in a simple continuous process using a hot iron wire/CO/ammonia system.

Optical absorption and Raman spectroscopy were performed on samples synthesized with varying amounts of ammonia. The nitrogen content was examined with

x-ray photoelectron spectroscopy and the corresponding line-shape analysis will be shown. Additionally, TEM/EELS observations were combined with STM/STS in order to locally understand the role of N atoms at the dopant sites. Furthermore, the electrical properties of the nanotube films were studied for possible application as transparent conducting films and as thin films transistors, where intrinsic n-type conduction was achieved. A well structured photoluminescence signal was also observed, demonstrating that low enough doping level preserves the electronic structure of the carbon nanotubes.

**THU 34****Continuous, Repeatable Separation of Metallic and Semiconducting Carbon Nanotubes Using Agarose Gel**

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Single wall carbon nanotubes (SWCNTs) have attracted a great deal of attention towards versatile applications, especially in the field of electronics. However, electrical heterogeneity of as-produced SWCNTs (metal/semiconductor) is one of the most crucial problems preventing useful application of SWCNTs. Previously, we reported novel separation methods of metallic and semiconducting SWCNTs (MS separation) using agarose gel. In this presentation, we report an improved method for the MS separation with high purities. When an SWCNTs/sodium dodecyl sulfate dispersion was applied to a column containing agarose gel beads, semiconducting SWCNTs were trapped by the beads, while metallic SWCNTs passed through the column. After the semiconducting SWCNTs adsorbed to the beads were eluted with sodium deoxycholate solution, the column could be used for repeated separation (1). Because this continuous, repeatable separation method is applicable to a low-cost, large-scale process, it should enable the industrial production of metallic and semiconducting SWCNTs.

This study was supported by the industrial technology research grant program of the New Energy and Industrial Technology Development Organization (NEDO) of Japan. (1) T. Tanaka et al., Appl. Phys. Express 2009, 2, 125002.

**THU 35****Raman intensities of the radial-breathing mode in carbon nanotubes: (n,m) abundances versus scattering efficiencies**

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Nanotube ensembles show strong variations in Raman intensities of the different tubes (n,m) which can either be interpreted as variations in the (n,m) abundances



or variations in the scattering efficiencies. In order to address this issue we collected Raman intensities of the radial breathing mode from a large number of different tubes (n,m) (HiPCO). To collect Raman intensities from resonantly excited tubes we varied the excitation energy between 1.15 and 2.15 eV. We observe systematic variations of the Raman intensities for different (n,m) including dependences on the optical transition, diameter  $d$ , family  $\nu$ , and chiral angle  $\theta$ . Here we focus on intensity variations depending on  $\nu$  and  $\theta$  which we contribute to variations in the exciton-phonon coupling. In particular, we observe an intensity minimum for nanotubes with  $\theta = 20$ . This finding corresponds to a minimum in the exciton-phonon coupling along the K-K direction in the Brillouin zone of graphene. Furthermore we discuss intensity variations which are due to different electronic broadening. The line width shows a dependence on  $d$  and varies between metallic and semiconducting tubes.

#### THU 36

##### **Nanostructured Devices Based on Graphene**

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Graphene is a two-dimensional form of crystalline carbon with unique electrical properties. This allotrope of carbon exhibits a high carrier mobility making it a prime-candidate for novel nano-electronic devices. Several graphene quantum devices have been recently reported, such as for example graphene nanoribbons, quantum interference devices and graphene single electron transistors. In this work, we report on the fabrication and characterization of several nanostructured graphene devices based on an effective band gap engineering approach. We show that the device functionality can be mostly determined by the shape of the nanostructured device. The graphene nanodevices are fabricated by mechanical exfoliation, lithography and dry etching techniques. Transport properties and electrostatic tunability of the graphene nanodevices are discussed.

#### THU 37

##### **Prostate cancer cells viability by Cisplatin-functionalized Multi-wall and Fe-filled Multi-wall carbon nanotubes treatment**

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The introduction of drug-carriers at the cellular level in the cure of cancer is necessary to embank the untoward side-effects caused by the chemotherapeutics administration: being not cell-selective, drug molecules affect every kind of tissue. Carbon

nanotubes inner space can be utilized to place those molecules within to be carried in a selective way. Moreover, tubes' magnetic properties are crucial to provide a driving force for the external magnetic fields: they can penetrate the body and localized in a target area where the uptake and the drug release are proper. The encapsulation of Cisplatin (CDDP) already involved SWNT, and its anticancer effect was recently reported by our group[1]. Here, we discuss the toxicity of MWNT and Fe-filled-MWNT endohedrally functionalized by CDDP. The CDDP release in physiological solution showed to be fast and complete after 48 h. In vitro experiments, performed using 2 different prostate cancer cell lines, confirmed the results obtained from the release analysis and indicated the drug efficacy preservation or lack of interaction with the tubes' inner wall. These data suggest the validity and higher efficiency of MWNT and Fe-MWNT as anticancer drug vectors in respect of SWNT. [1] C.Tripisciano et al., Chem.Phys.Lett., 478, (2009) 200-205.

#### THU 38

##### **The influence of incorporated $\beta$ -carotene on the radial breathing mode of carbon nanotubes**

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The extraordinary properties of carbon nanotubes (CNTs) make them attractive components for future optoelectronic devices. Nevertheless, to develop these very efficient devices the ability to tune the electronic properties of the CNTs *via* functionalization is required. Abe et al.[1] showed that the encapsulation of  $\beta$ -carotene, a molecule with a well known light-harvesting function in photosynthesis, into a CNT leads to a very fast excitation energy transfer from the  $\beta$ -carotene to the CNT, when the system is excited in the blue regime.

In this study we compare Raman data taken from CNTs incorporated with  $\beta$ -carotene with data derived from empty CNTs. We focus our analysis on the radial breathing mode (RBM) of the CNTs with respect to intensity and lineshape. Corresponding resonance profiles of the RBMs are presented and discussed in terms of changes in the nanotube electronic transition energies.

[1]Abe et al., Phys. Rev. B **77**, 165436 (2008)

**THU 39****Infrared and Raman investigation of carbon nanotube-based hybrid systems**Hajnalka Tóháti<sup>1</sup> Bea Botka<sup>2</sup> Katalin Németh<sup>1</sup> Áron Pekker<sup>1</sup> Katalin Kamarás<sup>1</sup><sup>1</sup>Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, Budapest, Hungary<sup>2</sup>Walther Meissner Institute for Low Temperature Research, Garching, Germany

Non-covalent functionalization of carbon nanotubes by polymers or aromatic systems is a rapidly emerging field. Its importance originates in the possibility of combining special (optical, electric or dispersive) properties of the added molecules with the mechanical stability of nanotubes. Crucial to all applications is a method to investigate the strength of interaction between nanotubes and the associated species. We use IR transmission and ATR spectroscopy as well as Raman spectroscopy to understand how these compounds cover the surface of the nanotube: the interaction of the evanescent field on the surface of the nanotube with the vibrations of the adsorbed species causes surface-attenuated infrared absorption (SAIRA) or surface-enhanced Raman scattering (SERS). We will demonstrate these effects on poly(allylamine hydrochloride) (PAH) that is widely used as a molecular glue between nanotubes and attached nanoparticles, on pyrene-based luminescent dye systems, and on luminescent rare-earth complexes with aromatic rings.

**THU 40****Functionalization of CNTs with luminescent Eu and Tb complexes**Anna Usoltseva<sup>1</sup> Andrea Parisini<sup>2</sup> Andrew Chuvilin<sup>3</sup> Arkadyi Ishenko<sup>4</sup> Hassan Tra-boulsi<sup>5</sup> Davide Bonifazi<sup>5</sup> Julien Amadou<sup>1</sup><sup>1</sup>Nanocyl S.A., Sambreville, Belgium<sup>2</sup>CNR-IMM, Bologna, Italy<sup>3</sup>nanoGUNE, Donostia - San Sebastian, Spain<sup>4</sup>Boreskov Institute of catalysis, Novosibirsk, Russia<sup>5</sup>FUNDP, Namur, Belgium

Functionalization of carbon nanotubes (CNTs) has now attracted increasing attention due to considerable improvement of their properties allowed development of new CNT-based materials in the fields of sensors, photoactive materials, and nanodevices. Here we present the results concerning opening of multi-wall carbon nanotubes with following their functionalization with luminescent complexes of rare-earth elements. The influence of type of oxidative treatment on the availability of carbon nanotubes for filling or decoration with Eu and Tb complexes was investigated. The structure of "CNTs-luminescent complexes" composites and the position of lanthanide-containing particles were studied with using of HR TEM, UV-Vis and X-ray photoelectron spectroscopy. It was shown that via variation of conditions of opening and functionalization of CNTs the luminescent material can be deposited as inside nanotubes as on their outer surface. Photoluminescent

properties of obtained composites made them perspective objects for development of new CNT-based materials.

**THU 41****Conductivity Versus Gate Voltage Hysteresis in Graphene Field Effect Transistors Due to Water Doping**

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A recent discovery that the conductance of graphene can be manipulated by a few molecules assembled on its surface opened a new direction of investigations: graphene-based sensors. However the influence of water adsorbates on the graphene's transport properties in the presence of a SiO<sub>2</sub> substrate is not yet fully understood. We show that the main cause of hysteresis observed in electrical measurements on graphene devices are indeed water molecules absorbed on the graphene and/or SiO<sub>2</sub> surfaces. Our experiments indicate two types of mechanisms: (1). The re-orientation of water dipoles located between graphene and substrate under an applied electrical field. (2). The electrochemical charge transfer between graphene and reduction/oxidation couple introduced by the exposure of graphene to humid environment. The final answer to the role of the SiO<sub>2</sub> substrate in the changes of graphene conductance under exposure to water molecules can be found by repeating the same experiments on free standing graphene membranes. Here the system is simplified to graphene and H<sub>2</sub>O only.

**THU 42****Emergence of local magnetic moments in doped graphene-related materials**

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Motivated by recent studies reporting the formation of localized magnetic moments in doped graphene, we investigate the energetic cost for spin polarizing isolated impurities embedded in this material. When a well-known criterion for the formation of local magnetic moments in metals is applied to graphene we are able to predict the existence of magnetic moments in cases that are in clear contrast to previously reported Density Functional Theory (DFT) results. When generalized to periodically repeated impurities, a geometry so commonly used in most DFT-calculations, this criterion shows that the energy balance involved in such calculations contains unavoidable contributions from the long-ranged pairwise magnetic interactions between all impurities. This proves the fundamental inadequacy of

the DFT-assumption of independent unit cells in the case of magnetically doped low-dimensional graphene-based materials. We show that this can be circumvented if more than one impurity per unit cell is considered, in which case the DFT results agree perfectly well with the criterion-based predictions for the onset of localized magnetic moments in graphene.

#### THU 43

##### **In situ ultra-HRTEM electrical investigations of graphene**

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Specially designed sample supports have been developed to permit in situ investigation of the electrical conductivity of sheets of graphene - either partially free standing or suspended between metal electrodes - in a transmission electron microscope (TEM). High-resolution (HR) imaging revealed the desorption of impurity deposits from graphene flakes at sufficiently high applied currents. We investigated the dependence of local heat development on current density as well as on the immediate sample vicinity. To date, maximum sheet current densities of about  $3 \cdot 10^8$  A/cm<sup>2</sup> were reached during these studies. In the case of perforated SiN membranes acting as sample supports, we clearly observed the occurrence of phase transitions and the sublimation of freestanding SiN beneath graphene flakes, indicating sheet temperatures in the range of 2000°C. In this manner, the temperature required for our current-induced cleaning procedure was estimated to be on the order of 1000°C. In addition to real-time observations of microstructure during graphene annealing, our efforts are now focused on other indicators and consequences of the resulting temperature profiles.

#### THU 44

##### **Exploring magnetism in graphene**

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Magnetism of carbon-based materials, containing only s and p electrons, as a counterpart of ferromagnetism in d, f orbital metals (Fe, Co etc.), is of theoretical and technological interest. It is often explained by the alternation between sp<sup>2</sup> and sp<sup>3</sup>-hybridized carbon orbitals, due to impurities, boundaries or defects [1]. Making graphene ferromagnetic (e.g. by H-plasma exposure) would give new prospects for spintronics, in addition to the spin-transport already shown in pure graphene [2]. The magnetisation of ferromagnetic graphene cannot be measured by stan-

dard SQUID or MFM as the expected signal is too small. I aim to measure the magnetisation in an indirect way, by the non-local spin-valve technique [2]. Particularly, in the Hanle spin precession experiment we can observe how spin-relaxation times are modified by an external field and/or localized magnetic moments inside the material. I will present theoretical predictions on how to turn graphene to a ferromagnetic state and how to detect magnetism in all-electrical studies. The experimental progress will be reported.

[1] Yazyev, O.V. & Helm, L. Phys.Rev.B 75,125408(2007)

[2] Tombros, N. et al., Nature 448, 571(2007)

#### THU 45

##### **High-density growth of horizontally-aligned carbon nanotubes for interconnects**

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Carbon Nanotubes (CNTs) are promising candidates to replace copper in interconnects in integrated circuit beyond the 22 nm node. Recently, there have been significant progresses made in achieving vertical CNT interconnects. In contrast, the fabrication of horizontal CNT interconnects is at a much earlier stage of development, which is largely due to the difficulties in patterning catalyst and its support material on a vertical surface.

In this study, we demonstrate the growth of horizontally aligned carbon nanotubes (CNTs) from a vertical, conductive surface for use as horizontal interconnects. This is achieved by using a CMOS compatible metal, CoSi<sub>2</sub>, as the catalyst support and contact, and Fe as the catalyst. The CoSi<sub>2</sub> and Fe are patterned on a vertical surface using a self-aligned silicidation and tilt evaporation technique, respectively. Cold-wall chemical vapor deposition achieves a multi-walled CNT density of  $\sim 510^{10}/cm^2$  that corresponds to a wall density of  $\sim 610^{11}/cm^2$ . Electrical measurements show that both outer and some inner walls carry current, demonstrating a promising method for growing nanoscale horizontal interconnects.

#### THU 46

##### **Fullerene-induced magnetization training effect in single molecular magnet**

V.S. Zagaynova<sup>1</sup> T.L. Makarova<sup>1</sup> N.G. Spitsina<sup>2</sup> E.B. Yagubskii<sup>2</sup>

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Mn12-based single molecular magnets have been intensively investigated during the last decade. It was demonstrated that their magnetic properties are strongly dependent on the magnetic core environment that makes it possible to produce

magnets with desirable properties. We report on the dramatic qualitative changes of magnetic properties of Mn12-based magnets complexated with C60 molecules in 1:1 ratio. After the cycle of 1T - -1T - 1T measurements the magnetization curve does not return to the initial point but progressively increases after each cycle of such measurements. The effect is reproducible, and we call it "magnetization training" emphasizing that magnetization rather than coercivity is trained in our system. We have studied several variations of Mn12-based molecular magnet with different ligands, containing and non-containing fullerenes, and confirmed that the effect is induced by C60 complexation.

**THU 47****Theoretical Studies of the Conductance of Copper-Contacted Carbon Nanotubes**

Andreas Zienert<sup>1</sup> Jörg Schuster<sup>2</sup> Reinhard Streiter<sup>1</sup> Thomas Geßner<sup>1</sup>

<sup>1</sup>Center for Microtechnologies, Chemnitz University of Technology, Chemnitz, Germany

<sup>2</sup>Fraunhofer Research Institution for Electronic Nano Systems, Chemnitz, Germany

Carbon nanotubes show unique electrical properties due to their precisely defined atomistic structure. The ability to conduct extremely high current densities ballistically makes them promising candidates for replacing copper interconnects in future microelectronic devices. In real devices the large contact resistance between carbon nanotubes and metal leads forms a serious obstacle for applications.

We investigate the conductance of copper-contacted carbon nanotubes in different levels of theory. To get a qualitative physical understanding, we use the tight-binding approximation in combination with the Landauer formalism. As first approach simple model Hamiltonians are used and missing constants are obtained from DFT simulations as suggested by [1]. Different contact geometries and nanotube types are examined. In future work results will be compared with pure ab-initio calculations combined with nonequilibrium Green's function methods.

[1] N. Nemec, D. Tománek, G. Cuniberti. Phys. Rev. Lett. 96, 076802 (2006)

**THU 48****Functionalization of graphene with 4d and 5d transition metals**

Viktor Zólyomi<sup>1</sup> Ádám Ruzsnyák<sup>2</sup> Jenő Kúrti<sup>2</sup> Colin J. Lambert<sup>1</sup>

<sup>1</sup>Department of Physics, Lancaster University, Lancaster, UK

<sup>2</sup>Department of Biological Physics, Loránd Eötvös University, Budapest, Hungary

We study the strength of the binding of 4d and 5d transition metals on a graphene sheet in the limit of low- and high-coverage using first principles density functional theory. A database of the binding energies is presented. Our results show that Mo, Hf, Ta, and W bind strongest to the graphene sheet. We find a charge transfer of  $\approx 0.01$  electrons per carbon atom from the transition metal to the graphene sheet.

The strong binding to Hf suggests that strong binding with  $\text{HfO}_2$  can be achieved which should make it possible to effectively interface graphene with silicon, allowing for an integration of graphene-based nanoelectronic components into existing silicon-based technology.

**THU 49****Spin transport in nanopatterned graphene devices**

P. J. Zomer<sup>1</sup> C. Józsa<sup>1</sup> N. Tombros<sup>2</sup> B. J. van Wees<sup>1</sup>

<sup>1</sup>Physis of Nanodevices, Zernike Institute for Advanced Materials, University of Groningen, The Netherlands

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Recent experiments show that graphene is a promising material for spintronic devices [1]. Spin relaxation times of 150 ps are measured, shorter than expected from theory. Long spin coherence times can be used for spin qubits in graphene quantum dots [2]. Successful measurements on charge transport in etched quantum dots have already been reported [3]. We now combine spin transport with confined graphene structures, using side gates to locally control the charge carrier density. Due to (quantum) confinement an enhancement of the spin relaxation time is expected. Currently we control graphene flake dimensions down to sizes below 50 nm. For this we use a PMMA etch mask in combination with oxygen plasma reactive ion etching. We measured charge transport in constrictions at room temperature and at liquid nitrogen temperature, using both back- and sidegates to tune the charge carrier density. We will also show our first measurements on spin transport in side-gated graphene constrictions [4].

1 N. Tombros et al. Nat. 448, 571 (2007)

2 B. Trauzettel et al. Nat. Phys. 3, 192 (2007)

3 C. Stampfer et al. Appl. Phys. Lett. 92, 012102 (2008)

4 P. J. Zomer et al. in preparation









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Friday, March 12

## Carbon nanotube chemistry applications

- 8:30 – 9:30     **A. Hirsch, DE**  
*Functionalization of Synthetic Carbon Allotropes*
- 9:30 – 10:00    **Y. Maeda, JP**  
*Dispersion, separation, and reaction of single-walled carbon nanotubes*
- 10:00 – 10:30   **Coffee break**
- 10:30 – 11:00   **D. M. Guldi, DE**  
*Nanotubes see the light (!)*
- 11:00 – 11:30   **M. Prato, IT**  
*Carbon Nanotubes: Fundamental Components for Materials Science and Bionanotechnology*
- 11:30 – 12:00   **H. Riel, CH**  
*Towards Ultimate Scaling – Semiconducting Nanowires and Molecular Electronics*
- 12:00 – 17:00   **Mini Workshops**
- 17:00 – 17:30   **T. Hertel, DE**  
*Nanotube and nanotube-surface spectroscopy*
- 17:30 – 18:00   **R. Krupke, DE**  
*Phonon assisted electroluminescence from metallic carbon nanotubes and graphene*
- 18:00 – 18:30   **A. Jorio, BR**  
*IWEPNM 2010 - Conference Summary*
- 20:00    **Bauernbuffet - Farewell**

Friday, March 12

**8:30****Functionalization of Synthetic Carbon Allotropes**Andreas Hirsch

Department of Chemistry and Pharmacy, Erlangen, Erlangen

Chemical functionalization of new C-allotropes is of fundamental interest and opens the door to unprecedented materials applications. In principal, the physical and chemical properties of fullerenes, carbon nanotubes (CNTs) and graphene are related to each other. In order to efficiently explore the reactivity of the less developed CNTs and especially that of graphene it is our goal to provide a unifying approach for the chemistry of all three new carbon allotropes. The fullerenes present the first family of synthetic carbon allotropes. Since their availability in macroscopic quantities numerous investigations with respect to their physical characterization and chemical functionalization have been carried out. CNTs - the second new family of C-allotropes - exhibit at least the same potential for unprecedented applications. Their chemistry, however, is much less developed. Finally, the youngest representative in the list of new C-allotropes is graphene and the exploration of its chemistry has just begun to start. We will present a series of new results of covalent and non-covalent functionalizations of fullerenes, carbon nanotubes and graphene.

**9:30****Dispersion, separation, and reaction of single-walled carbon nanotubes**Yutaka Maeda<sup>1</sup> Tadashi Hasegawa<sup>2</sup> Hanxan Qiu<sup>3</sup> Takeshi Akasaka<sup>3</sup> Jing Lu<sup>4</sup> Shigeru Nagase<sup>5</sup><sup>1</sup>Tokyo Gakugei University, PRESTO, JST, Japan<sup>2</sup>Tokyo Gakugei University, Tokyo, Japan<sup>3</sup>Center for Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Japan<sup>4</sup>Department of Physics, Peking University, Beijing, P. R. China<sup>5</sup>Department of Theoretical and Computational Molecular Science, Institute for Molecular Science, Okazaki, Japan

Many potential applications of single-walled carbon nanotubes (SWNTs) have been strongly expected because of their excellent mechanical and electrical properties. The SWNTs are typically grown as bundles of metallic and semiconducting tubes. This is a great hindrance to their widespread applications. The dispersion and exfoliation of SWNTs in an organic solvent enable complexation and functionalization of SWNTs with organic materials under homogenous conditions. In this context, we report the dispersion, separation, and reaction of SWNTs in organic solvents. A typical procedure for the dispersion of SWNTs is as follows: SWNTs was added to a tetrahydrofuran solution containing an amine, and then sonicated followed by centrifugation. When SWNTs were treated in THF with 1-octylamine, a black-colored transparent supernatant solution was obtained. The supernatant showed the characteristic absorption bands in the vis-NIR spectra of SWNTs. The addition of amines is an effective way to disperse SWNTs in organic solvents without changing their electronic structure. We also studied chemical reaction of SWNTs with organic compounds.



**10:30**

**Nanotubes see the light (!)**

Dirk M Guldi

Department of Chemistry and Pharmacy, Friedrich-Alexander-Universitaet Erlangen-Nuernberg, Erlangen

Multifunctional carbon nanostructures are currently under active investigation for producing innovative materials, composites, and optoelectronic devices, whose unique properties originate at the molecular level. Among the wide variety of carbon allotropes recently discovered, C60 and single wall carbon nanotubes (SWNT) are of particular interest.

I will highlight the opportunities that rest on carbon nanotubes within the context of charge transfer reactions in novel chemical as well as light driven systems with high tensile strength. A fundamental aspect of our research is to integrate such functions without sacrificing the structural and electronic integrity of the material. In this context, I will survey our concepts to design, manipulate, characterize, examine, and understand the potential of carbon materials as a novel platform for stable electron donor-acceptor hybrids and conjugates. Important aspects will include the impact, the benefits and some of the promises that evolve from charge transfer reactions involving carbon nanostructures with high tensile strength.

**11:00****Carbon Nanotubes: Fundamental Components for Materials Science and Bionanotechnology**Maurizio Prato

Department of Pharmaceutical Sciences, University of Trieste, Trieste

Processing of carbon nanotubes is severely limited by a number of inherent problems: purification from a variety of byproducts, difficult manipulation and low solubility in organic solvents and in water are only some of these problems. For these reasons, several strategies have been devised to make nanotubes “easier” materials. The combination of nanotubes with various electron donors has led to a new generation of donor-acceptor nanohybrids which can be used for the development of carbon-based photovoltaic cells. Also in biomedical applications carbon nanotubes are set to play an important role. Their use as drug delivery scaffolds and substrates for vaccines has already been demonstrated. Nanotubes functionalized with bioactive moieties are particularly suited for targeted drug delivery. In fact, not only they become less toxic, but also exhibit a high propensity to cross cell membranes. The use of carbon nanotubes as active substrates for neuronal growth has given so far very exciting results. Not only nanotubes are compatible with neurons, but they play a very interesting role in interneuron communication.

**11:30****Towards Ultimate Scaling – Semiconducting Nanowires and Molecular Electronics**Heike Riel

IBM Research GmbH, Rüschlikon

In this presentation two possible future candidates of post-CMOS technologies, such as semiconducting nanowires and molecular electronics will be discussed. Owing to their potential compatibility with existing CMOS technology, SiNWs are considered to be one of the most promising candidates for future logic elements. Results on the control and optimization of NW growth and in-situ doping, charge transport properties as well as the benefits of a gate-all-around structure will be presented. Furthermore, it is shown that the free carrier density in doped nanoscale semiconductor wires is size dependent due to a reduction in the amount of ionized impurities as a consequence of the dielectric mismatch between the NW core and the surrounding. The second part will cover molecular electronics which is aimed at the use of molecules as functional building blocks in electronic circuits. We are investigating the transport through individually contacted and addressed molecules using the MCBJ technique. Using this technique, we demonstrated reversible and controllable switching between two distinct conductive states of a single molecule thus successfully accomplishing memory operation.

**17:00****Nanotube and nanotube-surface spectroscopy**Tobias Hertel<sup>1</sup> Jared Crochet<sup>1</sup> Kristin Kröker<sup>1</sup> Tilman Hain<sup>1</sup> Timo Hefner<sup>1</sup> Nicolas Rühl<sup>1</sup> Friedrich Schöppler<sup>1</sup> Florian Späth<sup>1</sup> Dominik Stich<sup>1</sup><sup>1</sup>Institut für Physikalische und Theoretische Chemie, Julius-Maximilians-Universität Würzburg, Würzburg

Processes at carbon nanotube surfaces are essential for their behavior in various applications from thin film networks for flexible electronics, their use as membranes, sensors or biomedical contrast agents, biochemical vectors, pigments and more. However, information on solvent-nanotube interface structure as well as the kinetics and dynamics of interfacial processes is scarce and sometimes experimentally difficult to come by. Here we discuss recent investigations of nanotube-surface properties and processes. Specifically we have studied the formation, stability and properties of different supramolecular SWNT assemblies, from the commonly used ionic surfactant structures, over homo-aggregates to DNA-hairpin nanotube complexes. Their structure and photophysical properties are determined using a combination of CW and time-resolved spectroscopic probes. The experiments reveal an incredible wealth of unexplored phenomena at nanotube surfaces in aqueous and organic environments.

**17:30****Phonon assisted electroluminescence from metallic carbon nanotubes and graphene**

R. Krupke<sup>1</sup> C.W. Marquardt<sup>1</sup> A. Vijayaraghavan<sup>1</sup> M. Ganzhorn<sup>1</sup> S. Dehm<sup>1</sup> F. Hennrich<sup>1</sup> F. Ou<sup>2</sup> A.A. Green<sup>3</sup> C. Sciascia<sup>4</sup> F. Bonaccorso<sup>4</sup> K.P. Bohnen<sup>5</sup> H. v. Löhneysen<sup>6</sup> M.M. Kappes<sup>7</sup> P. Ajayan<sup>2</sup> M.C. Hersam<sup>3</sup> A.C. Ferrari<sup>4</sup> S. Essig<sup>1</sup>

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<sup>5</sup>Institut für Festkörperphysik, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany

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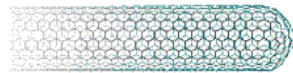
<sup>7</sup>Institut für Physikalische Chemie, Karlsruhe Institute of Technology, 76128 Karlsruhe, Germany

We report on light emission from biased metallic single wall carbon nanotubes (SWNT), multi wall carbon nanotube (MWNT) and few layer graphene (FLG) devices. SWNT devices were assembled from tubes with different diameters ranging from 0.7-1.5 nm. They emit light in the visible spectrum with peaks at 1.4 and 1.8 eV. Similar peaks are observed for MWNT and FLG devices. We propose that the light emission is due to phonon assisted radiative decay from populated  $\pi^*$  band states at the M point to the Fermi level at the K point. Since for most carbon nanotubes as well as for graphene, the energy of unoccupied states at the M point is close to 1.6 eV, we consider the observation of two emission peaks at  $1.6 \pm 0.2$  eV as evidence for radiative decay under emission or absorption of optical phonons, respectively.





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