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Verein zur Durchführung der International Winterschool on Electronic Properties of Novel Materials

Verein zur Förderung der Internationalen Winterschulen in Kirchberg Austria

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Dear Friend:

Welcome to the 25<sup>th</sup> International Winterschool on:  
**Electronic Properties of Novel Materials: "Molecular nanostructures"**

This Winterschool is a sequel of twenty-four 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 Staiger, Matthias Müller	accommodation
Patrick May	accommodation, sponsoring
Nils Rosenkranz	registration, finance
Marcel Mohr, Katharina Brose	video transfer and recording, internet
Niculina Peica, Sevak Khachadorian	general assistance
Harald Scheel	receipts, technical assistance
Dirk Heinrich	technical assistance
Norman Tschirner	website, e-payment
Jan Laudenbach	abstract booklet

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.

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 (Seoul)

## Program Committee

E. Andrei (US)	F. Mauri (FR)
A. Bachtold (ES)	M. Mehring (DE)
P. Dinse (DE)	K. S. Novoselov (UK)
M. Dresselhaus (US)	E. Obraztsova (RU)
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H. W. Kroto (UK)	Z. K. Tang (CN)
H. Kuzmany (AT)	C. Thomsen (DE)
Y. H. Lee (KR)	A. Zettl (US)
A. Loiseau (FR)	

## 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 IWEPM 2011 starts on Saturday, 26 February, evening, at the hotel Sonnalp in Kirchberg/Tirol, Austria and extends to Saturday, 5 March, breakfast. There will be a reception party on 26 February, after dinner, and a farewell party including dinner on Friday, 4 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:

IWEPM 2011, Hotel Sonnalp, A-6365 Kirchberg/Tirol, Austria

Tel: ++43 5357 2741, 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 IWEPM 2011 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: [iwepm-info@physik.tu-berlin.de](mailto:iwepm-info@physik.tu-berlin.de), Web: <http://www.iwepm.org>

### Participation

Participation at the IWEPM 2011 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 IWEPM 2011 will be published by Wiley in *physica status solidi*. The expected date for the appearance of the proceedings is October 2011. **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/group/home/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 2011  
CHAIRPERSONS FOR THE ORAL SESSIONS

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

Sunday, 27.02.	morning	Kuzmany
	morning, after coffee break	Jorio
	evening	Thomsen
Monday, 28.02.	morning	Obratzsova
	morning, after coffee break	Hofmann, S.
	evening	Kataura
Tuesday, 1.03.	morning	Heinz
	morning, after coffee break	Reich
	evening	Swan
Wednesday, 2.03.	morning	Mauri
	morning, after coffee break	van der Zant
	evening	Ensslin
Thursday, 3.03.	morning	Andrei
	morning, after coffee break	Kaiser, A.
	evening	Forro
Friday, 4.03.	morning	Roth
	morning, after coffee break	Arepalli
	evening	Dinse

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 Feb. 27	Monday Feb. 28	Tuesday March 1	Wednesday March 2	Thursday March 3	Friday March 4
Topics	graphene	nanotube growth and separation	graphene & nanotubes spectroscopy	topological insulators, graphene transport I	graphene electronic properties and transport II	Carbon nanomaterials growth and spin properties
8:30	Seeing electrons in two-dimensions: Optical spectroscopy of single- and few-layer graphene HEINZ	High sensitivity detection of surfactant molecules on SWCNTs by Raman spectroscopy KATAURA	Ab-initio calculation of resonant Raman spectra in graphene MAURI	Dirac Fermions in HgTe Quantum Wells MOLENKAMP	Coherent phonons in graphene double dots ENSSLIN	KIM
9:00	Interaction induced gap in high-mobility suspended bilayer graphene SCHÖNENBERGER	Fundamentals and applications of monodisperse carbon nanomaterials HERSAM			Electronic Properties of functionalized Graphene GRÜNEIS	Selective Growth of SWNTs and Type Separation Experiments AREPALLI
9:30	Graphene Nanomembranes and Quantum Dots MORGENSTERN	Controlled CVD Growth and Fabrication of SWNTs Array on Surface ZHANG	Raman intensity and absolute scattering efficiency of graphene CASIRAGHI	Magnetoelectric, thermoelectric, and spintronic properties of three-dimensional topological insulators MOORE	Plasmaron in quasi-free-standing graphene BOSTWICK	Thermal Properties of Graphene and Low-Dimensional Carbon Materials BALANDIN
10:00	Coffee break					
10:30	Raman Spectroscopy and Photonics of Graphene FERRARI	Challenges for selective growth of carbon nanotubes: Role of catalyst morphology HARUTYUNYAN	Il buono, il brutto, il cattivo JORIO	Carbon Nanoelectronics BOCKRATH	Disorder scattering in large-scale graphene nanodevices LIBISCH	Graphene Foam: A Three-Dimensional Inter-connected Graphene Network CHENG
11:00	Raman study of free standing single layer graphene at high hydrostatic pressure SOLDATOV	Concepts for technical synthesis of novel carbon materials MLECZKO	Optical Excitation and Energy dissipation in carbon nanotubes SWAN	Quantum spintronics systems based on diamond nanostructures WRACHTRUP	Ab initio quantum transport in defective and chemically-modified graphene CHARLIER	Nanostructured Carbon in Catalysis SCHLÖGL
11:30	The vanishing magneto resistance of polyacetylene nanofibers: Supermagnetoconductivity PARK	Separation, diameter sorting, and spectroscopy of empty (closed) and water-filled (open) SWNTs WENSELEERS	Formation and Dynamics of bound excitonic states in single walled carbon nanotubes LOUNIS	Spin qubits in silicon MORLEY	Probing Dirac fermions in graphene with STM and magneto-transport ANDREI	Carbon Nanotubes Based Stimuli Responsive Controlled-Release System BOROWIAK-PALEN

12:00-17:00	Mini workshops					
17:00 - 18:30	Dinner					17:00 Kondo ground state of organic charge-transfer salts on a metal surface PASCAL
18:30	special session	Carbon Nanotubes for advanced Interconnects ROBERTSON	Selective functionalization of carbon nanotubes MÜLLER	Graphene: Scratching the Surface FUHRER	Graphene NEMS resonators and self-oscillators: High-bandwidth electrical readout and magnetometry in the quantum Hall regime DESHPANDE	
19:00	Dirac Physics in Bilayer Graphene NOVOSELOV	Growth of aligned multi-walled carbon nanotubes: First in-situ X-ray diffraction and absorption analyses LAUNOIS	Molecular switches functionalization: Tailoring the properties of carbon nanotubes SETARO		Graphene nanopores: Structure, Properties and Function DRNDIC	17:30 New type of carbon-based superconductors: metal intercalated hydrocarbons KUBOZONO
19:30	Large-area graphene AHN	New concepts in molecular and energy transport within carbon nanotubes: thermopower waves and stochastically resonant ion channels STRANO	Wave functions and many-body effects in carbon nanotubes measured by STM LOISEAU	Gauge fields in graphene GUINEA	Intermolecular hybridization governs molecular doping of organic semiconductors KOCH	18:00 IWEPM11 - Conference summary PICHLER
20:00	CVD growth and processing graphene for electronic applications DUESBERG	Poster I Monday	Poster II Tuesday	Probing Graphene at the Atomic Scale: Adatoms, Strain, and Edges CROMMIE	Poster III Thursday	Bauernbuffet Farewell
20:30						
Topics	graphene	nanotube growth and separation	graphene & nanotubes spectroscopy	topological insulators, graphene transport I	graphene electronic properties and transport II	Carbon nanomaterials growth and spin properties
	Sunday Feb. 27	Monday Feb. 28	Tuesday March 1	Wednesday March 2	Thursday March 3	Friday March 4



**PROGRAM**

**AND**

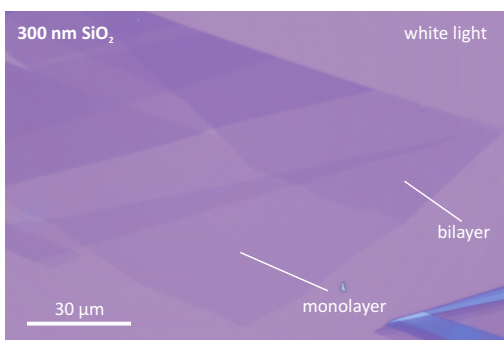
**ABSTRACTS**



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.

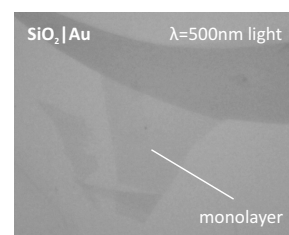
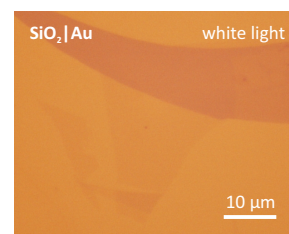


<b>Flake sizes</b>	Typically < 2000 μm <sup>2</sup> ; largest monolayer found to date: 1.5 mm <sup>2</sup>
<b>Pricing guide</b>	≈ € 0.50 per μm <sup>2</sup> area (decreases significantly for v. large flakes), with reductions if the flake is difficult to use for lithography, e.g. close to the wafer's 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



Visit [GRAPHENEINDUSTRIES.COM](http://GRAPHENEINDUSTRIES.COM) for more details and to see our current stock. **CVD grown graphene** will be available from March 2011. If you have any questions, please do not hesitate to contact Peter Blake: [peter@grapheneindustries.com](mailto:peter@grapheneindustries.com)

Graphene Industries Ltd, 24 Ellerslie Court, Upper Park Road, Manchester, M14 5RH, UK

Sunday, February 27

## Graphene

- 8:30 – 9:00 T. F. Heinz, US  
*Seeing electrons in two-dimensions: Optical spectroscopy of single- and few-layer graphene*
- 9:00 – 9:30 C. Schönenberger, CH  
*Interaction induced gap in high-mobility suspended bilayer graphene*
- 9:30 – 10:00 M. Morgenstern, DE  
*Graphene Nanomembranes and Quantum Dots*
- 10:00 – 10:30 Coffee break
- 10:30 – 11:00 A. C. Ferrari, GB  
*Raman Spectroscopy and Photonics of Graphene*
- 11:00 – 11:30 A. V. Soldatov, SE  
*Raman study of free standing single layer graphene at high hydrostatic pressure*
- 11:30 – 12:00 Y. W. Park, KR  
*The vanishing magneto resistance of polyacetylene nanofibers: Supermagnetoconductivity*
- 12:00 – 17:00 Mini Workshops
- 17:00 – 18:30 Dinner
- 18:30 – 19:00 Special session
- 19:00 – 19:30 K. Novoselov, GB  
*Dirac Physics in Bilayer Graphene*
- 19:30 – 20:00 J.-H. Ahn, KR  
*Graphene Films for Unusual Format Electronics*
- 20:00 – 20:30 G. S. Duesberg, IE  
*CVD growth and processing graphene for electronic applications*

Sunday, February 27

**8:30****Seeing electrons in two-dimensions: Optical spectroscopy of single- and few-layer graphene**Tony F Heinz

Department of Physics, Columbia University, New York, USA

Optical spectroscopy provides an excellent means of understanding the distinctive properties of electrons in the two-dimensional system of graphene. Within the simplest picture, one has a (zero-gap) semiconductor with direct transitions between the well-known conical bands. This picture gives rise to a predicted frequency-depedendent absorption of  $\alpha = 2.3\%$ , where  $\alpha$  is the fine-structure constant. We will demonstrate that this relation is indeed satisfied in an appropriate spectral range in the near infrared, but that at higher photon energies electron-hole interactions significantly modify this result through the formation of saddle-point excitons. Optical spectroscopy also permits a detailed analysis of how the linear bands of graphene are modified to yield massive electrons through interlayer interactions in bilayer and few-layer graphene sheets. The observation of a tunable band gap in bilayer and trilayer graphene will also be discussed. Recent measurements in which the electron and phonon dynamics are investigated by ultrafast pump-probe spectroscopy will also be presented.

**9:00****Interaction induced gap in high-mobility suspended bilayer graphene**Christian Schönenberger<sup>1</sup> Frank Freitag<sup>1</sup> Jelena Trbovic<sup>1</sup> Markus Weiss<sup>1</sup> Andreas Baumgartner<sup>1</sup><sup>1</sup>Department of Physics, University of Basel, Basel

Bilayer graphene is an exciting material, widely extending the range of phenomena. Interestingly, Coulomb interactions are expected to be much larger in bilayer as compared to monolayer graphene. The eight-fold ground-state degeneracy of the zero-energy Landau level provides a large Hilbert space with novel composite particles. It has already been shown that this degeneracy can be lifted in a large magnetic field. Here we show that high-mobility suspended bilayer graphene devices allow for a spontaneous gap formation at zero magnetic field.

The properties of this gap are investigated by means of electronic transport measurements in magnetic field as a function of gate-voltage, source-drain bias voltage, and temperature. We find a very pronounced dip in the conductance at the charge neutrality point in a rather narrow gate-voltage window. Although resembling a clear gap both in gate-voltage and as a function of source-drain bias, the conductance does not vanish at the charge-neutrality point. It rather appears to saturate at low temperatures at a value that is independent of the applied magnetic field. This suggests a topological ground state with edges.

**9:30****Graphene Nanomembranes and Quantum Dots**

Markus Morgenstern

RWTH Aachen, Aachen

Scanning tunneling microscopy and spectroscopy at 4 K is used to probe graphene properties on the nanoscale. It is demonstrated that small valleys of down to 2 nm in diameter, which exist within graphene flakes on SiO<sub>2</sub>, can be lifted either continuously or hysteretically by the forces of the tip. During continuous lifting, a phase transition from the hexagonal graphene lattice to a triangular phase, which breaks sublattice symmetry, takes place. Possible origins of the controlled breaking of sublattice symmetry are discussed.

Moreover, graphene quantum dots with zig-zag edges prepared on Ir(111) are probed by STS. Confined states could be mapped and are favorably compared with third-nearest neighbor tight-binding calculations. The inverse life-time of these states increases linearly with energy. At the zig-zag edges we find a peak at the Fermi level resembling the characteristics expected from the edge state. However, local magnetization curves using spin polarized tunneling in B-field did not reveal a spin signal so far.

**10:30****Raman Spectroscopy and Photonics of Graphene**Andrea C Ferrari

Engineering Department, University of Cambridge, Cambridge

The richness of optical and electronic properties of graphene attracts enormous interest. Graphene has high mobility and optical transparency, in addition to flexibility, robustness and environmental stability. It has great potential for photonics and optoelectronics, where the combination of its unique optical and electronic properties can be fully exploited, even in the absence of a bandgap, and the linear dispersion of the Dirac electrons enables ultra-wide-band tunability. Raman spectroscopy is the most common and informative characterization technique in graphene science and technology. It is used to determine the number of layers, doping, strain, defects, functional groups, quality and type of edges. I will outline the state of the art in graphene Raman spectroscopy and photonics. I will highlight the potential of graphene for displays and ultrafast lasers, as well as stress the role of electron-phonon and electron-electron interactions in its Raman spectrum. I will also discuss the historical development of the identification of the main Raman bands in graphene, focussing on the peak around  $2450\text{cm}^{-1}$ , the UV Raman spectrum and the interlayer coupling E2g mode

**11:00****Raman study of free standing single layer graphene at high hydrostatic pressure**Shujie You<sup>1</sup> Ambroise Neuville<sup>1</sup> Mattias Mases<sup>1</sup> Konstantin S. Novoselov<sup>2</sup>  
Alexander V. Soldatov<sup>1</sup><sup>1</sup>Department of Engineering Sciences and Mathematics, Luleå University of Technology, SE - 97187 Luleå, Sweden<sup>2</sup>School of Physics and Astronomy, University of Manchester, Oxford Road, Manchester M13 9PL, UK

We report on the first Raman study of free standing (FS) single layer graphene (SLG) at high hydrostatic pressure in a diamond anvil cell (DAC). We were able to follow G- and G' band up to a pressure of 10 GPa. Both modes exhibit significant attenuation and linear hardening on pressure increase at a rate of 5.6-5.9 cm<sup>-1</sup>/GPa and 12 cm<sup>-1</sup>/GPa for G- and G' band respectively. The evolution of the bands frequency, width, and relative intensity with pressure is discussed in detail. The modes' Grüneisen parameter was determined and compared to that reported for uni- and bi-axial strain [1] and theoretical predictions.

[1] T. Mohiuddin, A. Lombardo, R. Nair, A. Bonetti, G. Savini, R. Jalil, N. Bonini, D. Basko, C. Galiotis, N. Marzari, K. Novoselov, A. Geim, and A. Ferrari, Phys. Rev. B 79, 205433 (2009).

**11:30****The vanishing magneto resistance of polyacetylene nanofibers: Supermagnetoconductivity**Ajeong Choi<sup>1</sup> Kyung Ho Kim<sup>1</sup> Sung Ju Hong<sup>1</sup> Yung Woo Park<sup>1</sup><sup>1</sup>Department of Physics and Astronomy and Nano Systems Institute - National Core Research Center, Seoul National University, Seoul

Results of nonlinear magneto resistance (MR) of polyacetylene nanofibers in high magnetic field up to  $H = 30$  tesla at low temperature  $T = 1.5$  K are presented. The MR was proven to be of the spin origin; it reaches 16% at highest  $H$ . Unexpectedly, the MR was suppressed by increasing electric field  $E$ , vanishing at  $E \geq 2 \times 10^4$  V/cm. It is understood that the doping induced spinless charged soliton pairs, which are initially confined to a certain distance because of the interchain phase correlations, are deconfined in high electric fields, resulting in a vanishing magneto resistance (VMR). The role of the specific, degenerate ground state of the polyacetylene is confirmed by parallel studies of the different magneto resistance of polyaniline nanofibers which contrarily is not affected by the electric field. The VMR in high electric field of polyacetylene nanofibers is named as the supermagnetoconductivity in analogy to the zero resistance of superconductivity.

1. A. Choi *et al.*, Synthetic Metals 160, 1349-1353 (2010).
2. Y. W. Park, Chemical Society Reviews 39, 2428-2438 (2010).

Graphene

Sunday, February 27

**18:30**

**Special Session**

**19:00**

**Dirac Physics in Bilayer Graphene**

Novoselov

School of Physics & Astronomy, University of Manchester, Manchester

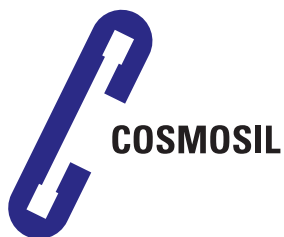
**19:30****Graphene Films for Unusual Format Electronics**Jong-Hyun Ahn

School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon

Unusual format electronics such as flexible and stretchable electronics are emerging as a technology that could be valuable for various applications. However, it is very difficult to accomplish such devices with conventional electronic materials. Graphene, the thinnest elastic material, has superb electronic and thermal properties that make it a promising host for device applications. In particular, graphene has an extremely good mechanical property, offering a great opportunity to flexible and stretchable electronics that should maintain a stable operation under a high strain. The recent advances in large-scale synthesis of graphene films by chemical vapor deposition are expected to enable various macroscopic applications such as semiconducting and transparent conducting films useful for flexible and stretchable electronics. In this talk, we present a large area growth of high-quality graphene films on metal films, and transfer printing method onto arbitrary substrates and examples for device applications. These large area synthesis and transfer methods provide improved scalability and processibility of graphene films ready for use in unusual format electronics.

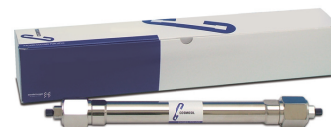
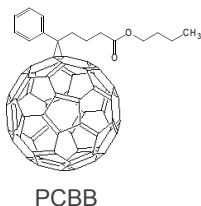
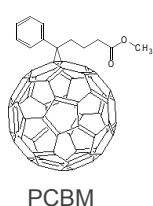
**20:00****CVD growth and processing graphene for electronic applications**Shishir Kumar<sup>1</sup> Nikos Peltekis<sup>2</sup> KangHo Lee<sup>2</sup> Hye-Young Kim<sup>2</sup> Niall McEvoy<sup>2</sup> Hugo Nolan<sup>1</sup> Georg S. Duesberg<sup>1</sup><sup>1</sup>School of Chemistry , Trinity College Dublin, Dublin<sup>2</sup>CRANN, Trinity College Dublin, Dublin

Graphene has potential applications in nano-electronics and sensing. The quality of graphene layers is of particular high importance as contamination, impurities, morphology and defects can substantially affect the electronic properties and the performance. After numerous studies on hand grafted graphene, processes that yield macro-scale samples which allow the fabrication of device arrays by structuring have been developed recently. However, there is a variation in the quality of the pristine films and each process step has an impact on the electronic properties of the samples. We present a comprehensive study on large scale CVD grown graphene films and investigate the effects of transfer, structuring and annealing procedures. A comparative study of Raman, AFM, and XPS with extensive analysis of high resolution C1s spectra, reveals that metallicity defect density and contaminations can be clearly identified. Furthermore, a new cleaning and reconstruction process of graphene is presented based on mild plasma cleaning, which can be used on in-situ contacted devices. Thus, carefully controlled processing conditions lead to the reproducible manufacture of graphene device arrays.

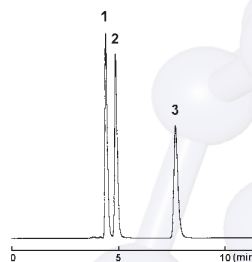
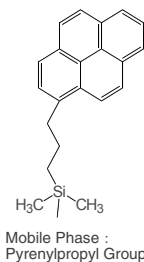


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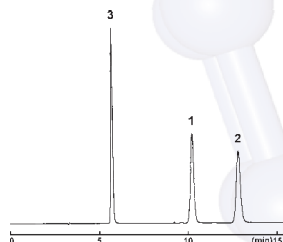
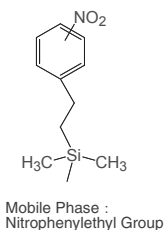
### COSMOSIL Buckyprep - Standard Column for Fullerene Separation



Column size 4.6mm I.D. x 250mm  
Mobile phase Toluene  
Flow rate 1.0ml/min  
Temperature 30°C  
Detection UV 325nm

Sample  
1. [6,6]-Phenyl-C<sub>61</sub> Butyric Acid Methyl Ester  
2. [6,6]-Phenyl-C<sub>61</sub> Butyric Acid Butyl Ester  
3. C<sub>60</sub>  
(1.5 µg each)

### COSMOSIL NPE - for Separation of Derivatized Fullerenes



Column size 4.6mm I.D. x 250mm  
Mobile phase Toluene/ Hexane = 25/75  
Flow rate 1.0ml/min  
Temperature 30°C  
Detection UV 325nm

Sample  
1. [6,6]-Phenyl-C<sub>61</sub> Butyric Acid Methyl Ester  
2. [6,6]-Phenyl-C<sub>61</sub> Butyric Acid Butyl Ester  
3. C<sub>60</sub>  
(1.5 µg each)

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Monday, February 28

## Nanotube growth and separation

- 8:30 – 9:00     **H. Kataura, JP**  
*High sensitivity detection of surfactant molecules on SW-CNTs by Raman spectroscopy*
- 9:00 – 9:30     **M. C. Hersam, US**  
*Fundamentals and applications of monodisperse carbon nanomaterials*
- 9:30 – 10:00    **J. Zhang, CN**  
*Controlled CVD Growth and Fabrication of Single-Walled Carbon Nanotubes Array on Surface*
- 10:00 – 10:30   **Coffee break**
- 10:30 – 11:00   **A. R. Harutyunyan, US**  
*Challenges for selective growth of carbon nanotubes: Role of catalyst morphology*
- 11:00 – 11:30   **Mleczko, DE**  
*Concepts for technical synthesis of novel carbon materials*
- 11:30 – 12:00   **W. Wenseleers, BE**  
*Separation, diameter sorting, and spectroscopy of empty (closed) and water-filled (open) single-wall carbon nanotubes*
- 12:00 – 17:00   **Mini Workshops**
- 17:00 – 18:30   **Dinner**
- 18:30 – 19:00   **J. Robertson, GB**  
*Carbon Nanotubes for advanced Interconnects*
- 19:00 – 19:30   **P. Launois, FR**  
*Growth of aligned multi-walled carbon nanotubes: First in-situ X-ray diffraction and absorption analyses*
- 19:30 – 20:00   **M. S. Strano, US**  
*New concepts in molecular and energy transport within carbon nanotubes: thermopower waves and stochastically resonant ion channels*

Monday, February 28

**8:30****High sensitivity detection of surfactant molecules on SWCNTs by Raman spectroscopy**Hiromichi Kataura<sup>1</sup> Daisuke Nishide<sup>1</sup> Huaping Liu<sup>1</sup> Shunjiro Fujii<sup>1</sup> Takeshi Tanaka<sup>2</sup><sup>1</sup>Nanosystem Res. Inst., Nat. Inst. of AIST, Tsukuba and CREST, JST<sup>2</sup>Nanosystem Res. Inst., Nat. Inst. of AIST, Tsukuba

Because most of metal-semiconductor separation methods of single-wall carbon nanotubes (SWCNTs) use specific interaction between SWCNT and surfactant molecules, high sensitive detection of surfactant molecule on the wall is crucial to know the separation mechanism. Recently, we found that the G-band Raman spectrum of SWCNTs is highly depending on the surfactant molecules on the side wall and thus the Raman spectrum can be used as a probe of surfactant. In this presentation, we will show the surfactant exchange process in the mixed surfactants system accompanied with separation results by the density gradient ultracentrifugation. We will also introduce the latest results of single chirality separation by the single-surfactant multi column gel chromatography method where we used only one kind of surfactant and the gel.

**9:00****Fundamentals and applications of monodisperse carbon nanomaterials**Mark C. Hersam

Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208-3108, USA

Carbon nanomaterials have attracted significant attention due to their potential to improve applications such as transistors, transparent conductors, solar cells, batteries, and biosensors. This talk will highlight our latest efforts to develop solution-phase strategies for purifying, functionalizing, and assembling carbon nanomaterials into functional arrays. For example, we have recently developed and commercialized a scalable technique for sorting surfactant-encapsulated single-walled carbon nanotubes (SWCNTs) by their physical and electronic structure using density gradient ultracentrifugation (DGU). The resulting monodisperse SWCNTs enhance the performance of thin film transistors, infrared optoelectronic devices, and transparent conductors. The DGU technique also enables multi-walled carbon nanotubes to be sorted by the number of walls, and solution phase graphene to be sorted by thickness, thus expanding the suite of monodisperse carbon nanomaterials. By extending our DGU efforts to carbon nanotubes and graphene dispersed in biocompatible polymers (e.g., DNA and poloxomers), new opportunities have emerged for monodisperse carbon nanomaterials in biomedical applications.

**9:30****Controlled CVD Growth and Fabrication of Single-Walled Carbon Nanotubes Array on Surface**Jin Zhang

Center for Nanochemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Due to their excellent properties, single-walled carbon nanotubes (SWNTs) have been regarded as one of the most potential materials for future applications in nanoelectronic devices. However, there is a huge gulf between production and applications. To meet the needs for applications, SWNTs diameter, chirality, and metallic/ semiconducting property should be controlled in the growth process. We present herein a brief review on the controlled growth and fabrication of SWNTs array on surface in our group, including 1) Temperature mediated chemical vapor deposition (CVD) growth of SWNTs with controlled diameter; 2) Cap engineering for SWNTs growth with controlled chirality; 3) Direct growth of semiconducting single-walled carbon nanotube array; and 4) Separation of semiconducting and metallic SWNTs by assistance of scotch tape.

**10:30****Challenges for selective growth of carbon nanotubes: Role of catalyst morphology**Avetik R. Harutyunyan

Honda Research Institute USA Inc., 1381 Kinnear Road, Columbus OH 43212, USA

Nowadays we still lack reasonably homogeneous SWCNT materials and importantly, a viable strategy for controllable growth of nanotubes. The latest fact is a major obstacle hindering SWCNTs broad applications. Ironically, the origin of this challenge is related to the most distinctive feature of the SWCNTs, which is the realization of the wide-ranging, energetically close, singular structures that can be transformed from one to another by very petite tuning of the chiral angle and vector. Among the proposed strategies for selectively growing SWCNTs, our recent studies on preferential growth of SWCNTs with metallic conductivity up to 90% lean toward the concept of definite relationship between catalyst structure and the grown tubes electronic properties. Here we examine whether the preferential grown metallic tubes chiralities can be understood in the terms of certain correlation with corresponding facet structure of the catalyst particle.

**11:00****Concepts for technical synthesis of novel carbon materials**Leslaw Mleczko

Bayer Technology Services GmbH, Leverkusen, E 41

In the last decades several novel carbon materials were described in the scientific literature. Everything started with fullerenes, grew with CNT (either SWNT or MWNT) and culminated with graphene. The Nobel Prize 2010 in Physics to Andre Geim and Konstantin Novoselov is the clear example of the expectation around this class of materials. However the availability of these materials with a constant quality is limiting the development of new applications. Also the price plays an important role outside of research and niche applications. Thus the need for scalable synthesis or processing technologies is necessary. We will illustrate how it is possible to overcome this limitation for CNTs, via CVD process and large scale catalyst production, for graphenes, via novel synthesis and pyrolysis method, and for fullerenes, via innovative functionalization and separation technology.

**11:30****Separation, diameter sorting, and spectroscopy of empty (closed) and water-filled (open) single-wall carbon nanotubes.**Wim Wenseleers<sup>1</sup> Sofie Cambré<sup>1</sup> Etienne Goovaerts<sup>1</sup><sup>1</sup>University of Antwerp, Universiteitsplein 1, B-2610 Antwerp, Belgium

The unusually efficient solubilization of carbon nanotubes using bile salt surfactants (cholates or steroid surfactants)<sup>1</sup> has enabled major advances in their processing and purification,<sup>2</sup> as well as their spectroscopic study. The regular, unperturbing micellar coating yields much narrower spectral linewidths than other surfactants,<sup>1</sup> which has allowed us to resolve the radial breathing modes of empty and water-filled SWCNTs, thus revealing that both coexist in aqueous solutions.<sup>3,4</sup> We show that both can be separated, and the empty tubes allow enhanced diameter sorting by density gradient ultracentrifugation.<sup>5</sup> The newly isolated empty nanotubes turn out to possess far more ideal properties.<sup>5</sup>

[1] W. Wenseleers *et al.*, *Adv. Funct. Mater.* 2004, 14, 1105

[2] M.S. Arnold, A.A. Green, J.F. Hulvat, S.I. Stupp, M.C. Hersam, *Nature; Nano.*; 2006, 1, 60

[3] W. Wenseleers, S. Camb, J.lin, A. Bouwen, E. Goovaerts, *Adv.: Mater.*; 2007, 19, 2274

[4] S. Camb, B. Schoeters, S. Luyckx, E. Goovaerts, W. Wenseleers, *Phys. ;Rev. ; Lett.*; 2010, 104, 207401

[5] S. Cambré, W. Wenseleers, *Angew.: Chem.: Int.: Ed.*; 2011, in press

**18:30****Carbon Nanotubes for advanced Interconnects**John Robertson

Cambridge, UK

Continuous scaling of integrated circuits means that carbon must eventually replace copper for interconnects in future integrated circuits. However, this requires carbon nanotubes with a density of over  $3 \times 10^{13} \text{ cm}^{-2}$  to reduce their resistance to comparable to that of copper, and this has been a serious impediment to their actual use. The CNTs grow from Fe or Co catalyst nanoparticles created by de-wetting. This mechanism limits the maximum achievable nanoparticle density, because it is difficult to reduce further the catalyst average thickness. Existing work [1] achieves  $6 \times 10^{11} \text{ cm}^{-2}$  for high density aligned CNT forests, well below the needed value, whereas the highest value for interconnects is typically  $1 \times 10^{11}$  to  $1 \times 10^{12} \text{ cm}^{-2}$  [2]. We have developed ways to increase the CNT density by over an order of magnitude to  $1 \times 10^{13} \text{ cm}^{-2}$  for simple forests [3]. Further, coworkers [4] have achieved  $2 \times 10^{12} \text{ cm}^{-2}$  within Via structures. These values show that one of the major applications of CNTs in microelectronics is possible. 1. K Hata et al, Science (2004) 2. Nihei et al, Jpn J App Phys (2004) 3. S Esconjaugui et al, ACS Nano (2010) 4. J Dijon et al, Tech Digest IEDM (2010)

**19:00****GROWTH OF ALIGNED MULTI-WALLED CARBON NANOTUBES: FIRST IN-SITU X-RAY DIFFRACTION AND ABSORPTION ANALYSES**

Périne Landois<sup>1</sup> Mathieu Pinault<sup>2</sup> Stéphan Rouzière<sup>1</sup> Dominique Porterat<sup>2</sup> Cristian Mocuta<sup>3</sup> Erik Elkaim<sup>3</sup> Quingyu Kong<sup>3</sup> François Baudelet<sup>3</sup> Martine Mayne<sup>2</sup> Pascale Launois<sup>1</sup>

<sup>1</sup>Laboratoire de Physique des Solides, UMR CNRS 8502, Université de Paris Sud 11, 91405 Orsay, FRANCE

<sup>2</sup>Laboratoire Francis Perrin, CEA/DSM/IRAMIS/SPAM, CNRS URA 2453, 91191 Gif-sur-Yvette, FRANCE

<sup>3</sup>SOLEIL synchrotron, Orme des Merisiers, Saint-Aubin, 91192, Gif-sur-Yvette, France

Catalytic chemical vapor deposition (CCVD) has become a method of choice to produce carbon nanotubes (CNT), with in particular the synthesis of aligned CNT forests. But a thorough understanding of the mechanisms for CNT nucleation, growth and alignment is still missing. To study these mechanisms, in-situ experiments are required. We have developed specific reactor and furnace to perform such experiments using synchrotron complementary techniques, X-Ray Diffraction (XRD) and X-Ray Absorption Spectroscopy (XAS), yet never used to study in-situ CNT growth. Technological challenges and solutions developed will be discussed. Experiments were performed at synchrotron SOLEIL, at 850 °C, a standard temperature for CCVD synthesis of aligned multi-walled CNT (Pinault et al, Nano Lett. 2005). XRD patterns and XAS spectra were recorded as a function of time, during nucleation and growth. These pioneer experiments reveal the nature of the catalyst iron-based nanoparticles and allow one to quantify CNT growth and alignment rates as a function of time, which give access to energies into play.

**19:30****New concepts in molecular and energy transport within carbon nanotubes: thermopower waves and stochastically resonant ion channels**Michael S. Strano

Massachusetts Institute of Technology, Cambridge

Our laboratory has been interested in how carbon nanotubes can be utilized to illustrate new concepts in molecular and energy transfer. In the first example, we predict and demonstrate the concept of thermopower waves for energy generation(1). Coupling an exothermic chemical reaction with a thermally conductive CNT creates a self-propagating reactive wave driven along its length. We realize such waves in MWNT and show that they produce concomitant electrical pulses of high specific power  $> 7 \text{ kW/kg}$ . Such waves of high power density may find uses as unique energy sources. In the second system, we fabricate and study SWNT ion channels for the first time(2) and show that the longest, highest aspect ratio, and smallest diameter synthetic nanopore examined to date, a 500 nm SWNT, demonstrates oscillations in electro-osmotic current at specific ranges of electric field, that are the signatures of coherence resonance, yielding self-generated rhythmic and frequency locked transport. The observed oscillations in the current occur due to a coupling between stochastic pore blocking and a diffusion limitation that develops at the pore mouth during proton transport.

1. Choi W, Hong S, Abrahamson JT, Han JH, Song C, Nair N, Baik S, Strano MS: Chemically driven carbon-nanotube-guided th

**MON 1****Electron Paramagnetic Resonance of conduction electrons in single-walled carbon nanotubes**

Aida Abiad<sup>1</sup> Núria Ferrer-Anglada<sup>1</sup> Vega Lloveras<sup>2</sup> José Vidal-Gancedo<sup>2</sup> Siegmund Roth<sup>3</sup>

<sup>1</sup>Applied Physics Department, CRNE, Universitat Politècnica de Catalunya (UPC), Campus Nord B4, J. Girona 3-5, 08034 Barcelona, Spain

<sup>2</sup>Institut de Ciència de Materials de Barcelona (CSIC), Campus Universitari, 08193 Bellaterra, Spain

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

Studies of Electron Paramagnetic Resonance (EPR) have been reported on several kinds of single walled carbon nanotubes (SWCNTs) synthesized by different methods. We worked both with the obtained samples, which contained a randomly distributed semiconducting and metallic SWCNTs, and with selected 99% semiconducting or metallic SWCNTs. The EPR spectroscopy was used to assess the quality of carbon nanotubes.

We analyzed the thermal variations of EPR signal in the range 160 K – 300 K. The signal intensity at room temperature assigned to magnetic catalyst ions weakened as temperature decreases and is no longer detectable at low temperatures. The amplitude of the asymmetric lines assigned to SWCNTs conduction electrons decrease when the T decreases from room temperature to 160 K in most samples, following an Arrhenius law with activation energy of 47 meV whereas the linewidth increases. Besides, for carbon nanotubes produced by arc discharge using non-magnetic catalyst Pt/Rh, the amplitude of the asymmetric line does not show an exponential behavior, only a slightly dependence on T and shows a constant narrow linewidth of 4 Gauss.

**MON 2****Comparison of two models of dissolution and cluster growth in fullerene  $C_{60}$  solutions in polar nitrogen-containing solvents**

Victor L. Aksenov<sup>1</sup> Timur V. Tropin<sup>1</sup> Mikhail V. Avdeev<sup>1</sup> Mikhail V. Korobov<sup>2</sup> Roman A. Yerebin<sup>3</sup> N. Jargalan<sup>4</sup>

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

<sup>2</sup>Chemical Department, Lomonosov Moscow State University, Moscow, Russia

<sup>3</sup>Samara State University, Samara, Russia

<sup>4</sup>Institute of Physics and Technology, Mongolian Academy of Science, Ulaanbaatar, Mongolia

In fullerene  $C_{60}$  solutions in polar nitrogen-containing solvents, like N-methylpyrrolidone (NMP), slow growth of large stable clusters is observed. These solutions

can be considered as a convenient model transitional system between molecular non-polar solutions and colloidal dispersions of  $C_{60}$  in water. The study of this model system is an important step towards control of cluster state in fullerene-water solutions. If prepared, molecular  $C_{60}$  solutions in water will be important for practical biomedical applications.

In present work we consider two simple models to describe the kinetics of cluster growth in  $C_{60}$ /NMP. Kinetic equations are based on approach of the nucleation theory. In first model the initial solution is considered to be extremely supersaturated. In second model cluster growth is a two-step process: fullerene dissolution and subsequent cluster growth. Cluster state of  $C_{60}$  in NMP is considered as different from solid state, with its own equilibrium parameters. In both models new  $C_{60}$ -NMP complex formation eventually limits cluster growth. Comparison of these two kinetic models results with each other and experimental data is presented.

### MON 3

#### **n-type doping of carbon nanotubes by encapsulation of conjugated oligomers**

Laurent Alvarez<sup>1</sup> Yann Almadori<sup>1</sup> Thierry Michel<sup>1</sup> Rozenn Le Parc<sup>1</sup> Jean-Louis Bantignies<sup>1</sup> Patrick Hermet<sup>1</sup> Rachid Babaa<sup>2</sup> Raul Arenal<sup>3</sup> Bruno Jousselmé<sup>4</sup> Serge Palacin<sup>4</sup> Pascale Jégou<sup>4</sup> Stéphane Rols<sup>5</sup> Jean-Louis Sauvajol<sup>1</sup>

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<sup>2</sup>Chemical Engineering Department, University of Technology PETRONAS, (UTP), Ipoh- Perak, Malaysia

<sup>3</sup>LEM, CNRS-ONERA, 92322 Chatillon, France

<sup>4</sup>CEA, IRAMIS, SPCSI, Chemistry of Surfaces and Interfaces Group, F-91191 Gif sur Yvette Cedex, France

<sup>5</sup>Inst Laue Langevin, F-38042 Grenoble, France

An hybrid system consisting in conjugated oligomers inserted into carbon nanotube samples is studied. Encapsulation of the conjugated oligomers in the hollow core of nanotube is investigated by Transmission Electron Microscopy (TEM) and spatial resolved electron energy loss spectroscopy (SR-EELS). The interaction, especially the charge transfer, between the oligomer and the nanotube is probed by means of Raman scattering and infrared absorption. Raman spectroscopy is known to be a powerful tool to investigate phonons in carbon nanotubes whereas infra-red spectroscopy is well-suited to study phonons in conjugated oligomers. Raman data reveals that the interaction between the nanotubes and oligomers deeply depends on the metallic or semiconducting nature of the nanotubes. The charge transfer is shown to be significantly stronger for semiconducting tubes than for metallic ones. The spectral features of the Raman-active G and 2D modes of the nanotubes state a n-type doping of the nanotubes. Complementary, the infrared spectra evidence a p-type doping of the oligomer.

**MON 4****Linear and Bimorph Bucky Gel Actuators from Cross-Linked Super-Growth Carbon Nanotubes**

Alberto Ansaldo<sup>1</sup> Maurizio Bisio<sup>1</sup> Don N. Futaba<sup>2</sup> Kenji Hata<sup>2</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

<sup>2</sup>Nanotube Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

In 2003 Takuzo Aida and coworkers reported that, when ground with imidazolium based ionic liquids (ILs), single-walled carbon nanotubes (SWCNTs) create a physical gel, named “bucky gel”. This gel was used to prepare bimorph dry electrochemical actuators that can operate in air at low voltage, having an internal solid electrolyte layer and two bucky gel electrodes used alternatively as cathode or anode thus producing a bending motion. This kind of motion limits the application range, especially when linear strain and motion are required.

We present a novel actuator capable of both linear and bending motion that relies on a three electrode configuration i.e. two bucky gel electrodes and a third passive one, made from a metal spring, acting as counter plate. Moreover we have cross-linked Super-Growth SWCNTs and used the resulting material for making the bucky gel actuators. This cross-linking gives rise to an increase in the specific capacitance of the composite material that results in a dramatic improvement in strain and efficiency of the bucky gel actuators. Our latest results on linear and bimorph bucky gel actuators composed of chemically modified CNTs will be given.

**MON 5****Inspection of n- and p- type substitutional dopants in SWCNTs and disentanglement of their bonding environment**

Paola Ayala<sup>1</sup> Duncan Mowbray<sup>2</sup> Georgina Ruiz-Soria<sup>1</sup> Jessica Campos-Delgado<sup>3</sup> Mauricio Terrones<sup>4</sup> Angel Rubio<sup>2</sup> Thomas Pichler<sup>1</sup>

<sup>1</sup>University of Vienna, Faculty of Physics, Strudlhofgasse 4, A-1090Vienna, Austria

<sup>2</sup>Nano-bio spectroscopy group and ETSF, University of the Basque Country and DIPIC, E-20018 San Sebastian, Spain

<sup>3</sup>INMETRO, Xerém, 25250-020 Rio de Janeiro, Brazil

<sup>4</sup>Department of Physics, The Pennsylvania State University, USA

The controlled modification of the electronic structure of SWCNTs doped with less than 1 at%. with N, B and P heteroatoms was inspected via spectroscopic methods. Samples produced via high and low temperature synthesis methods were probed. Multi-frequency Raman spectroscopy was used to monitor the dopant induced changes in the intensity of the RBM and changes in the G' band. Direct detection of dopants below 0.01% at in the SWCNT lattice from core level photo-

emission and X-ray absorption on purified samples will be shown to identify the different elemental bonding environments, which are substantially supported by ab-initio calculations. Further studies on the correlation between the changes in the electronic properties of the doped SWCNTs with Raman spectroscopy and optical absorption are shown to illustrate the site selective bonding environments and the influence on the electronic transport properties with unprecedented detail.

Work supported by FWF and EU.

## MON 6

### **Deposition of nanocrystalline diamond films on temperature sensitive substrates for grazing angle reflectance spectroscopy**

Oleg Babchenko<sup>1</sup> Zdenek Remes<sup>1</sup> Bohuslav Rezek<sup>1</sup> Alexander Kromka<sup>1</sup>

<sup>1</sup>Institute of Physics ASCR, v.v.i., Prague

Due to diamond chemical and abrasion resistance, it is often used as a protective material for brittle and soft substrates. On the other hand, low diamond adhesion or substrate damaging during a harsh chemical vapor deposition (CVD) are the limiting factors for wider commercial uses of these films [Costello et al: Diamond & Relat. Mater. 3 (1994) 1137]. In the present work we report on optimized deposition of thin nano-crystalline diamond films on mirror substrates (Al/glass). Top SiO<sub>2</sub> layer was used to improve the diamond adhesion and to protect Al layer during the CVD growth. Standard focused microwave plasma system results in damaging substrates due to high temperature gradient between plasma and the substrate holder. A homogenous, high quality diamond growth was achieved in CO<sub>2</sub>/CH<sub>4</sub>/H<sub>2</sub> gas mixture by linear antenna pulsed microwave plasma system. Mirror coated with diamond layer were successfully used as chemically functionable substrates for detection of adsorbed molecules (i.e. proteins) by grazing angle reflectance spectroscopy.

## MON 7

### **Optimizing the response of gas sensor based on SWCNTs film by using sorted SWCNTs**

yann Battie<sup>1</sup> O. Ducloux<sup>2</sup> P. Thobois<sup>2</sup> A. Loiseau<sup>1</sup>

<sup>1</sup>ONERA, LEM, Chatillon

<sup>2</sup>DMPH-CMT, ONERA, Chatillon

Single walled carbon nanotubes (SWCNTs) show extreme sensitivity towards changes in their local chemical environment. The sensitivity of gas sensor based on SWCNTs films is currently explained by two theories: the modification of the Schottky barrier between the semi-conducting nanotubes and the electrical contacts and the chemical doping on the surface of carbon nanotubes.

In this communication, density gradient ultracentrifugation (DGU) is used to separate semiconducting SWCNTs to metallic ones in order to determine the intrinsic

effect of the electronic structure of SWCNTs on the gas sensing mechanism. The sensors used, consist of sorted SWCNTs films deposited on a transmission line structure (TLM). TLM analysis is a common and reliable technique to simultaneously extract the contact resistance and the sheet resistance of the film from measurements. The tested gases are NH<sub>3</sub> or NO<sub>2</sub>. In this work, we firstly clarify the origin of the response of gas sensors based on SWCNT films and then we propose new ways for optimizing the gas sensors response taking advantage of using sorted semi-conducting tubes.

**MON 8****Differences and similarities in adsorption of a single photochromic molecule on Cu(111) and Si(100)**

Maciej Bazarnik<sup>1</sup> Ryszard Czajka<sup>1</sup> Karina Morgenstern<sup>2</sup>

<sup>1</sup>Institute of Physics, Poznan University of Technology, Nieszawska 13A, 60-965 Poznan, Poland

<sup>2</sup>Division of Atomic and Molecular Structures (ATMOS), Leibniz University of Hannover, Appelstr. 2, D-30167 Hannover, Germany

Molecular electronics proposes to use single molecules as functional units within larger circuits. As a possible switch the cis-trans isomerisation of azobenzene derivative stimulated mostly by electrons and by photons has been extensively studied. On surfaces, this molecule class was mostly investigated on Au(111) because it is known to weakly interact with adsorbed molecules. However, electronic industry is based on semiconductor monocrystalline surfaces, in particular Si(100), which interact more strongly with molecules. Therefore in order to incorporating molecular switches into devices we must find molecules which can act as a switch on silicon. In order to contribute to the understanding of switches based on isomerisation reactions adsorbed on the silicon surface we want to create a transfer rules for the research done on metals to Si surfaces. In this presentation, we compare the adsorption configurations of 4-anilino-4'-nitroazobenzene molecules adsorbed on Cu(111) and on Si(100). We discuss the differences in isomerisation capabilities of adsorbed molecules arising from interactions between the molecules and the substrates.

Acknowledgments: MSHE N N202 482739, COST CM0601

**MON 9****Substitutional doping of BN-sheets with carbon: a first principles study**

Natalia Berseneva<sup>1</sup> Arkady Krashenninikov<sup>1</sup> Risto Nieminen<sup>1</sup>

<sup>1</sup>Electronic Properties of Mathetial Group, Department of Applied physics, Aalto University School of Science and technology, Finland

In this work we investigate the combination of graphene and hexagonal boron nitride in one structure since they have several common characteristic features, such as crystal lattice, thermal properties, and hardness. We propose structures of different

sizes with carbon nano-islands being the defects in boron nitride systems.

Theoretical study of these materials involving Vienna Ab-initio Simulation Package (VASP) was accomplished with calculations based on Density Functional Theory (DFT), Generalized Gradient Approximation (GGA). Since the energy gap values obtained with GGA calculations are underestimated, the results with more accurate method involving hybrid potentials (HSE) are provided.

Formation energy of various substitutional defects was computed as a function of system charge. It was found that it has a minimum value in the systems where more B (N) atoms are substituted by C and system charge is positive (negative). In addition we presented that systems with triangular substitutional defects, formed by carbon islands, have interesting magnetic properties; magnetic moments are agreed well with Lieb's theorem.

#### **MON 10**

##### **Angle- and time-resolved XUV photoemission from graphene using high harmonic generation**

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Two-photon photoemission is a widely diffused technique to investigate electron dynamics at surfaces and allows to acquire information on the unoccupied electronic bandstructure. High-order Harmonic radiation of visible or near-IR ultra short laser pulses are a XUV radiation source with fs-pulse duration. We performed time- and angle-resolved photoemission on graphene epitaxially grown on Ni(111). The graphene is deposited on the Ni surface by cracking of ethylene in UHV at high temperature. Polarization dependent final state effects have been observed in the photoelectron cross section of graphene states. The band structure has been investigated and time resolution of about 37 fs has been achieved in a first XUV pump IR probe experiment.

#### **MON 11**

##### **Magnetoelectric properties of bulk materials and nanoparticles**

Robert Blinc

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The spontaneous polarization is a polar vector which is invariant against time reversal, but not space reversal. The spontaneous magnetization on the other hand is an axial vector which is invariant against space reversal, but not time reversal. Therefore the simultaneous existence of the spontaneous polarization and the spontaneous magnetization is usually forbidden. In magnetoelectric systems on the other hand the electric polarization and the ferromagnetic magnetization are simultaneously allowed in 58 magnetic classes in the bulk and 90 magnetic classes in

surface-dominated nanosystems. Here we present the properties of the bulk magnetoelectric K<sub>3</sub>Fe<sub>5</sub>F<sub>15</sub> with a ferroelectric transition at  $T_c = 490$  K and a magnetic transition at  $T_1 = 125$  K. We also discuss the properties of superparamagnetic Er<sub>2</sub>O<sub>3</sub> nanoparticles with an average size of 5 nm embedded in a SiO<sub>2</sub> glass matrix. Here a ferroelectric transition takes place around 275 K and the dielectric properties are strongly magnetic field dependent. The system seems to be determined by surface rather than by bulk symmetry. The theory of this effect is presented.

**MON 12****Anchor Engineering for Noncovalent Nanotube Functionalization**

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When functionalizing carbon nanotubes noncovalently, the interaction strength between the tubes and the attached moiety typically depends on the chirality of the nanotube as well as a specially designed anchor part of the molecules. Many aromatic molecules like pyrene, porphyrine, perylene and flavine as well as simple alkyl chains incorporated into molecules have been demonstrated to allow adsorption onto carbon nanotubes. Furthermore, the design of the anchor group can bring about a chiral selectivity towards a certain type of nanotube and thus allow engineering functional molecules to target specific nanotube chiralities.

We report our results on investigating aqueous dispersions of carbon nanotubes using a series of molecules with different anchor groups. We show that the interaction between amphiphiles and tubes, as well as the efficiency to solubilize and debundle carbon nanotubes can be tuned by varying the dimension of the hydrophilic and hydrophobic parts of the molecules and by inserting aromatic moieties. The sample composition and thus molecules' chiral selectivity are probed with various methods, in particular photoluminescence excitation and absorption spectroscopy.

**MON 13****Exciton-phonon induced side-bands in absorption spectra of carbon nanotubes**

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We present results on microscopic calculations of linear absorption spectra in carbon nanotubes (CNTs) and graphene. Our approach is based on the density matrix formalism, which allows a straight-forward inclusion of the carrier-carrier and carrier-phonon interaction. First, we investigate the absorption spectra by compu-

ting graphene- and CNT-Bloch equations: We find clear excitonic features in the spectra of metallic and semiconducting carbon nanotubes in agreement with recent experimental and theoretical studies. In graphene, we observe the formation of excitons around the M point in the Brillouin zone with significant binding energies. Around the K point, however, the excitonic effects are negligibly small.

Second, we investigate the influence of the exciton-phonon interaction on the absorption spectra of CNTs. Our approach is based on an excitonic basis set. We observe a polaron shift and a formation of pronounced exciton-phonon induced sidebands approximately 200 meV above and below the zero-phonon line depending on the temperature.

#### MON 14

##### **Influence of Pd-Au/MWCNTs surface treatment on catalytic activity in the formic acid electrooxidation**

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The catalytic activity in the formic acid electrooxidation reaction of the Pd-Au multiwall carbon nanotubes (MWCNTs) supported catalyst, prepared by a microwave-assisted polyol method, was investigated. Prior the electrochemical tests, the catalysts were submitted to several surface treatments, i.e. under different gas atmospheres and temperatures (200 °C and 300 °C), which resulted in different catalytic activities. To explain this behaviour, the electron spectroscopy methods were applied for characterizing the catalyst surface quantitatively and qualitatively by analyzing (i) the content of nanometallic particles (Pd and Au) and their chemical forms, (ii) the nanoparticles dimensions and (iii) the surface 3D nanostructure. Analysis showed that catalytic activity of Pd-Au/MWCNTs catalysts is attributed to the metallic nanoparticles size and distribution, as well as the content, coverage and thickness of contamination overlayer on Pd nanocrystallites.

**MON 15****Optical and Raman investigation of luminescent Eu complex - nanotube hybrids**

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Eu(III) complexes are among the light-emitting devices with the highest quantum efficiency. However, their low thermal and photochemical stability, poor mechanical properties and aggregation issues still represent important disadvantages concerning their technological applicability. To overcome these difficulties hybrid materials were prepared from carbon nanotubes and luminescent Eu complexes [1]. These materials combine the luminescent properties of the lanthanide complexes and the physico-mechanical properties of the nanotubes.

Model systems of different types of complexes (with and without aromatic ligands) adsorbed on single-walled carbon nanotubes were prepared and studied by optical and Raman spectroscopy with the focus placed on the interaction between the nanotubes and the Eu complexes. Raman spectroscopy is particularly useful to detect changes of the host nanotubes. With optical spectroscopy, the lanthanide complexes and the changes of the nanotubes' electronic transitions can be investigated. The adsorption process results in significant changes detectable by all methods.

[1] G. Accorsi et al. Adv. Funct. Mater. 2007, 17, 2975–2982

**MON 16****First measurement of the sound velocity within 1D fullerene chains inside single-walled carbon nanotubes**

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The fullerene peapods possess a high fundamental interest since they allow studying the physics of a truly 1D molecular chain that cannot be obtained in another environment. Whereas the original rotational dynamics of the encapsulated C<sub>60</sub> has already been observed (S. Rols et al., Phys. Rev. Lett., 2008, 101), their translational dynamics has never been measured until now. In order to observe this motion using inelastic neutron scattering (INS), we recently synthesized a large amount of

peapods under the form of buckypapers – in which the tubes are mainly oriented along the buckypaper's plane. In a recent experiment on the time of flight spectrometer IN5 at the ILL, we showed that the translational motion of the confined fullerenes is characterized by an additional quasielastic signal in the configuration where the Q corresponding to the 1D chain is set parallel to the paper's plane. This signal is actually due to the density of states of the longitudinal 1D phonons, whose analytical formula has been calculated, allowing to determine, for the first time, the sound velocity within the 1D fullerenes chains, and thus shedding light on the interaction between neighbor fullerenes.

#### MON 17

##### **Nanochemical Reactions by Laser Annealing of Ferrocene Filled Metallicity Selected Single-Wall Carbon Nanotubes**

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Thermal annealing of Fe(Cp)<sub>2</sub> filled SWCNTs yield to doped DWCNTs via a catalytic reaction. The annealing time and temperature allows to control their doping level. Here we present an additional approach of in-situ laser annealing setup in order to control the dynamics of the transformation of metallicity sorted Fe(Cp)<sub>2</sub> filled SWCNTs to doped DWCNTs. A Nd:Yag infrared laser was used for both: 1) anneal the sample in high vacuum and 2) to monitor the Raman response of the formation of DWCNTs and analyze the kinetic of the reaction. These results will be compared with photoemission and Raman results of furnace annealed metallicity sorted samples in order to pinpoint the doping level, DWCNTs diameters and metallicity dependence electronic properties. In addition the sample morphology was analyzed by electron microscopy. This work is supported by FWF.

#### MON 18

##### **BN monolayer - Graphene Heterostructures**

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Micromechanical exfoliation was important historically to isolate single atomic planes – graphene – from the layered material graphite. Usually this produces flakes of many thicknesses and optical contrast and Raman spectroscopy are indispensable tools to locate and identify the number of layers. As an insulating counterpart to graphene, few layer boron nitride (BN) is of interest. In this work we have applied similar techniques to identify the thickness of few layer BN down to its monolayer by utilizing its optical contrast on a silicon/silicon oxide substrate. We model the

interference conditions and determine the optimal spacer thickness to maximize contrast of few layer BN. We use Raman spectroscopy as a tool to confirm thickness with BN monolayers showing a  $4\text{ cm}^{-1}$  upshift of the fundamental Raman mode frequency in agreement with theory. The number of layers can be counted as the Raman intensity and optical contrast increase in a linear step-like fashion with thickness. This allows us to produce BN - graphene heterostructures with finely tuned properties by transfer procedures meaning we can investigate phenomena not possible in graphene on common substrates.

**MON 19****Simulations of the polarisation-dependent Raman intensity of photosystem II crystals**

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The photosystem II molecule complex, being found in almost every plant, is responsible for the absorption of light and the transport of charge carriers. The unit cell of the photosystem II (PSII) crystals consists of eight monomers containing twelve carotene molecules each. The polarisation-dependent Raman intensities for all 96 molecules were simulated taking into account the orientation and symmetry axis of each molecule. The crystal structure model of cyanobacterial photosystem II at 2.9-Å resolution [1] was used for the simulation of the Raman intensities. The calculated polarisation dependence is compared with polarisation-dependent Raman experiments on PSII crystals. The emphasis in the comparison of theory and experiment is on the symmetry of the monomers in the PSII crystal. Groups of carotenes with nearly the same orientation can be distinguished by their polarisation dependence of the  $\nu_1$  modes. The possibility to identify the orientation of one carotene molecule will be discussed.

**MON 20****Electronic state of polyaniline deposited on porous carbon nanomaterial**

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Combination of polyaniline (PANI) and porous carbon material allows developing supercapacitors with high specific capacity and long-term ability. Charge transport in composite electrode depends on the form of PANI deposited on the carbon surface. The most conductive form is leucoemeraldine where all nitrogen atoms are linked with protons from solution. Here we use methods of x-ray photoelectron spectroscopy and near-edge x-ray absorption spectroscopy for probing the electronic structure of composites from PANI and carbon nanomaterial. PANI was deposited chemically or electrochemically on two types of supports: array of aligned carbon nanotubes or ordered mesoporous carbon. The interpretation of experimental data was done based on DFT quantum-chemical calculations of different forms of PANI. We found that chemical state of PANI is very sensitive to the procedure of electrode preparation.

**MON 21****CNTs yield versus substrate chemistry and morphology**

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We performed Fe catalyst mediated Chemical Vapour Deposition (CVD) to grow Carbon Nanotubes (CNTs) on different TiN films, grown by Atomic Layer and Magnetron Sputtering deposition (ALD, SD). Studying each step of the CVD process via in situ photoemission and ex situ SEM and Raman measurements, we show that a good CNTs yield can be obtained only under certain conditions. Outside of these conditions a strong Fe-TiN interaction and Fe diffusion occur, which inhibit the CNTs growth. Fe diffusion is strongly dependent by the TiN growth method, it is present also at RT and it is strongly enhanced at 600°C. As a consequence, substrate reproducibility and quality are fundamental requirements to fix the process parameters to reach a reproducible growth of CNTs.

**MON 22****Growth of Curved Graphene Sheets on Graphite by Chemical Vapor Deposition**

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We report the synthesis of a new carbon-based nanostructure - curved graphene sheet (CGS), an intermediate structure between carbon nanotubes and graphene. The CGS grows by catalytic chemical vapor deposition auto-selectively at the stacked bilayer edges of graphite support, providing an atomically smooth connection of the edges. We propose a growth mechanism based on Fe nanoparticle diffusion along the step edges, acting as a nan zipper. The results may have a significant impact on the fabrication of new carbon nanostructures and their integration into nanoelectronics.

**MON 23****Single Molecule Magnets on Graphene**

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We report the first results towards the combination of carbon and molecular nanostructures for spintronics. In particular, we introduce hybrids made of Single Molecule Magnets (SMMs), which present unique quantum signatures in their magnetic behavior. We study hybrid nanostructures obtained from graphene and the  $\text{Fe}_4(\text{OMe})_6(\text{dpm})_6$  molecular magnet, which was functionalized with specifically-designed groups. Grafting is achieved by  $\pi$ -stacking interactions, with the idea of preserving the electronic properties of graphene and the quantum behavior of the SMMs. We investigate the formation of the hybrids on both graphene produced by micro-mechanical exfoliation and RGO. The properties of the hybrid material are then analyzed by means of AFM, XPS, TOFSIMS and SQUID. We evidence different reactivity of differently-produced graphene substrates. Control on the coverage density and on the creation of aggregates is achieved and reorganization of pyrene on graphene can be followed. Eventually we discuss the perspective of these systems for spintronic and for the realization of new devices for single molecule detection.

**MON 24****ALKALI-METAL DOPED GRAPHITE AND NANOTUBES: Exfoliation vs. Intercalation compound formation**

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In this work we introduce an experimental and theoretical approach to understand alkali-metal doping in graphite and MWNT. We present a combined ARPES and Raman study on three stages of graphite intercalation compounds (GIC)  $KC_{36}$ ,  $KC_{24}$ , and  $KC_8$ . A charge transfer to the graphene layer and a shift of the occupied  $\pi$  bands with respect to the Fermi level was monitored and compared with ab-initio results including electronic correlation effects. In the case of nanotubes, density functional theory (DFT) and molecular dynamics calculations were performed with Li atoms inside of a (5,5@10,10) DWNT. This part of the study provides relevant information about intercalation mechanism which is expected to be as efficient as in the case of GIC.

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**MON 25****EXAFS study of polyiodide chains confined inside carbon nanotubes**

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Carbon nanotubes are promising candidates in the development of new electronics devices [1]. Their electronic properties, can be controlled and tuned by inserting atoms or molecules in the hollow core of the tubes. When iodine atoms are inserted, a p-doping of the nanotubes is induced via a charge transfer from the tubes to the iodine atoms leading to the formation of polyiodides chains [2].

Depending on the nanotubes diameter, it has been shown that different kinds of structures are formed. In nanotubes of small diameter only single chains are found while in thicker nanotubes, double helix and triple helix chains are observed [3]. Although structural informations on the long range order are available, less is known on the local order and the nature of the polyiodides formed inside the carbon nano-

tubes. To go further in the understanding of these confined systems, we have used EXAFS spectroscopy to study of local order of polyiodides chains as function of the nanotube diameter.

[1] Santhosh et. al., Carbon 47 2436 (2009)

[2] L.Grignorian et. al., Phys. Rev. Lett, 80, (1998), 5560.

[3] L. Guan, Nanoletters 7, 1532, (2007)

## MON 26

### Faraday rotation in single and multilayer epitaxial graphene

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Placed in a magnetic field, the Dirac cones of graphene split up in non-equidistant Landau levels with a non-trivial zero energy. Transitions between various Landau levels give rise to a spectacular series of absorption peaks in the magneto-optical response [1]. One of the most striking consequences of time-reversal symmetry breaking is Faraday rotation: the rotation of the polarization of light after passing a medium in a magnetic field. Faraday rotation is directly related to the AC Hall conductivity and reveals the sign of charge carriers and provides a broad range optical response.

We present for the first time experimentally obtained Faraday rotation of multilayer and single layer graphene on the carbon and silicon side of SiC [2]. The cyclotron resonance observed in highly doped graphene strongly enhances the rotation, leading to a rotation of 6° in modest magnetic fields. Individual inter LL transitions are identified and we show that the sensitivity to the sign of charge carriers involved in the inter LL transitions delivers unexpected insights.

[1] M.L. Sadowski et al. Phys. Rev. Lett. 97, 266405 (2006).

[2] I. Crassee et al. Nature Physics 7, 48-51 (2011).

## MON 27

### Are carbon nanotubes commensurate?

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The nearest neighbor bonds in simply rolled up single-wall carbon nanotubes are not of the same length, as in graphene or graphite. This causes strains, which are only partly compensated within relaxation procedure. In fact, one degree of free-

dom, a torsion of nanotube, cannot be numerically relaxed: arbitrary small torsion tremendously enlarges nanotube translational period, making number of atoms to be considered beyond technical capabilities of the usual codes (treating translational cell). Even more, there is no justification that SWCNT is commensurate at all.

Line group symmetry [1] of nanotubes includes helical operation with two continual parameters: translation ( $f$ ) and rotation ( $Q$ ), corresponding to elongation and torsion. A simple geometrical model, enabling analytical optimization of these parameters, and afterwards, full symmetry implemented POLSym DFTB code confirm a torsion, and possible incommensurability except for achiral tubes. However, the angle may be tiny enough to be measurable, unless there is an effect clearly distinguishing commensurable and incommensurable structures.

[1] M. Damnjanovic and I. Milosevic, *Line Groups in Physics* (Springer, Berlin, 2010)

## MON 28

### **n-Type doping of single-walled carbon nanotubes or just de-doping?**

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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 is expected to transfer electrons to the nanotubes as already observed for alkali metals. The NEXAFS spectra show that the deposition of TMP and TMPD molecules on the nanotube surface strongly modifies the absorption features, especially the electron density of the weakly bonding and the density at the Fermi level (zero energy) increases with the molecule adsorption regarding to that in the pristine SWNTs. Rather intensive feature between  $\pi^*$  and  $\sigma^*$  resonances in the NEXAFS C-K-edge of the pristine SWNTs attributed to oxidized carbon functional groups are suppressed in the modified networks. This fact suggests that the aromatic amines remove or replace oxygen species responsible for the p-type doping of SWNTs and thus acting as a de-doping agent. Even though the n-type doping effect has been confirmed by the electronic structure calculations based on the first-principles density functional theory, the available experimental results provide only the evidence for the de-doping of the naturally p-type semiconducting SWNTs.

**MON 29****Vibrational properties of ZnO nanowires**Edib Dobardzic<sup>1</sup> Milan Damnjanovic<sup>1</sup><sup>1</sup>University of Belgrade, Belgrade

Standard Ewald summation method is amended to enable calculations for crystals periodical along only one direction. Slowly convergent Coulomb series is divided into three series. Two of them rapidly converge, and with high precision can be approximated by a few leading terms. The remaining one (comprising slowly convergent terms) is calculated analytically. The part of the dynamical matrix related to Coulomb interaction is subdued to analogous simplification.

We applied this method to hexagonal ZnO nanowires. It turns out that only the first neighbor core-core interaction is sufficient to stabilize system. Using the experimental value of the bulk modulus, model parameters are derived. Finally, we use valence-force-field model (stretching and bond-bending interactions) together with Coulomb and core-core interactions to calculate dynamical matrix and phonon dispersions. As it is expected, there is no discontinuity in phonon branches like LO-TO splitting characteristic for ionic three dimensional crystals.

**MON 30****Phenomenological Quantum Confinement Models for Excitons and Phonons of Silicon Nanocrystals.**Manuel DOSSOT<sup>1</sup> Patrice MISKA<sup>2</sup> Hervé RINNERT<sup>2</sup> Michel VERGNAT<sup>2</sup> Bernard HUMBERT<sup>3</sup><sup>1</sup>Laboratory of Physical Chemistry and Microbiology for the Environment (LCP-ME), UMR 7564 CNRS-Nancy University, F-54600 Villers-lès-Nancy, FRANCE<sup>2</sup>Institut Jean Lamour (IJL), UMR 7198 CNRS-Nancy University, F-54506 Vandœuvre-lès-Nancy Cedex, FRANCE<sup>3</sup>Institut des Matériaux Jean Rouxel (IMN), UMR 6502 CNRS-Nantes University, F-44322 Nantes Cedex 3, FRANCE

Silicon (Si) nanostructures have attracted much attention since the discovery of a strong visible photoluminescence emitted by porous silicon. The rich potential of silicon nanocrystals lies in the fact that their optical properties are quite correlated to their size and morphology due to spatial confinement of electronic and phononic wavefunctions.

In the present study, the optical and vibrational properties of silicon nanocrystals are studied in two systems elaborated by evaporation. The first one is constituted by a thick SiO layers. The second one is a multilayered sample made by successive evaporations of SiO and SiO<sub>2</sub> layers with controlled thicknesses. The luminescence and Raman spectra are fitted by phenomenological exciton and phonon confinement models accounting for the size distribution of the embedded nanocrystals. The coherence between the two models and experimental data is demonstrated and

gives support to the notion of exciton and phonon confinement effect in silicon nanocrystals embedded within silicon matrix.

**MON 31****Mechanical and Electrical Tuning of a Molecular Quantum Dot**

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Most important in the understanding of electronic transport through single molecules is the exact nature of the metal-molecule-metal conformation. The overlap of the molecular orbital with the Fermi-levels determines both the initial level alignment, the level spacing, as well as the coherence of the transport. We present the simultaneous electrostatic and mechanical tunability of a molecular junction. The ability to tune the distance between the electrodes with pm precision over wide range (nm), and at the same time shift the energy levels in the molecule by using a gate electrode allows us to unambiguously monitor the influences on the transport. Our results show that depending on the particular geometry of the junction the electronic transport through both HOMO and LUMO molecular orbital can be observed. By elongating and compressing the contact, different conformations of the same molecule can be achieved which results in huge shift in the position of the same molecular orbital with respect to the Fermi level of the metal electrodes. Our findings demonstrate that the electronic transport in a molecule can be modulated by gradually changing the electrode-molecule conformation.

**MON 32****Bundles of Single-Wall Carbon Nanotubes: Studied by a van der Waals Density Functional**

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We study the binding energy, intertube distance and electronic structure of bundles consisting of carbon nanotubes of the same chirality. We model various nanotube structures (chiralities) and orientations with van der Waals density functional theory. The orientation of the tubes in the bundle strongly influences the properties of the bundles if the chirality of the tubes shares symmetry with the trigonal bundle structure, meaning chiralities which have a 60°-rotational symmetry ( $C_6$ -axis), e.g. (12,0) bundles. Here, the bundle structure creates a constraint for the arrangement of the neighboring tube surfaces. Small pseudo gaps open up for all metallic tubes in a bundle. For bundles of chiralities with  $C_6$ -axis the pseudo gap and intertube distance ( $\pm 5$ -10%) vary in dependence of the relative orientation of the tubes. The

van der Waals forces between tubes increase with increasing tube diameter. The van der Waals energy per atom decreases with increasing tube diameter and converges towards the value of the intersheet energy of graphene for tubes with diameters larger than  $\approx 3$  nm.

### MON 33

#### Non-equilibrium transport of Dirac electrons

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We present a unified view of electric transport in undoped graphene for finite electric field. The weak field results agree with the Kubo approach. For strong electric field, the current increases non-linearly with the electric field as  $E^{3/2}$ . As the Dirac point is moved around in reciprocal space by the field, excited states are generated. This is analogous to the generation of defects in a finite-rate quench through a quantum critical point, which we account for in the framework of the Kibble-Zurek mechanism. These results are also recast in terms of Schwinger's pair production and Landau-Zener tunneling. The (spin-) quantum Hall breakdown is also analyzed.

### MON 34

#### Gate hysteresis originating from atomic layer deposition of Al<sub>2</sub>O<sub>3</sub> onto suspended carbon nanotube field-effect transistors

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We recently demonstrated hysteresis-free suspended carbon nanotube transistors [1], which are here employed to investigate hysteresis induced by atomic-layer-deposited Al<sub>2</sub>O<sub>3</sub>, typically serving as gate separation or passivation [2]. As hysteretic effects are not desired for FETs and the readout of sensors but useful for memory devices if controlled, their origins are being heavily discussed. Ultraclean, non-passivated suspended CNFETs contacted by shadow mask evaporation do not exhibit hysteresis. In this study, 40 nm of Al<sub>2</sub>O<sub>3</sub> were deposited on such a CNFET by atomic layer deposition at 150 °C. A change from p- to n-type behavior was seen. For gate sweeps to  $\pm 20$  V, hysteresis on the order of volts occurred – retarding hysteresis at lower  $V_g$  and advancing hysteresis at higher  $V_g$ . These effects are suspected to be caused by trap states and enhanced water adsorption due to the large hydrophilic [3] Al<sub>2</sub>O<sub>3</sub> surface.

[1] Muoth M. et al., Nature Nanotech. 5, 589 (2010).

- [2] Helbling T. et al., Nanotechnology 20, 434010 (2009).  
[3] Deng X. et al., J. Phys. Chem. C 112, 9668 (2008).

**MON 35****Spontaneous formation and characterization of silicon carbide nanowires generated by thermolysis**

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Nanowires (NWs) often show distinct properties from their bulk counterparts because of the radial confinement. Since silicon carbide NWs can be used as interconnects in integrated circuits and they are compatible with the processing of CMOS devices, their synthesis has been extensively studied recently. Here, we propose a fast, simple, easy to operate, and one-step chemical synthesis of branched SiC nanostructures via a thermolysis route. The effect of a set of parameters, such as: reactant composition (powdered Si/PTFE or Si/PTFE/NaN<sub>3</sub> mixture), initial combustion pressure (1-20 atm) and atmosphere (air, argon, nitrogen) was studied. The morphology of the products has been characterized using XRD, SEM, TEM and Raman spectroscopy. The chemical purification procedure was tested. Finally, the mechanism of formation and possible applications in composite materials are currently under investigation.

Acknowledgement. The project is co-financed by the European Regional Development Fund within the Innovative Economy Operational Program 2007-2013, No UDA-POIG.01.03.01-14-071/08-04.

**MON 36****Structural analysis of electron beam-induced destruction of graphene membranes in electron microscopes**

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Observation of graphene membranes under exposure to electron beam irradiation in a high resolution transmission electron microscope (HRTEM) show that such

treatments can cause severe damage of the 2D hexagonal structure of graphene. In order to study the voltage dependence and the “knock on threshold” of beam induced defects and the structural rearrangements of the honeycomb like structure of graphene, atomically resolved image sequences have been taken at different voltages. Voltage dependences of beam induced defects in graphene membranes for various doses as well as the “knock on” voltage threshold for defect creation is measured and discussed. Furthermore the collision process between the beam electrons and their target is analyzed by comparing beam induced defects of C12 and C13 graphene layers. The difference in the knock-on threshold between ordinary (C12) graphene and heavy (C13) graphene allows to identify and differentiate the effects of knock-on damage (the collision of the beam electrons with the nucleus of the carbon atoms) and other damage mechanisms (ionization damage or beam-induced chemical etching).

**MON 37****Reinforcement of multi-walled carbon nanotubes by high temperature annealing**

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Despite the drastic improvement in the quality of the multi-walled carbon nanotubes (MWNTs) produced by CCVD over the last decade as grown MWNTs with large diameter still exhibit weak mechanical properties due to the presence of structural defects with high density. Consequently, post growth processes like heat treatment are necessary to anneal the defects. Here, we will present the effect of heat treatment at high temperature (2200-2800°C) on the mechanical properties of CCVD-grown MWNTs measured by AFM bending tests. Without annealing, E decreases systematically as the MWNT diameter increases in the range of 10-45nm. MWNT annealing at temperature above 2200°C yields to a drastic increase of E as compared to the pristine MWNTs with similar diameter. This effect results from the effective elimination of structural defects. However, E between MWNTs annealed at different temperature above 2200°C varies within the experimental error of the AFM measurements. The mechanism of defects' annealing will be discussed on the basis of TEM analysis and Raman scattering spectroscopy as well. They corroborate a steady improvement of the MWNT structure with the annealing temperature increase.

**MON 38****Versatile Approach Towards Covalent Graphene Functionalization**

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Although significant research activity in the field of functionalized graphene has been carried out, most work done yet focuses on the use of either graphene oxide or already processed and exfoliated graphene sheets deposited on substrates. In this work we report on the first wet chemical bulk functionalization route starting from graphite that does not require an initial oxidative damage of the pristine graphene basal planes accomplished by means of reductive activation. The activated intermediates are characterized by Raman spectroscopy as well as by atomic force microscopy. Furthermore electrostatic exfoliation can be observed coupled with unexpectedly high reactivity of the chemically inert graphite towards reoxidation by organic aryldiazonium salts. The successful covalent functionalization prevents reaggregation and can be verified by a combination of microscopic and spectroscopic techniques, namely spatial scanning Raman microscopy, atomic force microscopy, aberration corrected HRTEM, statistical Raman spectroscopy, EDX and XPS analysis as well as by mass spectrometric coupled thermal gravimetric analysis (TGA/MS)

**MON 39****Determination of the Local Chemical Structure of Graphene Oxide and Reduced Graphene Oxide via Ultra-High-Resolution Electron Microscopy**

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Graphene oxide (GO) and reduced and annealed graphene oxide (raGO) are studied via ultra-high-resolution transmission electron microscopy and the atomic structure of these materials is revealed. A return to graphene from GO is found to not be possible via the standard synthetic route which was employed. Many insights about the greatly debated structure of GO are revealed, showing few square nanometer

graphitic regions surrounded by a network of highly oxidized regions with occasional small holes. Individual oxygen functionalities are imaged and shown to have high mobility along the surface of GO. A redefinition of the structure of GO is proposed and raGO is shown to have significant structural instability under the electron beam.

#### MON 40

##### **Growth of ultrahigh density nanotube forests for interconnects**

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We present a general method of catalyst design to synthesise ultra-high density, vertically-aligned forests of carbon nanotubes by cyclic deposition and annealing of catalyst thin-films. This leads to nanotube forests with an area density of at least  $10^{13} \text{ cm}^{-2}$ , over an order of magnitude higher than existing values, and close to the limit of a fully dense forest. The technique consists of cycles of ultra-thin metal film deposition, annealing and oxidative immobilisation. These ultra-dense nanotube forests are needed to use carbon nanotubes as vias and interconnects in integrated circuits and thermal interface materials. Further density increase is possible by reducing nanotube diameter; the method is also applicable to nanowire synthesis.

#### MON 41

##### **Morfology of helically coiled carbon nanotubes prepared using Co/13X zeolite catalysts**

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There are different ways to classify CNTs, such as by number of walls, chirality or tube morphology (helix/straight). Various applications require different properties in CNTs therefore, controlling the structures and properties of CNTs has been one of the most important issues in CNTs synthesis. Since the insertion of pentagons and heptagons into the hexagonal sheet of a straight nanotube induces significant changes in the electronic structures, helical and toroidal forms possess remarkable electrical and magnetic properties, which are rather different than that of cylindrical tubes. The adhesion force at catalyst/substrate interface, catalyst particle size and substrate porosity as key factors affecting the growth modes. Our experiments focused on the production and development of catalysts for the synthesis of helically coiled CNTs. The catalysts were characterized by XRD, TGA, SEM

and were tested in the decomposition of acetylene at 720°C by CCVD method. For qualitative characterization of carbon deposit on the surface, products were imaged by transmission and scanning electron microscopy (TEM, HRTEM, SEM). The activity of each catalyst sample was characterized by carbon yield.

**MON 42****FLEXIBLE ELECTRODES USING CARBON NANOTUBES**

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We obtained a random network films of highly pure single-wall carbon nanotubes (SWCNTs) on a flexible silicone substrate by spraying an aqueous SDS carbon nanotubes suspension. We stretch uniaxially the samples at different elongations up to 20 percent the original length and measured the AC electrical conductivity in a frequency range up to 110 MHz. The electrical impedance increases with the stretching, recovering the initial value for small elongations. We analysed by polarised Raman spectroscopy on the same stretched samples, and we could observe a partial alignment of single-wall carbon nanotubes on the elongated samples. We correlate the local Raman information to the impedance  $Z(f)$  and cut off frequency.

**MON 43****Tailoring The Interface Thermal Resistance Between Copper Matrix and Carbon Nanotubes**

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The current trend in thermal management and electronic packaging is for smaller, low density materials with improved thermal behaviour performance. Carbon nanotubes (CNTs) with their superior thermal properties are ideal candidates for engineering, e.g., metal composites with high thermal conductivity. When it comes to metal composites, the interface thermal resistance between carbon nanotubes reinforcement and the matrix is one of the most critical factors which determine the overall thermal conductivity of the composites. The quality of this interface, however, might be improved by introducing an electron-coupling layer at the interface between the two phases. In this work we present various approaches for carbon nanotubes sidewalls modification in the fashion that decreases thermal interface resistance between CNTs and copper matrix. The influence of interface modification on the effective thermal conductivity and thermal diffusivity of the composites was evaluated by means on xenon flash method. Furthermore, experimental values were compared with analytical estimation of the thermal conductivity of Cu-CNTs composites based on effective medium however approximation (EMA).

**MON 44****Composites SU8-Carbon Nanotubes**

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SU8 polymer consists of rigid epoxy oligomers allowing the micro-fabrication of structures with vertical walls and with high aspect ratio. Thanks to its photo-patterning abilities, SU8 is widely used in nano-engineering for MEMS, sensors, batteries, flat panel displays, fluidic and packaging applications. However, SU8 is an insulating polymer and is brittle with high internal stress although it has high Young's modulus ( $E_y$ ) as compared to other polymers. Consequently, the synthesis of conducting SU8 composites with improved mechanical properties is highly demanded but remains very challenging. Here, we will report on the preparation of SU8-Carbon Nanotubes (CNTs) composites exhibiting homogeneous distribution of CNTs within the epoxy matrix. This is achieved by the use of block copolymers as CNTs' dispersant. Electrical percolating network of CNTs is formed below 0.2w% of CNTs, so the photo-patterning abilities of the composites are preserved.  $E_y$  is improved by more than 50% as compared to pure SU8. The thermal management of composites with aligned carbon nanotubes will be presented as well. This work is done in collaboration with T. Stora, A. Karsa, L. Brocher and A. Akrap.

**MON 45****Use of plasma treatment to grow carbon nanotube forests on TiN**

Martin Fouquet<sup>1</sup> Santiago Esconjauregui<sup>1</sup> Bernhard Bayer<sup>1</sup> John Robertson<sup>1</sup>

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Hydrogen plasma pretreatment is used to enforce the growth of vertically-aligned carbon nanotube forests on TiN substrates. The evolution of the substrate, catalyst, and nanotubes are studied by in-situ and ex-situ X-ray photoemission spectroscopy and diffraction in order to understand the growth mechanism. We find that TiN retains its crystallographic structure and its conductivity during plasma pretreatment and nanotube growth, which is confirmed by electrical measurements. Plasma pretreatment is found to favour the growth of nanotube forests by root growth mechanism, as it binds the catalyst nanoparticles more strongly to the substrate than thermal pretreatment. We find that plasma pretreatment time should be limited, otherwise poor or no growth is found.

**MON 46****Infrared spectroscopic studies on  $K_4C_{60}$  under pressure**E. A. Francis<sup>1</sup> C. A. Kuntscher<sup>1</sup><sup>1</sup>Experimentalphysik II, Universität Augsburg, D-86159 Augsburg, Germany

Alkali fullerides have attracted interest due to their fascinating electronic and structural properties.  $A_4C_{60}$ , with  $A$  being an alkali metal, was predicted to be metallic by DFT calculations, while it is a narrow-gap insulator: The crystal field splits the conduction band to open a gap and the Jahn-Teller distortion enhances the stability of the insulating state. By applying external pressure on  $A_4C_{60}$  the band gap can be tuned. The possibility of an insulator-to-metal transition under pressure is reported controversially. Recently, the appearance of the metallic nature of  $Rb_4C_{60}$  under pressure was attributed to a nanoscale phase separation into metallic  $Rb_3C_{60}$  and insulating  $Rb_6C_{60}$  [1]. Similar results are expected for  $K_4C_{60}$ . In order to address this issue, we carried out high-pressure transmission studies on  $K_4C_{60}$  up to 8 GPa. The vibrational properties and interband transitions under pressure will be discussed, as well as the possibility of a pressure-induced metallic state.

[1] M. G. Yao et al., Phys. Rev. B **79**, 081403(R) (2009).

**MON 47****Raman 2D-peak splitting in graphene: theory and experiment**

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We present a systematic experimental and theoretical study of the two-phonon (2D) Raman scattering in graphene monolayers under a variable uniaxial tensile strain [1]. The external perturbation unveils that the 2D peak excited with 785 nm (1.58 eV) has a complex line-shape due to the contribution of two distinct double resonance scattering processes (inner and outer) in the Raman signal [2]. The two components can even be clearly distinguished in the spectra measured at zero strain. Taking into account previous experiments [3] conducted with 514.5 nm (2.41 eV) excitation, our study strongly suggests that the 2D mode lineshape depends on

the excitation energy. Additionally, the detected splitting depends on the direction of the applied strain and the polarization of the incident light. Independent first principles calculations performed for strained graphene with lattice orientations corresponding to the measured flakes confirm the observed 2D band behavior.

[1] O. Frank et al. submitted. [2] M. Mohr et al. Phys. Rev. B 82, 201409(R) (2010). [3] G. Tsoukleri et al. Small 5, 2397 (2009).

#### MON 48

##### **Correlating different characterization methods on individual carbon nanotubes**

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Carbon nanotubes (CNTs) can be chemically functionalized in many ways by attaching molecules to the outside wall, to the tube ends or inside the inner hollow. Such modification of CNT transport devices leads to new applications as e.g. chemical sensors or detectors. In order to understand the changes in transport behavior due to functionalization, information about the atomic structure is necessary.

Here we present an approach to perform transport measurements, transmission electron microscopy (TEM) as well as Raman spectroscopy all on a single CNT. Electron beam lithography patterning and reactive ion beam etching open windows on a Si<sub>3</sub>N<sub>4</sub> TEM membrane. CNTs are then grown by means of chemical vapor deposition on well-defined places and are finally contacted. With this method we obtain isolated (functionalized) CNTs which can be used ready for correlated transport, Raman and TEM measurements. This process does not limit to CNTs but may readily be applied to other nanomaterial systems.

#### MON 49

##### **Excited state spectroscopy on a bilayer graphene double quantum dot**

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Graphene double quantum dots are promising candidates for future spin-based quantum information technology. We present tunneling spectroscopy experiments on a bilayer graphene double quantum dot device which can be tuned by 5 graphene

lateral gates.

The device has been prepared by exfoliation of natural bulk graphite, electron beam lithography and reactive ion etching. The diameter of the graphene quantum dots are roughly 60 nm and the graphene constrictions acting as tunneling barriers are approximately 30 nm wide and 100 nm long.

Low noise charge stability measurements have been carried out in order to determine the gate lever arms and the addition energies of the two coupled quantum dots. Periodically ordered triple points of high conductance are present on a wide energy range. Yielding addition energies of approximately 20 meV for the two dots. High resolution measurements of individual triple points allow to resolve the energy spectra of excited states (level spacing 1.8 meV) and the interdot coupling energy (in the order of 2-4 meV). By varying the central-gate-voltage the interdot coupling can be tuned.

#### **MON 50**

##### **High performance thin-film transistors using aligned semiconducting single-wall carbon nanotubes separated by agarose gel chromatography**

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Thin-film transistors (TFTs) using single-wall carbon nanotubes (SWCNTs) have attracted a great deal of attention for their possible use in transparent, flexible, and high-speed electronics. Recently, we found that TFT using a slightly aligned semiconductor enriched SWCNT (s-SWCNT) thin film shows drastically improved transfer characteristics. In this work, the s-SWCNT solution was prepared by the agarose gel chromatography and was dropped onto a SiO<sub>2</sub>/Si substrate covered with self-assembled monolayer of 3-aminopropyltriethoxysilane. The aligned thin film was prepared by N<sub>2</sub> blow in the drying process. AFM observation showed that s-SWCNTs were aligned in the direction of N<sub>2</sub> blow, although they are still forming random network. Back-gated TFT exhibited p-type behavior with much better transport characteristics than the previous random network TFT. Typically, the on-off current ratio and the mobility were higher than 10<sup>5</sup> and 10 cm<sup>2</sup>/Vs, respectively, although the purity of semiconductor used in this work was not higher than 90%. The alignment decreased the number of SWCNT-SWCNT junctions between source and drain and thus the hopping transport was thought to be improved.

**MON 51****A broadband and high throughput single-monochromator Raman spectrometer; application for single-wall carbon nanotubes**

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We present a high sensitivity single-monochromator Raman spectrometer which allows operation with a tunable laser source. The instrument is based on the modification of a commercial Raman spectrometer; such instruments operate with holographic Rayleigh filters which also act as a laser mirrors and are usually considered as inherently narrow-band. In our design, the two tasks are separated and the filter can be freely rotated without much effect on the light alignment. Since rotation shifts the filter passband, this modification allows tunable operation with efficient stray light filtering down to  $100\text{ cm}^{-1}$ . The design is optimized for single-wall carbon nanotubes, for which the performance is demonstrated using a tunable dye-laser source. The spectrometer thus combines the high sensitivity with the broadband characteristics of usual triple monochromator systems.

**MON 52****Chemical and optical doping of an inorganic molecular wire**

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Conjugated organic polymers (CPs) have revolutionised electronics by combining the electronic and optical properties of semiconductors and metals with the attractive mechanical properties and processing advantages of plastics. We show the remarkable behaviour of one-dimensional inorganic molecular cluster polymers which mimic the properties of CPs not only mechanically and electronically, but also in terms of fundamental physics. Aggregation-doping in solution, electrochemical doping and self-doping during synthesis and by high-temperature annealing are used to prepare materials with different behaviours ranging from a semiconductor, with a band gap of around 1.5 eV in single molecular wires, to metallic one-dimensional quantum fluids behaviour. The room temperature conductivity accordingly increases by several orders of magnitude. Optical spectroscopy reveals systematic and reversible changes in the electronic structure upon doping, with the appearance of intragap states in doped wire bundles. Transient changes of matching spectral shape are observed upon photoexcitation, indicating that the same intragap states are populated by chemical doping and photoexcitation.

**MON 53****Preferred Reductive Carboxylation of Semiconducting Single Walled Carbon Nanotubes**

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The oxidation of CNTs is the most applied functionalization sequence, yielding soluble, highly functionalized CNTs, bearing carboxylic acid functionalities. These moieties are the foundation for coupling reactions with organic entities or biomolecules, yielding highly functional CNT architectures for a broad range of applications. Herein a modified Birch reaction is reported, yielding reduced CNTn-intermediates in an inert environment, opening the door for a covalent carboxylation reaction on the CNT scaffold. This addition reaction of CO<sub>2</sub> occurs preferably on the sidewalls of semiconducting CNTs, which is depicted in a detailed analysis of the Raman-RBM region. The carboxylic acid functionalities are attached by a covalent linkage to a sp<sup>3</sup> carbon atom of the intact CNT scaffold. Therefore, they have only a minor influence on the integrity of the CNT framework, and the p-system can be restored by thermal or chemical cleavage of the acid groups. In a further step the carboxylated and fully characterized CNTs are esterified with functional molecules. These novel architectures are investigated by TGA-MS spectroscopy. All data depict the covalent attachment to the carboxylic anchors.

**MON 54****A graphene phase transition induced by compressing nanomembranes using STM.**

Alexander Georgi<sup>1</sup> Dinesh Subramaniam<sup>1</sup> Christian Pauly<sup>1</sup> Torge Mashoff<sup>1</sup> Ludger Wirtz<sup>2</sup> Viktor Geringer<sup>1</sup> Marcus Liebmann<sup>1</sup> Marco Pratzer<sup>1</sup> Markus Morgenstern<sup>1</sup>

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The variety of the different carbon allotropes is due to the energetic similarity between the sp<sub>2</sub> and sp<sub>3</sub> band. Even a metastable 3d structure of sp<sub>2</sub> bands called K<sub>4</sub> has been proposed [1].

Applying forces on the graphene flake exfoliated on SiO<sub>2</sub> substrate using a STM-tip the valleys of the intrinsic rippling can be lifted [2]. The induced compression during lifting leads to a transition from flat hexagonal graphene to a triangular appearance probably representing a buckled hexagonal structure resembling a diamond-like arrangement of the atoms. Further lifting leads to a reduction of the compression and a corresponding switch-back to the unbuckled phase. For valleys with 1.5 nm<sup>2</sup>, a buckling amplitude of 5 pm has been deduced, which is only 10% of the buckling

within a 2d-diamond crystal. The phase transition cannot be reproduced by DFT Calculations so far.

[1] Itoh et al. PRL, 102, 055703 (2009)

[2] mashoff et al. Nano Lett., 10, 461 (2010)

## MON 55

### **Environmental effects on the Raman resonance spectra of CoMoCAT single walled carbon nanotubes**

Ahmad J Ghandour

Queen Mary University of London, London

Nanotubes are formed in bundles with different tube diameters and chiralities. This has been a problem in high-pressure studies using Raman spectroscopy as the resonance energies depend on the tube parameters and also change with the pressure. We need to know the resonance spectra of the tubes in our sample both at zero pressure and as a function of pressure. Moreover, experiments are done on bundled and on unbundled tubes and in different pressure-transmitting media (solvents). We must also account for changes to the resonance spectra due to these experimental parameters. In this study we present as a first step, the resonance profiles of CoMoCAT tubes under different environmental conditions at ambient pressure.

## MON 56

### **Defect-induced magnetism in graphene within a hybrid DFT-approach**

Roland Gillen<sup>1</sup> John Robertson<sup>1</sup>

<sup>1</sup>Department of Engineering, Center of Advanced Photonics, University of Cambridge, Cambridge

The field of magnetism in light elements attracts much interest for a wide array of applications. The observation of magnetism in graphene materials is particularly encouraging due to their attractive electronic properties. While ideal graphene is non-magnetic, the presence of defects or edges can give rise to quasi-localized states near the Fermi level and induce Stoner-type magnetic order on the material. Such states have been predicted to appear near carbon vacancies and chemisorped hydrogen in graphene [1] and the edge states in zigzag nanoribbons. However, the reported results from density functional theory studies within the generalized gradient approximation (GGA) might suffer from self-interaction effects, an intrinsic shortcoming of these methods, which promotes artificial delocalization of electrons and leads to particular errors in the presence of localized states. We used the hybrid functional sX-LDA, where the self-interaction is reduced, to study the magnetism of various defects in graphene. Most notably, we found an increased localization of magnetic momenta around the defects compared to previous reports.

[1] O. V. Yazyev, Rep. Prog. Phys. 73, 056501 (2010)

**MON 57****Correlation of quantum transport and tip-enhanced Raman spectroscopy on carbon nanotubes**K. Goß<sup>1</sup> N. Peica<sup>2</sup> S. Smerat<sup>3</sup> M. Leijnse<sup>4</sup> M. R. Wegewijs<sup>5</sup> C. Thomsen<sup>2</sup>J. Maultzsch<sup>2</sup> C. M. Schneider<sup>1</sup> C. Meyer<sup>1</sup><sup>1</sup>Peter Grünberg Institute, Forschungszentrum Jülich & JARA Jülich Aachen Research Alliance, 52425 Jülich, Germany<sup>2</sup>Institut für Festkörperphysik, Technische Universität Berlin, 10623 Berlin, Germany<sup>3</sup>Physics Department, Arnold Sommerfeld Center for Theoretical Physics, Ludwig-Maximilians-Universität München, 80333 München, Germany<sup>4</sup>Niels Bohr Institute & Nano-Science Center, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen, Denmark<sup>5</sup>Peter Grünberg Institute, Forschungszentrum Jülich & Institut für Theoretische Physik A, RWTH Aachen, 52056 Aachen, Germany

Hybridization of electronic states on single molecules can be measured using quantum transport spectroscopy (QTS) [1]. Additional characterization is needed to understand the correlation of this hybridization with the interaction of molecular orbitals. Tip-enhanced Raman spectroscopy (TERS) offers an increased spatial resolution and a high signal enhancement and can thus be used as a probe for single molecules. We present the correlation of QTS with TERS on the same carbon nanotube rope. QTS shows the formation of several parallel quantum dots at low temperature, which are distinguishable by distinct interaction and hybridization properties. To attribute these quantum dots to different strands within the rope, it is characterized using TERS. We identify several carbon nanotubes with different diameters and electronic properties from the diameter dependent Raman modes in combination with a tentative chiral index assignment. Our correlation of QTS with TERS illustrates a useful principle for molecular electronics, where an additional characterization is beneficial for the interpretation of transport data.

[1] A. Eliassen et al., PRB 81, 155431; K. Goß et al., arXiv:1011.4004v1 (2010)





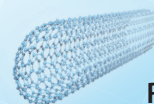
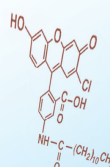
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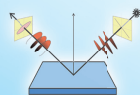


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Tuesday, March 1

## Graphene and nanotubes spectroscopy

- 8:30 – 9:30     **F. Mauri, FR**  
*Ab-initio calculation of resonant Raman spectra in graphene*
- 9:30 – 10:00    **C. Casiraghi, DE**  
*Raman intensity and absolute scattering efficiency of graphene*
- 10:00 – 10:30   **Coffee break**
- 10:30 – 11:00   **A. Jorio, BR**  
*Il buono, il brutto, il cattivo*
- 11:00 – 11:30   **A. K. Swan, US**  
*Optical Excitation and Energy dissipation in carbon nanotubes*
- 11:30 – 12:00   **B. Lounis, FR**  
*Formation and Dynamics of bound excitonic states in single walled carbon nanotubes*
- 12:00 – 17:00   **Mini Workshops**
- 17:00 – 18:30   **Dinner**
- 18:30 – 19:00   **M. Müller, DE**  
*Selective functionalization of carbon nanotubes*
- 19:00 – 19:30   **A. Setaro, DE**  
*Molecular switches functionalization: Tailoring the properties of carbon nanotubes*
- 19:30 – 20:00   **A. Loiseau, FR**  
*Wave functions and many-body effects in carbon nanotubes measured by STM*

Tuesday, March 1

**8:30**

**Ab-initio calculation of resonant Raman spectra in graphene**

Francesco Mauri<sup>1</sup> Pedro Venezuela<sup>2</sup> Michele Lazzeri<sup>1</sup>

<sup>1</sup>IMPMC, Universite Pierre et Marie Curie, Paris

<sup>2</sup>IMPMC, Universite Pierre et Marie Curie, Paris and Universidade Federal Fluminense, 24210-346 Niter

I will present an approach that allows the ab-initio calculation of shape, intensity and position of defect-activated (D, D', D'') and 2-phonon (D+D'', 2D, 2D') resonant Raman peaks in graphene. We also reproduce the weaker 2-phonon bands, that involve acoustic branches and that have recently been measured in graphene. Our (parameter-free) simulated spectra closely reproduce the measured spectra and their evolution with the laser energy and defect concentration. The detailed description of the Raman process allows us to identify the most relevant phonons, scattering events, and defect types involved in each peak.

**9:30****Raman intensity and absolute scattering efficiency of graphene**Cinzia Casiraghi

Freie Universitaet Berlin, Berlin; Manchester University, UK

Raman spectroscopy is a fast and non-destructive means to characterize graphene. However, little is known about the Raman intensity of graphene. Here, I will show a detailed analysis of the Raman intensities of graphene and their dependence on doping, type of substrate, amount of defects and excitation energy. In particular, I will show that the 2D peak intensity strongly changes with doping [1]. This dependence has been used to extract the electron-electron scattering rate, which is about  $60 \text{ ps}^{-1}$  at 2.41 eV [1,2]. Furthermore, the sample substitution method has been used to extract the absolute scattering efficiency from the Raman intensities [3]. A G peak Raman efficiency of about  $260 \times 10^{-5} \text{ m}^{-1} \text{ Sr}^{-1}$  is found [4], which is 40 times bigger than the first order diamond peak efficiency. Further results on the D and 2' peak intensity will be reported [5].

1. C. Casiraghi, PRB 80, 233407 (2009) 2. D. M. Basko et al. PRB 80, 165413 (2009) 3. M. Cardona, G. Guntherodt, Light scattering in solids II, Springer-Verlag 1982 4. P. Klar et al, submitted 5. A. Eckmann et al, submitted

**10:30**

**Il buono, il brutto, il cattivo**

Ado Jorio

Fisica, UFMG, Belo Horizonte

„Il buono, il brutto, il cattivo“ is the title of an Italian/Spanish epic western film, meaning "the good, the bad and the ugly". This talk is all about  $sp^2$  carbons, but devoted to three species which brought me to this title: nanotubes, graphene and amorphous carbon. Which is the good, the bad and the ugly is unimportant personal perspective, but the talk will address perturbations in carbon nanotubes and graphene, mostly from a Raman spectroscopy perspective, but with close connection with scanning probe microscopy and nanomanipulation. The step towards amorphous carbon is indeed big step, and it will be devoted to the discussion on how amorphous carbon, supposedly from Pre-Columbian civilizations, transformed the poor soil of the Amazonian forest into highly productive and stable earth.

**11:00****Optical Excitation and Energy dissipation in carbon nanotubes**Anna K Swan

Boston University, Boston

The intrinsic optical properties of carbon nanotubes have been surprisingly elusive, despite a large research effort. This is partially due to the problems of sample quality, and also the great variation in properties with varying chirality. Here I will discuss both pump probe measurements on a solution of near pure (6,5) nanotubes as well as Monte Carlo simulations. The studies show that even a pure (6,5) sample show complex dynamics behavior. Pump-probe saturation measurements reveal fluence dependent dephasing dynamics without concomitant lifetime effects. The pump-probe time decay dynamics is systematically fit with a predictive model for all fluence regimes, but requires unanticipated decay paths. Finally, very strong length dependence is found for the photoluminescence quantum yield based on a diffusion decay model, where the role of defects is explored for both time resolved measurement and stepwise quenching.

**11:30****Formation and Dynamics of bound excitonic states in single walled carbon nanotubes**Brahim Lounis

Laboratoire Photonique Nuriq et Nanosciences, Institut Optique Graduate School, CNRS and Universi de Bordeaux

Using time-resolved and cw luminescence spectroscopy, we have studied the excitons recombination dynamics in individual single walled carbon nanotubes. At low excitation regime (mono-excitonic regime), nanotubes can either display mono- or biexponential PL photoluminescence decays depending on the environmental conditions and nanotubes synthesis method. At high excitation regime (multi-excitonic regime), several theoretical works have predicted stable formation of multi-particle bound states. The formation of stable biexcitons (four-particle excitations consisting of two electrons and two holes bound together through Coulombic forces and exchange interactions) with binding energies larger than the thermal fluctuations at room temperature were predicted but never observed because of efficient exciton-exciton annihilations process. Moreover more recent calculations predicted that stable trions (three-particle excitations  $2e-1h$  or  $2h-1e$ ) can also be prepared in SWNT. The ensuing presentation will address our experimental progress on the study of the formation and dynamics of bound excitonic states in single walled carbon nanotubes using pump-probe spectroscopy.

**18:30**

**Selective functionalization of carbon nanotubes**

Matthias Müller<sup>1</sup> Benjamin Gebhardt<sup>2</sup> Ferdinand Hof<sup>2</sup> Reinhard Meinke<sup>1</sup> Frank Hauke<sup>2</sup> Janina Maultzsch<sup>1</sup> Andreas Hirsch<sup>3</sup> Christian Thomsen<sup>1</sup>

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<sup>2</sup>Zentralinstitut für Neue Materialien und Prozesstechnik Universität Erlangen-Nürnberg, Dr.-Mack-Str. 81, 90762 Fürth (Germany)

<sup>3</sup>Department of Chemistry and Pharmacy Universität Erlangen-Nürnberg, Henke-str. 42, 91054 Erlangen (Germany)

We show the selective chemistry of nanotubes with respect to their metallic and semiconducting character. Functionalized carbon nanotubes exhibiting selective addition reaching from preferred metallic to highly semiconducting are discussed. We will give an overview of the opportunities and the limitations for the spectroscopic evidence of an (n,m) selective functionalization. We discuss our results in the context of charge localization effects that may play a role as it is known in fullerene chemistry.

**19:00****Molecular switches functionalization: Tailoring the properties of carbon nanotubes**

Antonio Setaro<sup>1</sup> Pascal Bluemmel<sup>1</sup> Chris S Popeney<sup>2</sup> Christan Koerdel<sup>2</sup> Chandan Maity<sup>3</sup> Rainer Haag<sup>2</sup> Stefan Hecht<sup>3</sup> Stephanie Reich<sup>3</sup>

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

<sup>2</sup>Fachbereich Chemie, Freie Universitaet Berlin, Berlin

<sup>3</sup>Fachbereich Chemie, Humboldt-Universitaet, Berlin

One of the most intriguing features of carbon nanotubes is that their electronic structure shows different characters, exhibiting metallic or semiconducting behavior depending upon their chirality. Tuning the electronic character of a CNT could be the way of realizing a molecular conducting channel to be switched on and off at will. A possible way of getting this control is by functionalizing CNTs through molecular switches. Optical molecular switches could help tuning the CNTs' properties in a reversible and nondestructive way, just by exposing them to a proper radiation.

In this talk we will show our results on optical switch-functionalized CNTs. A non-covalent approach has been chosen to keep nanotubes' original properties, without considerable defectivity increase in the preparation steps. We will show our results on (a) switches whose state will directly affect CNT properties and (b) switches that play an auxiliary role, not altering the tubes properties. The first type of switches changes its dipole moment by passing from one isomer to the other (spiropyran derivatives); the second type of switches, the conformational ones, is based on azobenzene derivatives.

**19:30****WAVE FUNCTIONS AND MANY-BODY EFFECTS IN CARBON NANOTUBES MEASURED BY STM**Annick LOISEAU<sup>1</sup> Hong LIN<sup>1</sup> Vincent REPAIN<sup>2</sup> Francois DUCASTELLE<sup>1</sup> Hakim AMARA<sup>1</sup> Luc HENRARD<sup>3</sup> Jean-Sebastien LAURET<sup>4</sup> Sylvie ROUSSET<sup>2</sup><sup>1</sup>Laboratoire d'Etude des Microstructures, UMR 104-CNRS-ONERA, ONERA, BP 72, 92320 Chatillon, France<sup>2</sup>Laboratoire Matériaux et Phénomènes Quantiques, Université Paris Diderot-CNRS, Case 7021, 75205 Paris Cedex 13, France<sup>3</sup>Research Centre in Physics of Matter and Radiation (PMR), University of Namur (FUNDP). 5000 Namur, Belgium<sup>4</sup>LPQM, ENS Cachan -CNRS, Cachan France

We report here atomically resolved STM/STS investigations of local electronic properties of C-SWNTs. First, our novel approach demonstrates the existence of a screening effect of the substrate reducing the electronic gap measured by STS. We show how taking into account for this effect permits to determine the intrinsic gap from STS and the values of exciton binding energies [1]. These results provide a deeper knowledge of many-body interactions in these systems and solve the apparent controversy of the first STM measurements which reported the same gap values than optical experiments [2]. Second, we show the first complete experimental investigation of molecular orbitals of SWNTs [3]. Local conductance measurements show spectacular carbon-carbon bond asymmetry at the Van Hove singularities demonstrating the symmetry breaking of molecular orbitals in nanotubes. The observed features are perfectly described by an analytical tight-binding model and confirmed by ab initio calculations. [1] H. Lin et al, Nature Mat. 9, 235 (2010) [2] J. W. G. Wildoer et al Nature 391, 59 (1998) ; T. W. Odom, et al, Nature 391, 62 (1998) [3] H. Lin et al, Phys. Rev. B 81, 235412 (2010)

**TUE 1****CNTs selectivity, crystallinity and purity investigation: hydrocarbon kind effect**

O. Guellati<sup>1</sup> S. Boukhzar<sup>2</sup> S. Detriche<sup>3</sup> M. Guerioune<sup>3</sup> Z. Mekhalif<sup>3</sup> J. Delhalle<sup>3</sup> D. Bégin<sup>3</sup> I. Janowska<sup>3</sup> C. Pham-Huu<sup>3</sup>

<sup>1</sup>Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse (LMSPC), ECPM - CNRS, Uds, 25 rue Becquerel, 67087 Strasbourg, FRANCE.

<sup>2</sup>Laboratoire d'Etude et de Recherche des Etats Condensés (LEREC), Département de Physique, Université Badji Mokhtar BP, 12, Annaba 23000, ALGERIA.

<sup>3</sup>Laboratoire de Chimie et d'Électrochimie des Surfaces (CES), FUNDP rue de Bruxelles 61, B-5000 Namur, BELGIUM.

Different kind of CNTs have been synthesized over MgO/Fe-Co support using catalytic chemical vapor deposition *CCVD* process with various hydrocarbons, such as ethanol, acetylene and ethylene. Our aim in this investigation is to study the production condition (like temperature, period and gas flow rate) influence on the CNT features as product structure selectivity, crystallinity, purity and yield. In this interest, the crude and purified products have been characterized using low and high magnification TEM, FESEM, Raman spectroscopy and TGA analysis.

Key words: carbon nanotubes, SWNTs, DWNTs, MWNTs, EtOH decomposition, ACCVD synthesis.

**TUE 2****Electronic Properties of Functionalized Quasi-Free-Standing Graphene and Monolayer Boron Nitride**

D. Haberer<sup>1</sup> D. Usachov<sup>2</sup> C. Giusca<sup>3</sup> M. Farjam<sup>4</sup> S. A. Jafari<sup>4</sup> S. Taioli<sup>5</sup> Y. Wang<sup>6</sup> B. Dora<sup>7</sup> H. Sachdev<sup>8</sup> T. Pichler<sup>9</sup> S.R.P. Silva<sup>3</sup> S. Irle<sup>6</sup> M. Knupfer<sup>1</sup> B. Büchner<sup>1</sup> A. Grüneis<sup>9</sup>

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<sup>3</sup>Advanced Technology Institute, University of Surrey, Guildford GU2 7XH, United Kingdom

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<sup>6</sup>Department of Chemistry, Nagoya University, Japan

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<sup>8</sup>Anorganische Chemie 8.11, Universität des Saarlandes, 66041 Saarbrücken, Germany and Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany

<sup>9</sup>Faculty of Physics, University of Vienna, Strudlhofgasse 4, 1090 Wien, Austria

Regarding the application of graphene and monolayer hexagonal boron nitride (ML h-BN) in future electronic devices, chemical functionalization is one of the key strategies to tailor the electronic properties. We have carried out functionalization of CVD grown graphene monolayers with alkali and hydrogen atoms. This allows for tuning the energy bandgap as well as the electron concentration independently, which is crucial for device applications. The chemical bonding and the concentrations of the adsorbed H-atoms are determined with high accuracy using core level and angle-resolved photoemission spectroscopies (ARPES). We employ ARPES to access the electron-phonon coupling in n-doped graphene and further demonstrate that a peculiar electronic state arises when n-doped quasi-free-standing graphene is functionalized with atomic hydrogen. We further discuss the electronic properties of chemically functionalized CVD grown ML h-BN as well as graphene grown on h-BN.

### TUE 3

#### **Low-temperature growth of multi-walled carbon nanotubes on cobalt nanoparticles by thermal CVD**

Niina Halonen<sup>1</sup> Anne-Riikka Leino<sup>1</sup> Jani Mäklin<sup>1</sup> Jarmo Kukkola<sup>1</sup> Geza Toth<sup>1</sup> Andrey Schukarev<sup>2</sup> Jyri-Pekka Mikkola<sup>2</sup> Ákos Kukovecz<sup>3</sup> Zoltán Kónya<sup>3</sup> Krisztian Kordas<sup>1</sup>

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Low-temperature thermal chemical vapor deposition (thermal CVD) synthesis of multi-walled carbon nanotubes (MWCNT) was studied using cobalt and iron nanoparticles as catalyst, cyclopentene oxide and xylene:methanol (1:3) as precursors and Ar/H<sub>2</sub> (85%/15%) as carrier gas. When using drop cast cobalt nanoparticles as catalyst on Si/SiO<sub>2</sub> chips and cyclopentene oxide as precursor, considerable growth already at 470 °C was found. The structure and composition of the achieved MWCNTs films are studied by scanning and transmission electron microscopy as well as by Raman and X-ray photoelectron spectroscopy techniques. The successful MWCNT growth below 500 °C is promising from the point of view of integrating MWCNT materials into existing IC fabrication technologies.

**TUE 4****Application of single-walled carbon nanotubes as NO<sub>x</sub> sensors**

Miro Haluska<sup>1</sup> Moritz Mattmann<sup>1</sup> Marek Maciejewski<sup>2</sup> Kiran Chikkadi<sup>1</sup> Cosmin Roman<sup>1</sup> Christofer Hierold<sup>1</sup>

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In addition to investigating the sensing properties of field-effect transistors (FET) with individual SWNTs as active channels, we examine adsorption/desorption of NO<sub>x</sub> gas on SWNTs. SWNTs for sensors were directly grown on Si/SiO<sub>2</sub> chips and contacted by metal leads forming carbon nanotube FET (CNFET). Contacts were passivated with Al<sub>2</sub>O<sub>3</sub> for long term stability and to exclude their exposure to gas. These CNFET gas sensors with a 0.5  $\mu$  m long exposed SWNT channel can detect NO<sub>2</sub> gas in concentrations below 0.1 ppm in air. This sensor can be recovered by heating. A CNFET compact model was utilized to show that changes in Id-Vg characteristic upon NO<sub>2</sub> exposure are consistent with a shift of the charge neutrality level in the SWNT channel. Adsorption of NO<sub>x</sub> on nanotubes was monitored by a thermoanalyzer connected with a mass spectrometer. Up to 6 wt % of the mass increase was observed during exposure of SWNTs to NO<sub>x</sub> at room temperature. The temperature programmed desorption was monitored by simultaneous recording sample mass change and kind and quantity of evolved gasses. Applied adsorption-desorption method confirms the adsorption process of NO<sub>x</sub> on nanotubes.

**TUE 5****Towards plasmonic enhancement of carbon nanotube Raman signatures**

Sebastian Heeg<sup>1</sup> Kirsten Strain<sup>2</sup> Eleanor Campbell<sup>2</sup> Roberto Garcia<sup>3</sup> Stefan Maier<sup>3</sup> Stephanie Reich<sup>1</sup>

<sup>1</sup>Freie Universitaet Berlin, Berlin

<sup>2</sup>University of Edinburgh, Edinburgh, UK

<sup>3</sup>Imperial College London, London, UK

Raman spectroscopy is a well established tool in carbon nanotube characterization. It reveals properties such as diameter, defect concentration and optical transition energies. As Raman scattering in carbon nanotubes is a resonant process, its information content is somewhat limited if the optical transition energies are altered. This occurs for instance by applying a voltage to the nanotube during transport measurements. To overcome this limitation, Gold nanoparticles are placed next to an as grown nanotube. The field enhancement of their surface plasmons should enhance the Raman signal of the nanotube even if the energy of the excitation laser is away from the nanotube resonance. We present a first set of Raman measurements and discuss their implications from a conceptional and experimental point of view.

**TUE 6****The effect of alkaline doped catalysts on the CVD synthesis of carbon nanotubes**

Klara Hernadi<sup>1</sup> Krisztián Németh<sup>1</sup> Zoltán Németh<sup>1</sup> Zoltán Balogh<sup>2</sup>

<sup>1</sup>University of Szeged, Department of Applied and Environmental Chemistry, Szeged

<sup>2</sup>Center for Electron Nanoscopy, Technical University of Denmark,

Nowadays, the quality of CVD carbon nanotubes is a pressing problem to be solved and to improve catalytic process. Therefore, we investigated how potassium or cesium dopants modify the activity and selectivity of the original mono- and bimetallic CVD catalysts during carbon nanotube synthesis. Mono-(Co) and bimetallic (Fe-Co) catalysts supported by either 13X zeolite or CaCO<sub>3</sub> were doped with potassium or cesium compounds and tested in carbon nanotube production using the chemical vapor deposition method. The effect of alkaline dopant concentration and attendant anion was also investigated. In order to increase comparability, the evaluation of the performance of the catalysts a combinatorial arrangement was also used. Catalyst samples were characterized by carbon deposit and carbon yield values. For qualitative characterization, products were investigated by transmission and scanning electron microscopy.

**TUE 7****Sidewall Functionalization and Derivatization of Single Wall Carbon Nanotubes**

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Since the discovery of carbon nanotubes (CNTs) in 1991, many challenging aims are remaining. Depending on the production technique the samples contains several CNT chiralities. Therefore the development of scalable chemical separation techniques of CNTs is absolutely necessary. Moreover pristine CNTs are strongly interacting with each other and thus are obtained as large entangled bundles. One possible method to tackle these problematic is covalent chemical sidewall functionalization of CNTs. This can not only greatly improve the solubility of CNTs in a wide range of solvent polarities but is also directly dependent on the tubes electronic properties. Based on reductive treatment utilizing modified Birch reaction, we present a versatile and scalable reaction scheme that leads to sidewall carboxylated CNTs via abundant CO<sub>2</sub>. According to the reaction conditions, semiconducting CNTs are highly preferred. Our carboxylated CNT moieties can serve as an anchor

group for further chemical modification and derivatization. The successful modification of the CNTs scaffold was demonstrated by means of statistical Raman-, UV/vis- and IR- spectroscopy, TGA/MS, zetapotential measurements and AFM.

## TUE 8

### In-situ observations of graphene CVD

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The understanding of the role of transition metal templates in the chemical vapour deposition (CVD) of graphene and carbon nanotubes remains incomplete, which limits a widespread utilisation of these materials. We present a combination of high-pressure X-ray photoelectron spectroscopy (XPS)[1], environmental transmission electron microscopy (ETEM)[2], and in-situ X-ray diffraction (XRD) experiments analysing the behaviour of thick (> 300 nm) poly-crystalline and nanoparticulate catalysts during hydrocarbon exposure at temperatures ranging from 300-900°C. We focus on graphene nucleation and graphene domain size in relation to the catalyst grain size distribution and the C chemical potential. We compare (few-layer) graphene precipitation based on a solid C source to graphene CVD. Time-resolved XPS allows a detailed comparison of transient states prior to graphene formation and C/metal core level signatures for CVD and bulk precipitation experiments, based on which we model the growth process.

[1] Hofmann et al., J. Phys. Chem. C 113, 1648 (2009)

[2] Hofmann et al., Nano Lett. 7, 602 (2007)

## TUE 9

### In vitro investigation of the Toxicity of Boron Nitride Nanotubes

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Similar to carbon nanotubes (CNTs), boron nitride nanotubes (BNNTs) are one of the most promising tubular nanomaterials. Especially when applications are expected at high temperature or in a chemically active environment. Currently, their commercial production is scaling up and human exposure is very likely to increase dramatically. However, only very few studies have addressed the question of their

safety and the response of lung cells to BNNTs has not been studied yet. Here, we report on the toxic action of BNNTs on lung epithelial and macrophage cells, as well as fibroblasts and a kidney cell line. The in vitro assessment of BNNTs toxicity, based on cell proliferation and modification of cell metabolism and morphology, demonstrates an acute toxic action of BNNTs for all cell types studied. However, the degree of nanomaterial toxicity is cell-type dependent and strongly correlated with the endocytic (phagocytic) ability of the cells. On the other hand, straight BNNTs able to traversing the cell membrane, exhibit higher toxicity than curly CNTs. The results point the cellular accumulation of nanomaterials to determine the toxicity of tubular nanomaterials.

## TUE 10

### **High Efficiency Solid-state Dye-sensitized Solar Cells: Fast Charge Extraction Through Self-assembled 3D Fibrous Network of Crystalline TiO<sub>2</sub> Nanowires**

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The development of reliable and sustainable energy production is a major concern in the further facilitation of nation's economy. Dye-sensitized solar cells (DSCs) are one of the most promising photovoltaic technologies for production of cost-effective, renewable and non-polluting energy. The state of the art liquid electrolyte-based DSCs have reached efficiencies as high as 11.1%. However, these liquid-based DSCs may suffer from potential leakage and corrosion problems. These probable disadvantages have bred research towards the implementation of solid-state hole transport materials (HTMs) instead of liquid electrolytes in DSCs. Herein, we introduce a novel 3D cathode morphology for solid-state dye-sensitized solar cells consisting of oriented linear aggregates of anatase nanorod building blocks. This self-assembled fibrous network of fused single crystalline anatase nanorods offers a high roughness factor, significant light scattering and up to several orders of magnitude faster electron transport to reach a near-record breaking conversion efficiency of 4.9%.

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N. Tetreault et al, ACS Nano (2010) DOI: 10.1021/nm1024434

**TUE 11****Synthesis of Nb<sub>1-x</sub>W<sub>x</sub>S<sub>2</sub> Graphene-Like Sheets**

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Along with carbon 2D material graphene, stable graphene-like structures of transition-metal chalcogenides have sparked new discoveries in condensed-matter physics and electronics. In fact, the miniaturization of 2D structures by lateral confinements, makes them potential candidates not only for modulation of electron-transport phenomena, but also enhances their host capabilities arising from the enlarged surface area and improved diffusion properties upon the intercalation of guest molecules due to the finite lateral size and enhanced open-edge morphology of the 2D nanosheets. Herein, we demonstrated the formation of Nb<sub>0.33</sub>W<sub>0.66</sub>S<sub>2</sub> flying carpets, i.e. stacks of one to five layers, by lithiation and exfoliation of stacked niobium tungsten sulfide Coin-Roll Nanowires. The flying carpets can be successfully functionalised with ZnO colloids, demonstrating the reactivity of the sulphur atoms at the surface. We will present detailed investigations TEM investigations on the defect structure and transport properties by means of conductive-AFM studies.

**TUE 12****Ultra-fast efficient synthesis of one-dimensional nanostructures**

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Using the thermal-explosion mode of the redox reaction between the strong reducing agent and oxidant within a fraction of a second the process is terminated. A careful selection of powdered reactants, which are very basic chemicals, can result in the efficient formation of novel nanostructures. Different starting mixtures of magnesium powder with various carbonates (such as Na<sub>2</sub>CO<sub>3</sub>, CaCO<sub>3</sub>, FeCO<sub>3</sub>) were tried while the autothermal reaction was carried out under both reactive (air) and neutral atmosphere (argon) with an initial pressure of 1 or 10 atm, respectively. Spectral diagnostics was carried out to determine the combustion temperature (around 1900 K). Under those conditions the deep decomposition of carbonates was confirmed. The morphology of the products was studied using XRD, SEM, TEM and Raman spectroscopy. Both micro- and nanosized one-dimensional structures were efficiently formed. The morphology of some of the latter ones resembles multi-walled carbon nanotubes.

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### TUE 13

#### **Ionic doping of carbon nanotubes – a Raman scattering and electric conductivity study**

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In our contribution, we present results on doped single-wall carbon nanotubes. Combining Raman spectroscopy with measurements of electrical conductivity and the Hall coefficient, the influence of various stages of doping on Raman features is investigated. In particular, it is shown that for a proper characterisation of Breit-Wigner-Fano line of metallic nanotubes both a broader part of the Raman spectrum than usually used, and the spectrum background (“dark counts”) have to be taken into account. Furthermore, a characteristic energy for ionic doping in order of few tens of meV was obtained from thermal annealing experiments. We also focus on possible signatures of electronic Raman scattering in carbon nanotubes. For that, the basic parameters like screening length, plasma frequency, single-particle energy, etc. and their dependence on the charge carrier concentration are discussed.

### TUE 14

#### **Investigating the effect of heat pre-treatment and catalyst mixtures on the yield of epitaxially horizontally aligned carbon nanotubes grown over st-cut quartz**

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Single-walled carbon nanotubes (SWNT) are a promising material for nanoelectronics because of their physical and electrical properties. To this end, they should be synthesized with controlled orientation, alignment, yield and electronic type. Chemical vapor deposition (CVD) is widely used method for growing horizontally aligned SWCNT on selectively cut single crystal substrates such as ST-cut quartz. Thermal annealing of the substrates prior the CVD process is an often implemented step to improve yield. Nevertheless, the role of the annealing step has not been fully investigated. Here, we systematically investigate the effect of the annealing step on the morphology of the ST-cut quartz substrates, in order to provide excellent conditions for high nucleation yields and growth of long tubes (longer than 100

$\mu\text{m}$ ). Also, the surface morphology is shown to affect the catalyst nanoparticles size distribution which affects their propensity to nucleate SWNT. The ratio of the catalyst metal mix (Fe:Co) is shown to be a less important parameter. The successful transfer of the aligned SWCNTs onto other substrates without incurring damage or misalignment is also demonstrated.

## TUE 15

### Spin-orbit coupling in multi-electron carbon nanotube quantum dots

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The coupling of the spin of electrons with their orbital motion is a central theme in quantum dot research. For carbon nanotubes the coupling was overlooked in the first decade of experiments. Recently, spin-orbit interactions were observed in a disorder-free few-electron quantum dot[1]. I will present low-temperature measurements of the spin-orbit coupling in the general multi-electron regime of nanotube quantum dots in the presence of finite disorder [2]. The spin-orbit coupling is found to depend on the electron occupation of the dot in a systematic manner that follows from the curvature induced spin-orbit splitting of the Dirac cones for graphene. The modified spectrum is fully accounted for by a single-particle model.

The research was supported by the Carlsberg and Lundbeck Foundations, the Danish Research Council and University of Copenhagen Center of Excellence.

[1] F. Kuemmeth et al, Nature 452, 448 (2008).

[2] T.S. Jespersen et al, Nature Physics (in press)

## TUE 16

### Magneto-conductance of carbon nanotubes in parallel magnetic fields up to 60 T

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We have investigated the magneto-conductance (MC) of carbon nanotubes (CNTs) in pulsed, parallel magnetic fields up to 60 T. From the MC of semiconducting

CNTs, we report the direct observation of the predicted band-gap closure and the reopening of the gap under variation of the applied magnetic field. We also highlight the important influence of mechanical strain on the MC of the CNTs [1]. For chiral metallic CNTs, we find a peculiar split MC peak close to the charge neutrality point. Our analysis of the data reveals that this splitting is intimately connected to the spin-orbit interaction and the tube chirality. Band structure calculations suggest that the current in the peak regions is highly spin-polarized, which calls for application in future CNT-based spintronic devices [2].

References:

- [1] S. H. Jhang et al., arXiv:1011.3330v1 (accepted in Phys. Rev. Lett.)
- [2] S. H. Jhang et al., Phys. Rev. B **82**, 041404 (2010).

## TUE 17

### **Study of Optoelectronic properties of Nanostructures Lasers Based on Diluted Nitrides Antimonides Materials: $\text{Al}_x\text{Ga}_{1-x}\text{In}_y\text{N}_{1-y}\text{Sb}_1\text{Sb}_{1-x}$**

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Abstract:

In this work we have studied the optoelectronics properties of the nanostructures Lasers based on diluted Nitrides Antimonides III-N-Sb of  $\text{AlGaInNSb}/\text{GaNSb}$ , our goal is to evaluate the performance and the feasibility of the type-I structures Lasers with direct transition which can emit in Mid-InfraRed and Far-InfraRed. The interest of these materials reside in their promising properties that can offer to emit in Infra-Red wavelengths range with small quantities of Nitrogen incorporation and to emit in the Ultra-Violet wavelengths range with small quantities of antimony incorporation, Nitrides Antimonides are characterized by wide miscibility band at intermediate compositions, will make it difficult to prepare alloys with a large Nitrogen fraction and giant bowing parameter.

Keywords: Nitrides Antimonides, Optoelectronics, nanostructures, Laser,  $\text{GaNSb}$ ,  $\text{AlGaInNSb}$

## TUE 18

### **Direct synthesis of carbon based nanostructures**

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Carbon based nanostructures such as fullerenes and nanotubes attract considerable attention because of their unique properties and potential applications. The main task of direct synthesis is the controlled generation of the desired nanostructures by

rational chemical methods. This approach is of practical interest for the production of individual higher fullerenes and nanotubes with specific chiralities which cannot be obtained by the uncontrolled classical processes. Our direct methodology is based on the synthesis of polycyclic aromatic hydrocarbons (PAHs) which already contain all necessary carbon atoms in appropriate positions. The following intramolecular condensation leads to the desired nanostructures which carbon connectivity is fully predefined by the precursor molecule. The direct synthesis approach is not limited to fullerenes and carbon nanotubes but can be applied as well to the formation of other carbon based nanostructures including, but not limited to, endohedral, hetero or open cage fullerenes.

## TUE 19

### **Imaging of Fullerene and Functionalised Endohedral Fullerenes in Single-Walled Carbon Nanotubes - Current Status and Future Prospects**

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Carbon nanotubes are ideal low-contrast, atomically thin containers for visualising structurally complex and dynamically active molecules. At medium voltages of 100-300kV single-walled carbon nanotubes (SWNT) are quickly destroyed because of knock-on collisions between the beam electron and the graphene atoms. At 80 kV aberration-corrected high-resolution transmission electron microscopy (AC-TEM) simultaneously provides both, structural information about the exterior (functional groups) and/or the interior of individual fullerenes molecules, at the near-atomic level in direct space and real time. However, we demonstrate on the example SWNT filled with M3N@C80 functionalised with an organic group and with fullerenes that radiation damage effects at 80 kV still break fullerenes and functional groups hindering in the latter case their atomic resolution. We moreover show that fullerenes inside SWNTs can accept an about 100 times higher electron dose at 20kV than at 80kV and report the current status and future prospects of sub-Angstrom low-voltage electron (SALVE) microscopy.

## TUE 20

### **Comparison of conduction in graphene and carbon nanotube networks**

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We point out that there is a remarkable analogy between electronic conduction in reduced graphene oxide sheets (1), in graphene prepared by chemical-vapour deposition (2) and in thin single-wall carbon nanotube films measured by Ravi et al. (3). The conductance generally increases with temperature, showing the importance of variable-range hopping or fluctuation-assisted tunnelling. However, in each case there is a small nearly constant conductance at very low temperatures indicating the presence of a limited fraction of percolating metal-like conduction paths. We model this behaviour in terms of inhomogeneous disorder, with metallic conduction in more ordered regions interrupted by some thin barriers through which electric-field driven tunnelling can occur at all temperatures.

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(3) S. Ravi, A.B. Kaiser and C.W. Bumby, *Chem. Phys. Lett.* 496, 80 (2010).

## TUE 21

### **Raman spectroscopy and in situ Raman spectroelectrochemistry of individual single walled carbon nanotubes with engineered defects**

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Defects in a single walled carbon nanotube (SWCNT) can exhibit new interesting properties. For example, defects are reactive centers on a nanotube, so that they can be used as the sites for nanotube decoration or to improve the sensing of the attached species. A better understanding of the role of defects in SWCNTs can open a route toward engineering the properties of new electronic devices based on carbon nanotubes by controlling or creating defects.

Here we have studied long (more than 1 mm) individual single wall carbon nanotubes which were intentionally and only locally modified by defects while other parts of the tube remained defect-free. We use Raman spectroscopy and in situ Raman spectroelectrochemistry to investigate the changes in the electronic structure of a particular SWCNT by creation of the defect. We show that not only the increased D band is a signature of defects in carbon nanotubes Raman spectra. The creation

of a defect also caused a significant decrease of the intensity of other Raman features. In addition we show that defects leads to a broadening of the Raman resonance profile and also to a decrease of the resonance profile intensity maxima.

## TUE 22

### **Graphene as a substrate for cell cultivation**

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Graphene as a new material was not sufficiently tested for its biocompatibility and for application as a substrate material for cell cultivation so-far. The biocompatibility of large single layer graphene produced by chemical vapour deposition was investigated using human osteoblasts and mesenchymal stromal cells. Our study is focused on cellular adhesion, morphology and the ability to proliferate and differentiate on graphene substrates. It was found that both of the tested cell types adhered and proliferated better when cultured on graphene films than on a SiO<sub>2</sub> substrate and that there is a potential for better osteo-differentiation. Thus graphene due to its exceptional properties (mechanical and electrical) could be used for application in biomedicine and biosensing.

## TUE 23

### **Diameter dependence of the low-frequency gap in carbon nanotubes**

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The low-frequency optical behavior of carbon nanotubes is still a matter of controversy, lacking systematic studies. We will present wide range optical studies on freestanding transparent carbon nanotube films, made from nanotubes with different diameter distributions. From the wide-range spectra we determined the optical functions which are directly comparable among different samples. By a detailed analysis we determined the average diameters of both the semiconducting and metallic species. Comparing the spectral features in the far infrared and the near infrared/visible, we can demonstrate the diameter dependence of the low frequency gap-like behavior. Our results strongly support the explanation of the low-frequency feature as arising from a curvature-induced gap, instead of being the consequence of metallic particles in an effective medium.

**TUE 24****Synthesis and characterization of carbon nanofiber palladium composite**

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We present a synthesis approach to produce carbon nanofibers decorated with Pd nanoparticles. Helical carbon nanofibers were synthesized by a CVD process on Pd supported C60 catalyst. Their structure has a high and unique surface area. They are an ideal candidate to be decorated with metallic nanoparticles. The obtained nanofibers were functionalized by a H<sub>2</sub>O<sub>2</sub> treatment. This process introduced additional defect sites and oxygen functional groups thus reducing the hydrophobicity of the nanofibers. Pd nanoparticles were deposited by a polyol method. Transmission electron microscopy (TEM) images could clearly show the successful Pd decoration of the carbon support. The material was characterized by a variety of methods, such as Raman spectroscopy and scanning electron microscopy (SEM).

**TUE 25****The effect of oxide layers on the vibrational and optical properties of (111) silicon nanowires**

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Elastic properties of silicon nanowires (SiNWs), surrounded by SiO<sub>x</sub>-shells are of large interest due to their impact on vibration and optical properties of SiNWs. Raman frequencies of SiNWs with two different SiO<sub>x</sub>-shell thicknesses were studied. It is known that the oxidation of Si leads to a volume increase of the resulting SiO<sub>x</sub> shell, hence, the question about the nature of the emerging strain inside the remaining Si-core arises.

Our findings show that a thin oxide layer on the SiNWs results in tensile strained Si-core along the (111) growth direction, leading to a red shift in Raman frequencies, whereas for SiNWs covered by a thick SiO<sub>x</sub>-shell plastic deformation of the Si-SiO<sub>x</sub>-interface occurs leading to stress relaxation of the core region. The experiments are

accompanied by calculation of the strain-stress relation of the core-shell system in a linear continuum elasticity framework. The photoluminescence measurements on both SiNWs samples using various excitation powers provide us an insight into the Si- SiO<sub>x</sub>-interface formation.

## TUE 26

### Effect of chemical doping on electronic properties of carbon nanotube network thin film transistors

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Thin films of single-walled (SWNTs) are recognized as an ideal nanomaterial for making light, inexpensive, and flexible electronics. Despite of their remarkable properties, a precise assembly and control the deposition on substrates still remains a challenging task. Here we applied self-assembled films adsorbed on silicon substrate from the surfactant-water solution of the mixed and the type separated semiconducting and metallic SWNTs. We then investigated the effect of chemical doping on electronic properties of carbon nanotube networks by post-treatment with p- and n-type doping molecules.

## TUE 27

### 2D interband plasmons in free standing Graphene

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Two dimensional (2D) graphene is an exciting material both due to its unique properties and potential technological applications. As a result of its unique electronic structure graphene offers a means by which many-body interactions such as quasi-particle excitations (electron-hole pair interactions), collective excitations of valence electrons (plasmons) and lattice vibrations (phonons) can be studied [1]. We investigated the properties of the  $\pi$ -plasmon excitations in free-standing monolayer of graphene using electron energy loss spectroscopy (EELS). We study the dispersion of the  $\pi$  plasmon peak for momentum transfers  $0 \leq q \leq 0.5 \text{ \AA}^{-1}$  and in the energy loss range  $0 \leq \Delta E \leq 30 \text{ eV}$ . In this momentum transfer range we observe the  $\pi$  plasmon as being characterized by a quasi-linear dispersion. In addition, the  $\pi$  plasmon excitations are shown to lie above the interband single-particle excitations (SPE) in mono-layer graphene. These results are discussed and compared to results obtained from single wall carbon nano-tubes (SWCNT).

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## TUE 28

### **Surface structure and field emission properties of few-layer graphene flakes**

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Correlations between field emission (FE) properties and surface structure of few-layer graphene (FLG) flakes have been examined. Films consisting of the flakes oriented perpendicularly to the flat Si substrates were obtained by a PECVD method. FLG flakes had thickness of 5-10 nm and width and height of 1-3  $\mu\text{m}$ . The FE characteristics of the FLG films were studied depending on the various surface-sensitive effects: adsorption of residual gases, ion bombardment and thermal oxidation. It was found that thermal oxidation in air at temperatures up to 800 C produces a big amount of 100 nm sized through-hole defects in the lateral side of the flakes. Nevertheless the FE properties of the oxidized films remained almost the same as for as-grown material. At the same time electron emission in the harsh ion bombardment conditions led to the strong degradation of the FE properties. However it was revealed no considerable changes in the form and size of the flakes. Using the structural analysis of FLG performed by TEM, SEM and Raman techniques, the possible mechanisms responsible for the observed FE changes are discussed.

## TUE 29

### **Carbon nanotubes based poly(composites) for the fuel cell applications**

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Proton exchange membrane - membrane electrode assembly (PEM-PEAs) are commonly used as state of the art (green) technology in the fuel cell applications for powering portable devices, vehicles, bikes or small houses. They are still progressing toward better performances and the design of improved proton exchange membrane (PEM) is one of the key issues. In this contribution, we will report on the development of novel composites materials based on commercial perfluorosulfonic acid/PTFE copolymer poly(electrolyte) scaffold known as Nafion. Different types of fillers (carbon nanotubes, titanate nanotubes and nanowires to name but a few) will be used to improve the characteristics of Nafion. The performances of composites are evaluated in terms of water-uptake, hydration number, proton conductivity, electronic conductivity, thermal stability and mechanical properties. A special at-

tention will be given to composites with aligned fillers built from carpets of CNTs. These novel materials are promising candidates to take place as fuel cell electrodes as they exhibit high electronic and proton conductivity. This work is supported by the EC project MULTIPLAT

### TUE 30

#### **Metal complex encapsulation in carbon nanotubes: various methods of filling and investigation**

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We will present results on single-walled carbon nanotubes filled with ferrocene, prepared by two types of encapsulation: the gas-phase method and nano-extraction from ethanol. We performed a careful study with reference materials (pure nanotubes and ferrocene, respectively) included in every step. Characterization methods of the end products as well as the references included IR-ATR, Raman, UV-VIS and Mössbauer spectroscopy. By the latter method, other iron-containing phases were observed after high-temperature filling. We also prepared nanotubes filled with luminescent Eu complexes by nano-extraction from supercritical carbon dioxide. After thorough washing of the product to remove adsorbed material from the tube surface, we did not detect any luminescence; however, the Raman spectra were different from the pristine nanotubes. These results suggest encapsulation and subsequent quenching of luminescence.

### TUE 31

#### **Diameter Dependence of the Electrical Performance of Au-seeded Ge Nanowire Field Effect Transistors**

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Integration of low-dimensional materials into novel integrated circuitry has been a topic of ever-increasing interest over the last decades. In order to develop optimum performance nanowire devices, the fundamental charge-carrier transport properties of the structures need to be understood in detail. In this study, vapour-liquid-solid phase synthesized germanium nanowires using Au catalyst were contacted with metallic electrodes and electrically characterized. All devices showed a p-type electric-field effect characteristic which is attributed with the incorporation of metal catalyst during synthesis; Au being known for creating three acceptor states within the germanium band-gap. For nanowires with diameters ranging from 10 to 100 nm, the electrical resistivity and carrier mobility were measured, exhibiting a significant

diameter dependence. The study provides insight into the basic transport-related physical processes that occur in semiconductor nanowire systems, and moreover allows for an outlook on the potential impact of different material's combinations on the characteristics of germanium nanowire-based devices.

## TUE 32

### WO<sub>3</sub> nanowires - Preparation and application

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Much effort has been devoted to the synthesis of semiconductor nanowires, nanorods and nanobelts. WO<sub>3</sub> is a wide band gap semiconductor; it can be used in many applications like semiconductor gas sensing devices, electrochromic devices or photocatalysis. WO<sub>3</sub> nanowires are usually synthesized either by heating a tungsten foil in argon gas or by electrochemically etching a tungsten tip. In this contribution we report a simple hydrothermal method to prepare uniform nanowires in aqueous solution. In a typical synthesis sodium sulfate was added to aqueous sodium tungstate solution. Then hydrochloric acid solution was added until the pH value of the solution reached 1.5. The mixture was transferred into a Teflon-lined stainless steel autoclave and was heated at 180 °C for 48 h. The product was collected by centrifugation and washed and dried. The as-prepared sample was investigated by XRD. The diffraction peaks could be indexed to the hexagonal phase of WO<sub>3</sub>. SEM and TEM were utilized to assess the uniformity of the nanowire diameter and length distribution. We present the I-V characteristics and gas sensing properties of the synthesized WO<sub>3</sub> nanowires.

## TUE 33

### Formation of graphite/molybdenum sulfides hybrid materials using high temperature annealing.

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Combination of low dimensional carbon nanostructures, possessing high electrical conductivity, with semiconducting nanoparticles allows creating new group of hybrid materials with unique electronic, optical and luminescent properties. Procedure, based on high temperature annealing of components, was proposed to form hybrids from exfoliated graphite and different molybdenum sulfides.

The obtained samples were studied using high resolution transmission electron microscopy, optical absorption spectroscopy, Raman spectroscopy and x-ray photo-

electron spectroscopy. It was found that the shape and composition of molybdenum sulfide nanoparticles deposited on the graphitic surface depend on the structure of initial carbon material as well as annealing temperature and time. We were able to produce  $\text{MoS}_2$ ,  $\text{Mo}_2\text{S}_3$ , or  $\text{Mo}_3\text{S}_4$  compounds and formation of two latter species were found to proceed much faster if molybdenum sulfide is supported by graphitic substrate. Specific capacity of the obtained hybrids for lithium intercalation was also measured.

This work was supported by the Russian Foundation of Basic Research grant No. 10-03-00696.

### TUE 34

#### Rehybridization and filling of $\text{C}_{60}\text{s}' \text{T}_{1u}$ in metallic and semiconducting peapods

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We have investigated the C1s core level x-ray absorption of bulk samples of either metallic or semiconducting single-walled carbon nanotubes and the respective  $\text{C}_{60}$  peapods. The clear cut separation of the different species unveils their distinct electronic properties. We evidence in metallic peapods an enhanced metallicity due to half filled bands derived from the molecular  $\text{t}_{1u}$  orbital of  $\text{C}_{60}$ . This is strongly contrasted by an unoccupied  $\text{t}_{1u}$  orbital in semiconducting peapods. In the latter the hybridization of the nanotube and fullerene is manifested in one additional peak between the  $\text{t}_{1u}$  orbital of  $\text{C}_{60}$  and the first unoccupied van Hove singularities.

This work is supported by an APART fellowship (11456) from the Austrian Academy of Science.

### TUE 35

#### Diameter dependent Raman scattering of WS<sub>2</sub> nanotubes

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Metal dichalcogenide (MX<sub>2</sub>) nanotubes and particles, commonly classified as inorganic fullerene-like (IF) materials, represent the inorganic counterparts of carbon nanotubes and fullerenes. They are usually constituted of several MX<sub>2</sub> triple layers, whose curvature is provided by specific defect sites. WS<sub>2</sub> and MoS<sub>2</sub> IF's have recently attracted much interest as dry lubricants and grease additives due to friction coefficients lower than those of platelet based standard mineral oil additives.

In this study WS<sub>2</sub> nanotubes with diameters in the range of 28 nm to 290 nm are studied by electron microscopy and resonant 1st and 2nd order Raman spectroscopy. With decreasing tube diameter a disorder induced line in the A<sub>1g</sub> range, termed D-A<sub>1g</sub> line, is increasingly enhanced. For the thinnest tubes it is even stronger than the fundamental A<sub>1g</sub> crystal mode. The intensity ratio I(D-A<sub>1g</sub>)/ I(A<sub>1g</sub>) follows a simple functional relationship. It resembles that of the well known I(D)/ I(G) ratio in disordered carbon.

[1] M. Krause, M. Viršek, M. Remškar, N. Salacan, N. Fleischer, L. Chen, P. Hatto, A. Kolitsch, W. Möller, ChemPhysChem, 10, 2221-2225 (2009)

## TUE 36

### **Electrical conductivity of nanodiamond films deposited by oxygen-enhanced linear plasma chemistry**

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Recent studies have shown that hydrogen terminated intrinsic nanocrystalline diamond films reveal high enough and stable p-type surface conductivity for fabrication of electronic devices [H. Kozak et al., Diamond & Relat. Mat. 18 (2009) 722]. Electronically tested diamond films were grown by focused microwave (MW) plasma process using a CH<sub>4</sub>/H<sub>2</sub> gas mixture. Present work focuses on electrical performance of diamond films deposited by oxygen-enhanced linear plasma process in which CO<sub>2</sub> is added to the CH<sub>4</sub>/H<sub>2</sub> gas mixture to improve the film purity and growth rate. Grown diamond films were processed in hydrogen MW plasma (> 550°C, 10 min). We observed that diamond surface wettability changed from its hydrophilic (cont. angle, CA < 30°) to hydrophobic (CA > 70°) character indicating a successful hydrogen termination. However, diamond surface still reveals high resistivity (> 10<sup>9</sup> ohm). We propose that remaining oxygen in the film bulk acts as recombination centers for holes induced by hydrogen termination and no current transport can be achieved. We will show that this technological limitation can be partially solved by re-growing the diamond layer in the CH<sub>4</sub>/H<sub>2</sub> gas mixture.

**TUE 37****Low temperature CVD synthesis of multiwall carbon nanotubes**András Sápi<sup>1</sup> Akos Kukovecz<sup>1</sup> Krisztián Kordás<sup>2</sup> Géza Tóth<sup>2</sup> Zoltán Kónya<sup>1</sup><sup>1</sup>Dept. of Applied and Environmental Chemistry, University of Szeged, Szeged, Hungary<sup>2</sup>Microelectronics and Materials Physics Laboratories, University of Oulu, Oulu, Finland

Our aim was to synthesize multiwall carbon nanotubes in a cost effective, scalable and environmentally friendly route. Thus, a modified methanol precursor-based CCVD process was used for synthesizing such materials at low temperature. In a typical process, methanol was used as carbon precursor and N<sub>2</sub> was the carrier gas fed into a horizontal tube reactor. Several mono-, bi- and trimetallic catalysts with different metal to support ratios were tested at various synthesis temperatures. The products and the catalysts were investigated by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray diffractometry, Raman spectroscopy and BET surface area measurements. On a Ni-Co-Fe trimetallic catalyst carbon nanotube synthesis was achieved successfully at a temperature as low as 400 °C.

**TUE 38****Pressure studies on fullerene peapods**A. Abouelsayed<sup>1</sup> Á. Botos<sup>2</sup> Á. Pekker<sup>2</sup> K. Kamarás<sup>2</sup> C.A. Kuntscher<sup>1</sup><sup>1</sup>Experimentalphysik II, Universität Augsburg, D-86159 Augsburg, Germany<sup>2</sup>Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, P.O. Box 49, H-1525 Budapest, Hungary

Applying external pressure to single-walled carbon nanotubes (SWCNTs) causes a structural phase transition, where the tubes' cross-section is deformed to an oval shape. This phase transition is revealed by an anomaly in the pressure-induced frequency shifts of the optical transitions at a critical pressure  $P_c=2-3$  GPa, as observed by infrared spectroscopy [1]. Furthermore, a second anomaly in the frequency shifts signals a more drastic deformation of the nanotubes' cross-section above 5-6 GPa [2].

Filling the SWCNTs with molecules should influence the pressure-induced effects. In order to clarify this issue, we followed the optical transitions in fullerene peapods, i.e., SWCNTs filled with C<sub>60</sub> molecules, as a function of pressure. We will present our results in comparison with those for SWCNTs. The importance of the pressure transmitting medium used in the measurements will also be discussed.

[1] K. Thirunavukkuarasu et al., Phys. Rev. B 81, 045424 (2010). [2] C. A. Kuntscher et al., Phys. Stat. Sol. (b) 247, 2789 (2010).

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**TUE 39****Atomic structure of CVD graphene**

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Large area graphene can now be produced by chemical vapor deposition (CVD). Copper turned out to be an ideal substrate for the graphene growth as the process seems to be self-limiting resulting in predominantly single-layer sheets of polycrystalline graphene.

We use 80kV aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM) to study this new material on the single-atom level. We found that the grains are connected via pentagon-heptagon pairs and that the grain growth stops when two grains are approaching each other. However the grain sizes are in the range of a few tens up to a few hundreds of nanometres what is much smaller than the grain size of the copper substrate. Furthermore we find a large variety of tilt angles between the grains indicating that graphene did not grow on the substrate in an epitaxial way.

**TUE 40****A Composite of the Red-ox Conducting Polymer of the Ferrocene Adduct of C<sub>60</sub> and Single-Wall Carbon Nanotubes for a Symmetric Electrochemical Capacitor**

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A redox conducting (carbon nanotube)-fullerene composite was devised and tested as an electrode material for a symmetric electrochemical capacitor. It was prepared, first, by electrophoretic deposition of HiPCO single-wall CNTs modified with 1-pyrenebutyric acid (pyr-SWCNTs). Then, they were coated, by electropolymerization, with a Pd-doped polymer of 2'-ferrocenylpyrrolidino-[3'-4';1,2]C<sub>60</sub>,

C<sub>60</sub>Fc-Pd. The composite was electroactive at both positive ( $\geq 0.30$  V vs. Ag/AgCl) and negative ( $\leq -0.40$  V) potentials due to redox activity of its Fc and C<sub>60</sub> moiety, respectively. Interactions between the Pd and C<sub>60</sub> moiety and the mole ratio of C<sub>60</sub>:Fc:Pd  $\approx 1:1:3$  in the C<sub>60</sub>Fc-Pd film indicated formation of a 2D and 3D rather than 1D structure of C<sub>60</sub>Fc-Pd. The highest specific capacitance of the composite was 120 and  $\sim 300$  F g<sup>-1</sup> for negative and positive potentials, respectively. A potential dependence of redox capacity, charge-transfer resistance, and double-layer capacity mimicked that of redox conductivity of the composite. Galvanostatic 90- $\mu$ A composite charging and discharging was reproducible and pseudo-linear at least in the range of 2.25 V.

#### TUE 41

##### **A spin glass transition observed by low temperature ESR from fully metal-semiconductor separated SWCNTs**

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We report ESR measurements for fully metal-semiconductor separated SWCNTs in the temperature range from 0.39 to 300 K. The temperature dependence of the spin susceptibility  $\chi$  follows a ferromagnetic Curie-Weiss law. For well annealed samples  $\chi$  exhibits a maximum at a critical temperature and drops to almost zero below. The low temperature state is considered to be a spin glass, since no response from ferromagnetic spins could be detected. The spin glass transition is the same for metallic and semiconducting tubes, indicating localized spins as the source for the ESR signal. The temperature dependence of the line width is dramatically different for the semiconducting and metallic tubes. This is evidence that the spins originate from defects on the tubes and not from other contaminations.

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**TUE 42****Comparative study of reflectance properties of nanodiamonds, onion-like carbon and multiwalled carbon nanotubes**

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Carbon nanomaterials are promising candidates for potential broadband limiting applications and extremely low reflectance coatings, particularly in the infrared, visible and UV spectral regions. In this paper we have performed comparative study of diffuse reflectance of nanodiamond (ND), sp<sup>2</sup>/sp<sup>3</sup> composites and onion-like carbon (OLC) and multiwalled carbon nanotubes (MWNTs) in IR, visible and UV regions. ND and sp<sup>2</sup>/sp<sup>3</sup> composites and onion-like carbon (OLC) produced via high temperature annealing of the same set of NDs allow us to vary sp<sup>2</sup>/sp<sup>3</sup> carbon ration, size of primary particle agglomerates and concentration of defects while MWNT set provides possibility to vary NT diameters and length, order/disorder degree (via high temperature MWNTS annealing). The diffuse reflectance of carbon nanomaterials depends mainly on electronic configuration, defect concentration, size of graphene-like ordered fragments and agglomerates in nanocarbons along with their morphology. Incorporation of nanocarbons in polymer or ceramic matrix provides additional possibility to produce new optic materials.

**TUE 43****Infrared active modes in single walled carbon nanotubes - a theoretical study**

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The frequencies of infrared active modes of a large number of single walled carbon nanotubes have been calculated on the first principles level. We used density functional theory in the local density approximation. All semiconducting tubes were studied in the diameter range between 0.3 - 1.1 nm. Due to the fact that the number of carbon atoms in the traditional translational unit cell is several hundreds in many cases, we had to explicitly take into account the helical symmetry of the tubes when calculating the force constants. The identification of the infrared active modes was based on the representation theory of line groups. The frequencies of the 0A<sup>-</sup> 1 dimensional modes are around 860 cm<sup>-1</sup> and increase monotonically with increasing diameter - in good agreement with very recent experimental results (see contribution of Á. Pekker et al).

**TUE 44****Hybrid semiconductor-metal-polymer nanostructures**

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We present selected concepts to combine inorganic nanocrystals in functional polymers. The general route is a ligand exchange of the organic ligands used in the synthesis to hydrophilic copolymer pre-stages. This allows either the addition of further polymer chains or the embedding in polymer-based nanostructures. The focus of the presented work is on the structural characterization via Raman spectroscopy, AFM and new material properties arising from the combination of the organic and inorganic material.

**TUE 45****Raman investigation of the defect modes of metallic and semiconducting enriched single walled carbon nanotubes**

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Functionalization of single-walled carbon nanotubes (SWCNTs) typically leads to an increase in intensity of the defect induced Raman bands. A large intensity of the defect modes is therefore often used as an evidence for successful functionalization. However, there is no hint if a selective functionalization of metallic or semiconducting SWCNTs can be confirmed with the help of the intensity or position of the defect mode. A necessary condition for that would be that the resonance profiles of the defect modes are known in comparison to the profiles of the well-known radial-breathing modes.

Here we analyze the Raman defect modes of metallic and semiconducting enriched HiPCO SWCNT samples. By resonance Raman spectroscopy we study the evolution of the lineshape of the defect mode of SWCNTs for excitation energies in the range of 1.45 to 1.65 eV and 1.96 to 2.34 eV. Furthermore, we discuss differences of the defect modes between the semiconducting and metallic enriched samples.

**TUE 46****3D nanostructure analysis of Pd-Au/MWCNTs catalysts by QUASES**B. Lesiak<sup>1</sup> L. Stobinski<sup>1</sup> A. Borodzinski<sup>1</sup> J. Zemek<sup>2</sup> P. Jiricek<sup>2</sup> L. Kövér<sup>3</sup> J. Tóth<sup>3</sup><sup>1</sup>Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Kasprzaka 44/52, Poland<sup>2</sup>Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnicka 10, 162 53 Prague 6, Czech Republic<sup>3</sup>Institute of Nuclear Research, Hungarian Academy of Sciences (ATOMKI), H-4001 Debrecen, P. O. Box 51, Hungary

The Pd-Au multiwall carbon nanotubes (MWCNTs) supported catalysts were prepared using: (i) a polyol method and (ii) a microwave-assisted polyol method. The catalysts surface treatment under different gas atmospheres and temperatures resulted in changing their catalytic activities in the electrooxidation of formic acid. These activities were attributed to Pd and Au metallic nanoparticles size and their distribution, content, coverage and also thickness of palladium oxides and amorphous carbon overlayer on Pd nanocrystallites. In the present work, the 3D surface nanostructure was investigated using the QUASES software, with a special consideration to Pd and Au nanometallic particles structure due to: (i) preparation reaction and (ii) the catalysts pretreatment. Reasons for different activities of Pd/MWCNTs and Pd-Au/MWCNTs catalysts in the reaction of formic acid electrooxidation for Pd/MWCNTs were discussed.

**TUE 47****Direct Graphene Growth on Insulator**Gunther Lippert<sup>1</sup> Jarek Dabrowski<sup>1</sup> Max Lemme<sup>2</sup> Olaf Seifarth<sup>1</sup> Grzegorz Lupina<sup>1</sup><sup>1</sup>Innovations of High Performance microelectronics, Frankfurt (Oder)<sup>2</sup>KTH Royal Institute of Technology 16640 Kista Sweden

Fabrication of graphene devices is often hindered by incompatibility between the silicon technology and the available methods of graphene growth. Exfoliation from graphite yields excellent films but is good mainly for research. Graphene grown on metal has a technological potential but must be transferred mechanically. Growth by SiC decomposition requires a temperature budget exceeding the technological limits.

These issues could be circumvented by growing graphene directly on insulator. This implies van der Waals growth. During growth, the insulator acts as a support defining the growth plane. In the device, it insulates graphene from the Si substrate. We demonstrate planar growth of graphene on mica surface. This was achieved by molecular beam deposition at about 800°C. High resolution Raman scans illustrate the effect of growth parameters and substrate topology on the film perfection. Ab initio calculations suggest a growth model. Analysis of experimental and theo-

retical data highlights the competition between nucleation at surface steps and flat surface. As a proof of concept, we show the evidence of electric field effect in a transistor with a directly grown channel.

**TUE 48****Vibrational spectroscopy of layered  $\text{Li}_7\text{Ge}_{12}$  and its derivative compounds: theory and experiment**

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The results of experimental and theoretical (Density Functional Theory) studies on the vibrational properties of layered  $\text{Li}_7\text{Ge}_{12}$  and its derivative structures are presented. Li-removal from the structure and the “collapse” of the Ge-layers manifests itself in the appearance of Raman-active mode with higher frequency compared to the “Ge-Ge” bonds in cubic germanium single crystals and in  $\text{Li}_7\text{Ge}_{12}$ .

**TUE 49****Scalable Single-Chirality Separation of SWCNTs by Simple Gel Chromatography**

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

<sup>1</sup>NRI, AIST and Japan Science and Technology Agency (JST), CREST, Japan

<sup>2</sup>Nanosystem Research Institute (NRI), National Institute of advanced industrial science and Technology (AIST), Tsukuba, Japan

Here, we report a simple and effective method for large-scale chirality separation of single-wall carbon nanotubes (SWCNTs) using single-surfactant multicolumn gel chromatography (SS-MUGEC) that uses only one surfactant (sodium dodecyl sulfate) and a series of gel columns (commercial Sephacryl gel). We succeeded in isolating 13 kinds of single-chirality nanotubes from HiPco-SWCNTs just by injecting an excess of SWCNT dispersion into the gel column series. This simple method is based on the structure-dependent interaction of SWCNTs with the gel. The nanotubes with the highest interaction with the gel are preferentially adsorbed in the top column whereas the nanotubes with the lower interaction with the gel are adsorbed in the following gel columns. In this manner, chirality-separation of SWCNTs was achieved. Metallic SWCNTs were finally collected as unbound nanotubes because of their lowest interaction with the gel. Because this method is simple, quick, high-efficiency, continuous and low cost, separation in an industrial scale is expected. We believe that SS-MUGEC will open a new research field and applications of SWCNTs.

**TUE 50****Optical studies of ferrocene filled very thin single-walled carbon nanotubes**Xianjie Liu<sup>1</sup> Hans Kuzmany<sup>1</sup> Thomas Pichler<sup>1</sup><sup>1</sup>Faculty of Physics, University of Vienna, Austria

We present optical studies of ferrocene filled very thin single-walled carbon nanotubes (SWNTs) by photoluminescence, optical absorption and Raman spectroscopy. The mean diameter of selected SWNTs is close to the limitation given by the size of the ferrocene molecule. The filling effect was confirmed by conversion of ferrocene peapods into double-walled carbon nanotubes. The change of electronic properties of SWNTs during opening and filling processes was observed by the variation of optical responses from outer tubes. A p-type doping of SWNTs occurs in the opening process, however, when ferrocene was filled into SWNTs, the charge transfer from ferrocene to nanotubes can compensate p-type doping in the opening process. The corresponding optical and photoluminescence measurements confirm such different doping behaviors. Furthermore, a very low annealing temperature of 500 °C is enough to convert ferrocene peapods into double-walled carbon nanotube in such thin diameter SWNTs.

This work is supported by FWF project P21333-N20.

**TUE 51****Influence of agarose gel concentration on metallic/semiconducting separation of single-walled carbon nanotubes via chromatography**Pawel Lukaszczuk<sup>1</sup> Ewa Borowiak-Palen<sup>1</sup> Ryszard Kalenczuk<sup>1</sup><sup>1</sup>Institute of Chemical and Environment Engineering, West Pomeranian University of Technology, Szczecin

Here we report a systematic study on influence of agarose gel concentration on the efficiency of metallic and semiconducting fractionation of bulk single-walled carbon nanotubes (SWCNTs). It was found that the agarose gel concentration used in a chromatography has to be optimised in order to get one electronic type of SWCNTs in a relatively short process time. Therefore, we present the preparation of agarose gel beads used as a filling of chromatographic column which are tested in the separation. The highest yield of the process and the shortest separation was obtained using agarose gel with concentration of 1%. One step procedure results in the preparation of the sample containing 97% of semiconducting tubes. Additionally, the preparation cost of the agarose gel is approximately 0,49 \$ per single process with the chromatography column of 10 mL. It is worth pointing that the commercially available Sepharose® 2B used for the same process costs 16,99 7 \$ per 10 mL (Sigma-Aldrich). Therefore, this gel preparation route is an alternative method and could reduce the cost of this recently widely investigated technique.

**TUE 52****High-frequency suspended graphene resonators for tunable filters**

Dmitry Lyashenko<sup>1</sup> Xuefeng Song<sup>1</sup> Mika A. Sillanpää<sup>1</sup> Mika Oksanen<sup>1</sup> Pertti J. Hakonen<sup>1</sup>

<sup>1</sup>Aalto University, School of Science and Technology, Low Temperature Laboratory, Espoo, P.O. Box 15100, FI-00076

Mechanical oscillators are widely applied in digital and radio architectures. Recent trends require new oscillators with good stability and wide-tunable resonance. We have investigated suspended graphene as a tunable mechanical resonator in a low-capacitance scheme.

Graphene film is obtained by CVD technique on the copper surface. Graphene sheet is transferred onto a prepatterned electrodes scheme. To detect mechanical resonance, suspended graphene is actuated by applying a driving voltage. External AC voltage produces time-varying capacitance between graphene and the gate. An injected RF signal is modulated by the graphene capacitor and sideband peaks in the reflected signal are produced when crossing the mechanical resonance.

Presented electrical detection method is applicable for nanoscale mechanical resonators in a large frequency range. The fabrication method is promising to build complex graphene and carbon nanotubes nanoelectromechanical systems.

**TUE 53****Abnormal behavior of electron emission from graphite-based nanomaterials.**

Sergey Lyashenko<sup>1</sup> Dmitri Golberg<sup>2</sup> Alexander Obraztsov<sup>3</sup>

<sup>1</sup>Department of Physics, Moscow State University, Moscow, Russia

<sup>2</sup>International Center for Materials Nanoarchitectonics, National Institute for Materials Science, Tsukuba, Japan

<sup>3</sup>Department of Physics and Mathematics, University of Eastern Finland, Joensuu, Finland

Thermionic and field electron emissions governed by Richardson-Dushman and Fowler-Nordheim equations, correspondingly, are normally coexisting at usual experimental conditions. However, the carbon-based cathodes demonstrate deviations of temperature dependencies of the current-voltage characteristics from those predicted by these equations. This difference cannot be ascribed to very little variations of work function or surface topology which are resulted from temperature change. In this work the temperature dependencies of the electron emission characteristics were experimentally investigated for the nano-graphite film cathodes obtained by a chemical vapor deposition method. In addition, computer modeling of heat dissipation in the graphitic nano-emitters was performed. We found that self-consistent explanation of the experimental observations of the thermionic and field electron emissions from the nano-carbon cathodes may be obtained taking into account the temperature dependence of free carrier density.

**TUE 54****Long term stabilization of reaction center protein photochemistry by carbon nanotubes**

M. Magyar<sup>1</sup> K. Hajdu<sup>1</sup> T. Szabó<sup>1</sup> K. Hernádi<sup>2</sup> A. Dombi<sup>3</sup> E. Horváth<sup>4</sup> L. Forró<sup>4</sup>  
L. Nagy<sup>1</sup>

<sup>1</sup>Department of Medical Physics and Informatics, University of Szeged, Szeged, Hungary

<sup>2</sup>Department of Applied and Environmental Chemistry, University of Szeged, Szeged, Hungary

<sup>3</sup>Department of Inorganic and Analytical Chemistry, University of Szeged, Szeged, Hungary

<sup>4</sup>Institute of Physics of Complex Matter, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

The long term stability and the redox interaction between the single walled carbon nanotubes (SWNTs) and photosynthetic reaction center proteins (RCs) purified from purple bacterium *Rhodobacter sphaeroides* R-26 in the SWNT/RC complex has been investigated. The attachment of SWNT to RC results in an accumulation of positive (the oxidized primary electron donor, P(+)) and negative (semiquinone forms, QA(-) and QB(-), the reduced primary and secondary quinones, respectively) charges followed by slow reorganization of the protein structure after excitation. The photochemical activity of the SWNT/RC complexes remains stable for several weeks even in dried form. In the absence of SWNT the secondary quinone activity decays quickly as a function of time after drying the RC onto a glass surface. Polarography measurements support the idea that there is an electronic interaction between the RCs and SWNTs after light excitation, which was suggested earlier by optical measurements. The special electronic properties of the SWNT/protein complexes open the possibility for several applications, e.g. in microelectronics, analytics or energy conversion and storage.

**TUE 55****Magnetic properties of semifluorinated graphite**

T. L. Makarova<sup>1</sup> A. I. Shames<sup>2</sup> G. N. Chekhova<sup>3</sup> D. V. Pinakov<sup>3</sup> N. F. Yudanov<sup>3</sup>  
N. F. Yudanov<sup>3</sup> L. G. Bulusheva<sup>3</sup>

<sup>1</sup>Umea University, Umea, Sweden

<sup>2</sup>Ben Gurion Univ Negev, Beer Sheva, Israel

<sup>3</sup>Nikolaev Int. Inorganic Chemistry, Novosibirsk, Russia

A series of layered inclusion compounds based on fluorinated graphite C<sub>2</sub>F<sub>x</sub> (x?1) was obtained by a room temperature synthesis. Electronic and magnetic properties of graphene sheet can be delicately tuned by the fluorination degree and the nature of the inclusion compound in the layered fluorographene compounds. Magnetic phase transitions have been observed using both magnetic susceptibility measurements

and electron spin resonance. The semifluorinated graphite provides an opportunity to study the magnetism of two-dimensional system without metallic impurities.

**TUE 56****Donor and/or Acceptor Systems built around Graphene**

Jenny Malig<sup>1</sup> Dirk M. Guldi<sup>1</sup>

<sup>1</sup>University Erlangen-Nuremberg, Department of Chemistry and Pharmacy & Interdisciplinary Center of Molecular Materials (ICMM), Egerlandstraße 3, 91058 Erlangen, Germany.

Graphene's extraordinary electronic properties render it a promising material for electronics, material sciences, and photo conversion systems. In our group, we focus on integrating graphene into electron donor and/or acceptor hybrids by concomitant exfoliation of "natural graphite" as starting material. In this regard, we immobilized molecular building blocks, which are predestinated for  $\pi - \pi$  stacking, as exfoliation reagents, e.g. phthalocyanine oligomers or pyrene derivatives, onto graphene. In addition, the aforementioned building blocks are prone to react as either an electron acceptor or electron donor. A myriad of covalent or non-covalent means are at our disposal to combine graphene with appropriate functionalities resulting in complex electron donor-acceptor conjugates or hybrids, respectively. The energy and electron transfer interactions within these newly formed donor/acceptor nano-hybrids are examined in depth by time-resolved and steady-state techniques. Most importantly, their applicability as novel photoelectrodes in solar cells is tested by means of transferring them out of solution onto different substrates.

**TUE 57****MWCNTs-ZrO<sub>2</sub> nanoparticle hybrid materials**

A. Malolepszy<sup>1</sup> M. Mazurkiewicz<sup>1</sup> K.J. Kurzydowski<sup>1</sup> L. Stobinski<sup>2</sup>

<sup>1</sup>Faculty of Materials Science and Engineering, Warsaw University of Technology, Woloska 141, 02-507 Warsaw, Poland

<sup>2</sup>Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Kasprzaka 44/52, Poland

ZrO<sub>2</sub> nanoparticles were deposited on the purified multiwall carbon nanotubes (MWCNTs) surface by applying the hydrothermal method. Solution of ZrOCl<sub>2</sub> precursor and sodium hydroxide base were initially mixed and then heated in the Teflon reactor at temperature around 200 K and under 50 bars pressure for 30 min. A narrow size distribution (2-4 nm) of uniform deposited ZrO<sub>2</sub> nanoparticles on the MWCNTs surface was observed. The density of ZrO<sub>2</sub> nanoparticles distribution can be regulated by the concentration of the ZrOCl<sub>2</sub> precursor in the reaction mixture. The obtained hybrid MWCNTs-ZrO<sub>2</sub> nanomaterials can be a good candidate for a photo- and electro-catalysts support and different kind of sensors.







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Wednesday, March 2

## Topological insulators, graphene transport I

- 8:30 – 9:30     **L. W. Molenkamp, DE**  
*Dirac Fermions in HgTe Quantum Wells*
- 9:30 – 10:00    **J. Moore, US**  
*Magnetoelectric, thermoelectric, and spintronic properties of three-dimensional topological insulator*
- 10:00 – 10:30   **Coffee break**
- 10:30 – 11:00   **M. Bockrath, US**  
*Carbon Nanoelectronics*
- 11:00 – 11:30   **J. Wrachtrup, DE**  
*Quantum spintronics systems based on diamond nanostructures*
- 11:30 – 12:00   **G. W. Morley, GB**  
*Spin qubits in silicon*
- 12:00 – 17:00   **Mini Workshops**
- 17:00 – 18:30   **Dinner**
- 18:30 – 19:30   **M. S. Fuhrer, US**  
*Graphene: Scratching the Surface*
- 19:30 – 20:00   **F. Guinea, ES**  
*Gauge fields in graphene*
- 20:00 – 20:30   **M. F. Crommie, US**  
*Probing Graphene at the Atomic Scale: Adatoms, Strain, and Edges*

Wednesday, March 2

**8:30****Dirac Fermions in HgTe Quantum Wells**

Laurens W Molenkamp

Physikalisches Institut (EP3), Würzburg University, Würzburg

HgTe quantum wells have a linear band dispersion at low energies and thus mimic the Dirac Hamiltonian. Changing the well width tunes the band gap (i.e., the Dirac mass) from positive, through zero, to negative. Wells with a negative Dirac mass are 2-dimensional topological insulators and exhibit the quantum spin Hall effect, where a pair of spin polarized helical edge channels develops when the bulk of the material is insulating. Our transport data provide very direct evidence for the existence of this third quantum Hall effect. Wells with a thickness of 6.3 nm are zero gap Dirac systems, similar to graphene. However, zero gap HgTe wells possess only a single Dirac valley, which avoids inter-valley scattering. Finally, we demonstrate that strained bulk HgTe is a gapped 3-dimensional topological insulator, where transport occurs through Dirac fermions on the surfaces of the material.

**9:30****Magnetoelectric, thermoelectric, and spintronic properties of three-dimensional topological insulators**Joel E. Moore

University of California, Berkeley, and Lawrence Berkeley National Laboratory

Three-dimensional topological insulators are insulating in bulk but have protected metallic surface states as a consequence of spin-orbit coupling. In  $\text{Bi}_2\text{Te}_3$  and  $\text{Bi}_2\text{Se}_3$ , these surface states have the same Dirac electronic structure as graphene but with reduced degeneracy and spin-momentum locking. We discuss theoretical predictions of how these surface states lead to unusual transport effects that could be useful for thermoelectric and spintronic applications: a thin film of a topological insulator can show enhanced thermoelectric figure of merit at low temperature and support a large, switchable spin density induced by an applied electrical current. When the surface states are gapped by a time-reversal breaking perturbation, the result is a quantized magnetoelectric effect and understanding this effect leads to a general theory of orbital magnetoelectricity in crystals.

**10:30****Carbon Nanoelectronics**

Marc Bockrath<sup>1</sup> Vikram V. Deshpande<sup>2</sup> Bhupesh Chandra<sup>3</sup> Robert Caldwell<sup>2</sup>  
Dmitry S. Novikov<sup>4</sup> James Hone<sup>2</sup> Hang Zhang<sup>1</sup> Wenzhong Bao<sup>1</sup> Chun Ning Lau<sup>1</sup>

<sup>1</sup>University of California, Riverside, CA

<sup>2</sup>Columbia University, New York, NY

<sup>3</sup>IBM TJ Watson Research Center, Yorktown Heights, NY

<sup>4</sup>New York University School of Medicine, New York, NY

Evidence showing that the electrons in nominally metallic nanotubes comprise a 1D Mott insulator will be presented. This indicates that carbon nanotubes are never truly metallic, in agreement with theoretical predictions that account for umklapp scattering at half-filling due to electron-electron interactions. Using inelastic co-tunneling spectroscopy, we also observe neutral electronic excitations within the gap, yielding an additional signature of strong electron-electron interactions. Our results demonstrate nanotubes' promise for studying a variety of tunable correlated electron phenomena in one dimension. The talk will conclude with a discussion of our recent data showing voltage-programmable switching behavior in suspended graphene electromigration-driven break-junction devices.

**11:00**

**Quantum spintronics systems based on diamond nanostructures**

Jörg Wrachtrup

3. Institute of Physics and Research Center SCoPE, University of Stuttgart, Germany

Engineering and controlling quantum few body systems is a technical as well as intellectual challenge. Being led by quantum and atom optics initially, solid state based synthetic quantum systems like quantum dot molecules, interacting superconducting circuits or spin arrays in diamond have currently reached a high degree of sophistication. The talk will describe how to engineer spin arrays comprising few electron and nuclear spins into diamond and how to integrate them into diamond nanostructures. The quantum dynamics of those systems will be analyzed and their behavior in resonator structures in the single photon limit will be discussed. A perspective towards application in sensing and bioanalytics will be given.

**11:30****Spin qubits in silicon**Gavin W MorleyLondon Centre for Nanotechnology and Department of Physics and Astronomy,  
University College London, London

Spin qubits in silicon are interesting because of their long coherence times and the electrical readout of the state of one electron spin. In a single experiment we demonstrate initialization, manipulation, storage and electrical readout of quantum information with a small ensemble of phosphorus electron spins in silicon. Our electrical readout does not destroy the electron spin coherence, which is limited instead by naturally-occurring  $^{29}\text{Si}$  nuclear spins. This experiment required a pulsed electron spin resonance spectrometer operating at high magnetic fields. Additionally, we have extended our experiment to initialise, manipulate, store and electrically readout classical information in  $^{31}\text{P}$  nuclear spins.

Silicon quantum computers would benefit from having a second dopant species which can be addressed selectively, and we find that bismuth atoms are well suited for this role. They offer long spin coherence times as well as new opportunities when compared with phosphorus.

Wednesday, March 2

Topological insulators, graphene transport I

**18:30**

**Graphene: Scratching the Surface**

Michael S Fuhrer

Center for Nanophysics and Advanced Materials, University of Maryland, College Park, MD

Graphene, a single-atom thick plane of graphite, is composed entirely of surface atoms, making the techniques of surface science useful in studying its properties. In this talk, I will first discuss the electronic structure of graphene, and its implications for electronic properties. I will then discuss experiments which combine ultra-high vacuum (UHV) surface science with electronic transport measurements. Surface science techniques can be used to controllably modify graphene's properties: alkali or transition metal atoms can be deposited to form charged impurity scatterers; ice can be deposited to modify the dielectric environment of graphene and tune the electron-electron interaction strength; and ion irradiation can be used to create atomic vacancies which act as Kondo impurities, and at high densities induce strong localization. Graphene may also be used as a sensitive detector to observe chemical reactions occurring on its surface at concentrations below 1/1000th of a monolayer.

**19:30****Gauge fields in graphene**Francisco Guinea

Insitituto de Ciencia de Materiales de Madrid, CSIC, Madrid

Lattice deformations couple to electrons in graphene by giving rise to an effective gauge field[1,2]. This unique feature leads to the possibility of modifying the electronic properties by applying strain to the lattice[3,4]. The main properties of the interaction between electrons and long wavelength lattice deformations will be reviewed.

- [1] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, A. K. Geim, Rev. Mod. Phys. 81, 109 (2009)
- [2] M. A. H. Vozmediano, M. I. Katsnelson, F. Guinea, Phys. Rep., in press (2010).
- [3] F. Guinea, M. I. Katsnelson, A. K. Geim, Nature Phys. 6, 30 (2010).
- [4] N. Levy, S. A. Burke, K. L. Meaker, M. Panlasigui, A. Zettl, F. Guinea, A. H. Castro Neto, and M. F. Crommie, Science 329, 544 (2010).

**20:00****Probing Graphene at the Atomic Scale: Adatoms, Strain, and Edges**

M. F. Crommie<sup>1</sup> C. Tao<sup>1</sup> L. Jiao<sup>2</sup> O. V. Yazyev<sup>1</sup> Y.-C. Chen<sup>1</sup> J. Feng<sup>1</sup> X. Zhang<sup>1</sup>  
R. B. Capaz<sup>3</sup> J. M. Tour<sup>4</sup> A. Zettl<sup>1</sup> S. G. Louie<sup>1</sup> H. Dai<sup>2</sup> N. Levy<sup>5</sup> S. A. Burke<sup>6</sup>  
K. L. Meaker<sup>1</sup> M. Panlasigui<sup>1</sup> F. Guinea<sup>7</sup> A. H. Castro Neto<sup>8</sup> M. L. Cohen<sup>1</sup> V.  
W. Brar<sup>1</sup> R. Decker<sup>1</sup> K. T. Chan<sup>1</sup> H. Lee<sup>1</sup> C. Girit<sup>1</sup> H. M. Solowan<sup>1</sup> Y. Wang<sup>1</sup> L.  
Maserati<sup>1</sup>

<sup>1</sup>Physics Department, University of California at Berkeley, Berkeley

<sup>2</sup>Chemistry Department, Stanford University

<sup>3</sup>Instituto de Física, Universidade Federal do Rio de Janeiro

<sup>4</sup>Chemistry Department, Rice University

<sup>5</sup>Center for Nanoscale Science and Technology, NIST

<sup>6</sup>Physics Department, University of British Columbia

<sup>7</sup>Instituto de Ciencia de Materiales de Madrid

<sup>8</sup>Physics Department, Boston University

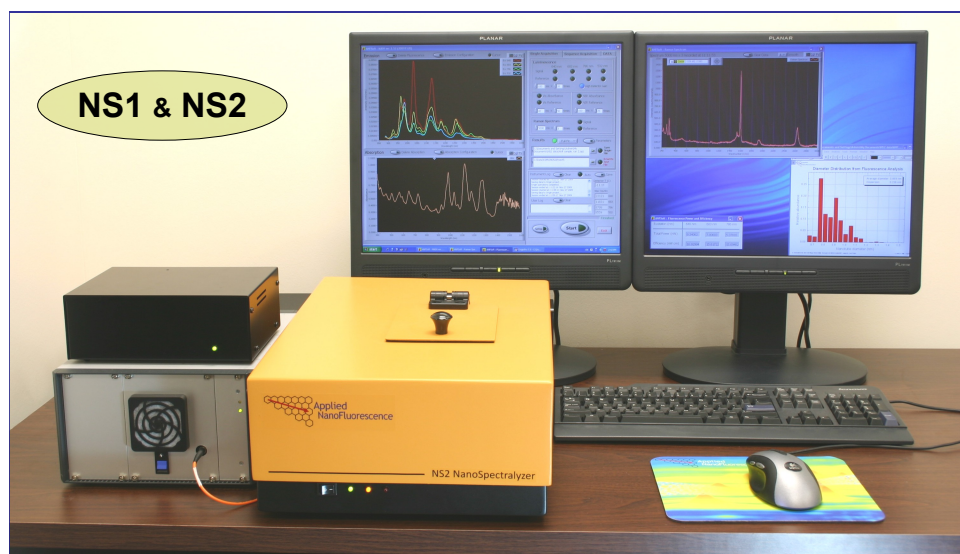
Novel phenomena arises from the interplay between Dirac fermions in graphene and imperfections such as adsorbed atoms, highly strained regions, and edges. Scanning tunneling microscopy (STM) is an ideal tool to study such phenomena at the atomic scale. We have used STM-based techniques to explore the local electronic properties of graphene that has been modified by the addition of transition metal adsorbates, the application of highly anisotropic strain, and the creation of well-defined chiral edges. We find that cobalt atoms added to graphene create electronic defect states that can be charged or discharged through the application of a back-gate voltage. Highly strained graphene grown on a metal surface was observed to produce pseudofields in excess of 350 Tesla. One-dimensional states were observed at the chiral edges of graphene nanoribbons and shown to exhibit a width-dependent energy gap consistent with predictions for spin-polarized nanoribbon edge-states.



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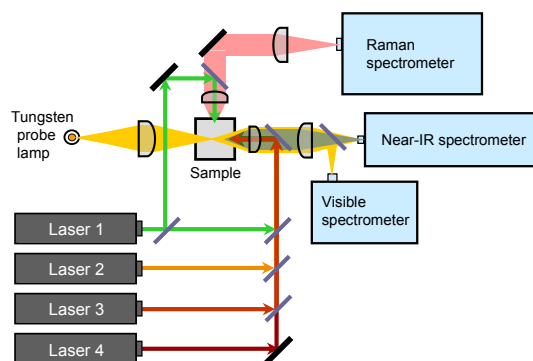
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Thursday, March 3

## Graphene electronic properties and transport II

- 8:30 – 9:00     **K. Ensslin, CH**  
*Coherent phonons in graphene double dots*
- 9:00 – 9:30     **A. Grüneis, DE**  
*Electronic Properties of functionalized Graphene*
- 9:30 – 10:00    **A. Bostwick, US**  
*Plasmaron in quasi-free-standing graphene*
- 10:00 – 10:30   **Coffee break**
- 10:30 – 11:00   **F. Libisch, AT**  
*Disorder scattering in large-scale graphene nanodevices*
- 11:00 – 11:30   **J.-C. Charlier, BE**  
*Ab initio quantum transport in defective and chemically-modified graphene*
- 11:30 – 12:00   **E. Andrei, US**  
*Probing Dirac fermions in graphene with STM and magneto-transport*
- 12:00 – 17:00   **Mini Workshops**
- 17:00 – 18:30   **Dinner**
- 18:30 – 19:00   **V. Deshpande, US**  
*Graphene NEMS resonators and self-oscillators: High-bandwidth electrical readout and magnetometry in the quantum Hall regime*
- 19:00 – 19:30   **M. Drndic, US**  
*Graphene nanopores: Structure, Properties and Function*
- 19:30 – 20:00   **N. Koch, DE**  
*Intermolecular hybridization governs molecular doping of organic semiconductors*

Thursday, March 3

**8:30****Coherent phonons in graphene double dots**

Klaus Ensslin<sup>1</sup> Francoise Molitor<sup>1</sup> Johannes Güttinger<sup>1</sup> Susanne Dröscher<sup>1</sup> Preden Roulleau<sup>1</sup> Stefan Baer<sup>1</sup> Thomas Ihn<sup>1</sup>

<sup>1</sup>ETH Zurich, Zurich

Coulomb blockade has been observed in single quantum dots. Double dots have also recently been realized in graphene and ground state and excited states have been experimentally detected. Here we demonstrate excited states which are almost periodic in energy. We argue that they arise from an interference effect including coherent phonons. Similar effects have meanwhile also been observed in a completely different material system, InAs nanowire double dots. We discuss the relevance of this phonon effect in view of the different dimensionality of graphene, nanowires and electron gases in standard semiconductors.

**9:00****Electronic Properties of functionalized Graphene**Alexander Grüneis

IFW-Dresden (Germany) and University of Vienna (Austria)

Chemical functionalization is one of the key strategies to tailor graphene's electronic properties. We have carried out functionalization of CVD grown graphene with alkali and hydrogen atoms. This allows for tuning of the electron energy bandgap as well as the electron concentration independently. Angle-resolved photoemission (ARPES) is employed to determine the electron-phonon coupling constant in alkali metal doped graphene and the size of the gap in hydrogenated graphene. We demonstrate that a peculiar midgap state arises when n-doped quasi-free-standing graphene is functionalized with atomic hydrogen. The chemical bonding and the concentrations of the chemisorbed hydrogen atoms are determined using x-ray photoemission spectroscopy (XPS) of the carbon core levels. By performing long hydrogenation cycles we show with XPS that the H coverage saturates at 25%. This stoichiometry is independently found from molecular dynamics simulations of graphene's hydrogenation kinetics. The simulations predict that repeated surface reorganization due to associative  $H_2$  elimination results in a para-type chemisorption pattern for this phase.

**9:30****Plasmaron in quasi-free-standing graphene**Aaron Bostwick

Advanced Light Source, Lawrence Berkeley National Lab, Berkeley

Graphene is a remarkable new electronic material with many unique properties. To realize its promise, it is essential to understand how its charge carriers interact. By measuring the spectral function of charge carriers in quasi-free-standing graphene, we show that at finite doping, the well-known linear Dirac spectrum does not provide a full description of the charge-carrying excitations. We find that there also exist composite "plasmaron" particles, consisting of holes coupled to density oscillations of the graphene electron gas. The Dirac crossing point is resolved into three crossings: the first between pure charge bands, the second between pure plasmaron bands, and the third a ring-shaped crossing between charge and plasmaron bands.

**10:30****Disorder scattering in large-scale graphene nanodevices**F. Libisch<sup>1</sup> S. Rotter<sup>1</sup> J. Burgdörfer<sup>1</sup><sup>1</sup>Institute for Theoretical Physics, Vienna University of Technology, Vienna

We investigate the role of disorder scattering in transport through graphene nanodevices of experimentally realizable size. We use a Fourier transformation of scattered states to disentangle the role of scattering between the two cones of the bandstructure ( $K - K'$ ) and the two sublattices ( $AB$ ). Varying the characteristic length scale of the disorder allows us to tune between symmetry breaking and symmetry-conserving potential landscapes. We find that short-range potentials introduce substantial differences between scattering states on the A and B sublattice, marking the breakdown of simple Dirac descriptions based on pseudospin as good quantum number. The visibility of size quantization plateaus in graphene is found to be strongly dependent on pseudo-spin conservation. We can thus offer an explanation why quantization effects have not yet been observed in the experiment: symmetry breaking disorder scattering washes out the quantization plateaus. Inclusion of a magnetic field allows us to investigate the interplay between magnetic length, correlation length of the disorder, and the lattice spacing.

**11:00****Ab initio quantum transport in defective and chemically-modified graphene**Jean-Christophe CharlierInstitute of Condensed Matter and Nanosciences, University of Louvain,  
Place Croix du Sud 1 (NAPS-ETSF-Boltzmann), Louvain-la-Neuve (Belgium)

Quantum transport properties of disordered graphene with structural point defects are investigated using tight-binding/ab initio calculations [PRL 106, 046803 (2011)]. Mean free paths and semiclassical conductivities are computed as a function of the nature and density of defects. By increasing the defect density, the decay of the semiclassical conductivities saturates to a minimum value over a large plateau of carrier density. Additionally, strong contributions of quantum interferences suggest that the Anderson localization regime could be experimentally measurable (for defect density  $< 1\%$ ). The transport properties of graphene after epoxide functionalization via ozone treatment is also studied [ACS Nano 4, 4033 (2010)]. The orbital rehybridization induced by the epoxide groups triggers a strong inter-valley scattering and changes dramatically the conduction properties of graphene. By varying the coverage density of epoxide defects from 0.1 to 4%, charge conduction can be tuned from a diffusive to a strongly localized regime, with localization lengths down to a few nm long. Our results provide a physical interpretation to the metal-insulator transition observed experimentally.

**11:30****Probing Dirac fermions in graphene with STM and magneto-transport.**Eva Y Andrei

Department of Physics and Astronomy, Rutgers University, Piscataway NJ

The strictly two dimensional structure of graphene results in 2D charge carriers that are readily accessible by surface probes such as STM or ARPES and in electronic properties that can be controlled through doping, strain and external potentials. I will describe STM and magneto-transport experiments showing that when graphene is decoupled from substrate-induced potential fluctuations the intrinsic properties of the carriers become apparent and measurable. This led to the direct observation of quantized Landau levels and the observation of a fractional quantum Hall Effect. When graphene is exposed to an external potential induced by a second graphene layer, we found that its electronic density of states undergoes a qualitative transformation from the linear spectrum characteristic of massless Dirac fermions to one that contains prominent Van Hove singularities which are controlled by the relative orientation of the layers.

**18:30****Graphene NEMS resonators and self-oscillators: High-bandwidth electrical readout and magnetometry in the quantum Hall regime**Vikram Deshpande<sup>1</sup> Changyao Chen<sup>1</sup> David Heinz<sup>1</sup> Yuehang Xu<sup>1</sup> Philip Kim<sup>1</sup> James Hone<sup>1</sup><sup>1</sup>Columbia University, New York

High-frequency graphene nanoelectromechanical systems (NEMS) are promising candidates for applications in wireless communication and sensing as well as for studying fundamental physics. However, electrical detection of carbon NEMS in general has only been possible by down-mixing the signals to low (kHz and DC) frequencies, due to the small displacements and large parasitics involved in such measurements. To this end, I will report on recent technological advances we have made at Columbia University and the physics they enable. One, we have developed a direct radio-frequency electrical readout for graphene NEMS which is three orders of magnitude faster than mixing techniques. Two, we have developed zero-bias purely-capacitive detection of resonance (readout in the absence of transconductance), which is useful in low-temperature regimes such as on a quantum Hall plateau. Three, we are able to amplify and feed back thermal vibrations and thus self-oscillate these devices without the need for external driving. Combining these techniques in the form of a unique application, we use graphene NEMS as magnetometers to detect their own magnetization in the quantum hall regime.

**19:00****Graphene nanopores: Structure, Properties and Function**Marija Drndic

David Rittenhouse Laboratory, University of Pennsylvania, Philadelphia

Graphene is an exceptional material for high-speed electronics, as well as a revolutionary membrane material due to its strength and atomic thickness. Nanopores in membranes of graphene are currently regarded as candidates for ultrafast DNA sequencing. The unique band structure of graphene dictates phenomena that affect its surface properties, electronic properties, and interactions with ions and molecules in a way that is to date poorly understood.

In this talk, we present results on the passage of individual DNA molecules through nanopores created in suspended graphene membranes. Unlike traditional solid-state nanopore materials that are insulating, graphene is an excellent electrical conductor, and its use opens the door to a new class of nanopore devices in which electronic sensing and control is performed directly at the nanopore. Due to the thin nature of the graphene membranes, and the reduced electrical resistance, we observe larger current signals than in the case of traditional solid-state nanopores. Signal to noise ratio can be improved with the atomic-layer deposition of a few nanometers of oxide over the graphene surface.

**19:30****Intermolecular hybridization governs molecular doping of organic semiconductors**Ingo Salzmann<sup>1</sup> Georg Heime<sup>1</sup> Norbert Koch<sup>1</sup><sup>1</sup>Institut für Physik, Humboldt-Universität zu Berlin, Berlin

Doping of semiconductors permits tuning their conductivity and the band alignment at interfaces with other materials. For inorganic semiconductors the development of controlled doping paved the way for the multitude of opto-electronic devices that are available today. Likewise, the field of organic electronics emerged with the discovery of metallic conduction in poly(acetylene) doped with iodine decades ago. However, using alkali metals or halides as dopants in organic semiconductors (OSC) causes problems, such as poor processability, limited stability, and diffusion. To overcome this problem strong organic donor and acceptor molecules are currently explored as dopants. The combined experimental and theoretical study presented resolves the mechanism of doping for OSCs. In contrast to previous models that involve direct OSC-to-dopant charge transfer and radical ion formation, we suggest that new hybrid molecular orbitals from the OSC and dopant frontier molecular orbitals are formed. Our results evidence that the hybridized OSC-dopant dimer is electronically stabilized compared to the individual components, and that it exhibits a reduced but non-vanishing energy gap.

**THU 1****Laser-induced modifications of HiPCO nanotubes in different gas environments**

Mattias Mases<sup>1</sup> Maxime Noël<sup>1</sup> Manuel Dossot<sup>2</sup> Edward McRae<sup>3</sup> Alexander V. Soldatov<sup>1</sup>

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We have studied the thermal and chemical stability of HiPCO-produced SWCNT bundles to high laser power in air and argon. The samples were exposed to 110 kW/cm<sup>2</sup> for 16 hours with 633 nm or 532 nm lasers. Evolution of the CNT structure caused by laser heating was monitored via recording the CNT Raman spectra under reference conditions to ensure unaltered resonance conditions. The Raman signal from large diameter CNTs irradiated at 633 nm first increases followed by a decrease in air likely due to desorption of adsorbates and CNT destruction respectively. The 532 nm laser irradiation in air quickly destroys CNTs independently of their diameters whereas in argon the Raman signal from large diameter CNTs increases for 6 hours with a subsequent decrease. The start temperature was estimated from the downshift of the G<sup>+</sup> peak to 400 °C and 600°C for the 633 and 532 nm laser respectively. For both lasers the temperature dropped notably with time due to destruction of the resonant CNTs in air but not in argon which clearly demonstrates the importance of oxidation. Small diameter CNTs are more easily destroyed than larger ones and higher photon energy facilitates the process.

**THU 2****Jahn-Teller distortion in Cs<sub>3</sub>C<sub>60</sub> detected by infrared spectroscopy**

Gyöngyi Klupp<sup>1</sup> Peter Matus<sup>1</sup> Katalin Kamarás<sup>1</sup> Alexey Y. Ganin<sup>2</sup> Alec McLennan<sup>2</sup> Matthew J. Rosseinsky<sup>2</sup> Yasuhiro Takabayashi<sup>3</sup> Martin T. McDonald<sup>3</sup> Kosmas Prassides<sup>3</sup>

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Recently both face-centered cubic (fcc) and A15 (body-centered cubic) structured Cs<sub>3</sub>C<sub>60</sub> were shown to become non-BCS superconductors under pressure [1,2]. The high symmetry of the lattice, the ordered arrangement of the fulleride ions, and the absence of phase transitions makes A15 Cs<sub>3</sub>C<sub>60</sub> ideal to study the physics of strongly correlated superconductors. In both fcc and A15 phases the fulleride ions were

found to be in the  $S = 1/2$  spin state, which was explained by the Jahn-Teller effect [1,2]. To study the Jahn-Teller distortion we carried out temperature-dependent infrared spectroscopic measurements on both the fcc and the A15 phases. Unlike  $K_3C_{60}$  and  $Rb_3C_{60}$ , we found splitting of the fulleride vibrational lines. Because of the high symmetry of the lattice, the potentially distorting crystal field will not produce any splitting, thus we see a clear signature of the Jahn-Teller distortion. In this contribution we will present the detailed evolution of the distortion with temperature.

[1] Y. Takabayashi, et al.: Science **323**, 1585 (2009).

[2] A.Y. Ganin, et al.: Nature **466**, 221 (2010).

### THU 3

#### Double-resonant Raman scattering in free-standing bilayer graphene

Patrick May<sup>1</sup> Felix Herziger<sup>1</sup> Biswajit Mukhopadhyay<sup>2</sup> Marcel Mohr<sup>1</sup>

Janina Maultzsch<sup>1</sup>

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We report on the contribution of different scattering processes in the double resonance Raman process of free-standing bilayer graphene. There is an ongoing debate about the so-called inner and outer processes, where inner (outer) refers to scattering by phonons with wave vector between  $\Gamma - K$  ( $K - M$ ). The bandstructure consists of two valence and two conduction bands in the visible regime and provides an ideal system for investigating the mechanisms of the double resonance process with Raman spectroscopy. We show the evolution of the double resonant 2D mode in free-standing bilayer graphene over a wide range of excitation energy. Compared to bilayer graphene on SiO<sub>2</sub> substrate, the linewidth is narrower and therefore the peaks are more distinct. This allows a more precise analysis of the evolution of the 2D peak. By comparing the Raman frequencies with simulated frequencies obtained from a calculation of the electronic structure of bilayer, we find best agreement for a contribution of both inner and outer processes. Further we compare the Raman intensities for the different contributions with the electronic density of states in one dimension.

### THU 4

#### Effects of functionalisation with a fluorescent group on arc-discharge single wall carbon nanotubes

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We have carried out extensive studies aimed at placing a fluorescent group on electric-arc carbon nanotubes (CNTs). The functionalisation involves three steps: an acid treatment to place carboxylic groups on the CNT walls, a second step to replace its hydroxyl function with chlorine, and then a final step to replace the chlorine with the chosen fluorescent group. In order to optimise the carboxylation step, three different treatment times with refluxed nitric acid have been tested: 2, 5 and 10 hours. We have initially investigated this first step in detail. Electron microscopy and EDX studies have allowed evaluating the microstructure changes and the chemical composition on a local level. On a more overall scale, TGA under dry air and under helium has been used to evaluate the initial sample and the carboxylated CNTs as a function of treatment time. Raman spectroscopy has revealed a number of interesting evolutions in the RBM, D, G and G' zones of the overall spectra as a function of treatment time. The results show that the nature of the attached group has a minor role in modifying the CNT structure, compared with treatment time.

#### THU 5

##### **Ferromagnetically contacted CNTs for spin injection**

Carola Meyer<sup>1</sup> C. Morgan<sup>1</sup> C. M. Schneider<sup>1</sup>

<sup>1</sup>Institute for Solid State Research, Research Centre Juelich, Juelich

In addition to exhibiting ballistic transport, carbon nanotubes (CNTs) have small spin-orbit interactions and relatively few spin nuclei (<sup>13</sup>C). These properties suggest a long spin relaxation length in CNTs, giving them a potential application in the field of spintronics.

We study spin injection in CNT-based devices. Samples are fabricated via CVD growth of CNTs onto lithographically prepatterned substrates. The CNTs are then contacted by ferromagnetic leads to form 2 and 4 terminal devices for spin injection. Special attention has been given to choosing a ferromagnetic material and shape for contacts. Permalloy and Co-based alloys have been studied in order to find a material with good magnetic properties that also forms a stable electronic interface with CNTs. SQUID and X-ray measurements of thin films were used to select good material systems. The shape and size of the contacts have been optimized to have only one in-plane magnetic domain. SQUID and atomic/magnetic force microscopy were used to study the magnetic properties of nanocontacts. Magnetoresistance measurements of contacted CNT samples are shown and discussed.

**THU 6****Lattice dynamics and piezoelectricity in bulk and in multilayers of hexagonal boron- nitride**Karl H. Michel<sup>1</sup> Bart Verberck<sup>1</sup><sup>1</sup>Departement Fysica, Universiteit Antwerpen, Antwerpen

A theory of phonon dispersions and piezoelectricity in bulk and in multilayers of hexagonal boron-nitride (h-BN) is derived. The dynamical matrix is calculated within an empirical force model of intra-layer valence and inter-layer van der Waals interactions. Coulomb forces are derived by Ewald's method. The deformation of the ionic charge distribution with long-wave lattice displacements is accounted for. The non-analytic Coulomb part of the dynamical matrix is different in the 3 dimensional (3D) crystal and in the multilayer case. In 3D h-BN a splitting of the transverse optical (TO) and longitudinal optical (LO) phonon branches of E<sub>1u</sub> symmetry and a discontinuity of the A<sub>2u</sub> branch is found at the Gamma point. No splitting and discontinuity exist in multilayers with a finite number N of layers. A diverging bundle of N overbending optical phonon branches emerges from Gamma. Born's long-wave theory is applied to the study of piezoelectricity in layered crystals. While 3D h-BN and multilayers with an even number of layers (symmetry D<sub>6h</sub>) are not piezoelectric, multilayers with an uneven number N<sub>u</sub> of layers (symmetry D<sub>3h</sub>) are piezoelectric, the piezoelectric coefficient  $e_{1,11}$  varies as  $1/N_u$ .

**THU 7****Optical Properties of Coiled Armchair Carbon Nanotubes**Ivanka Milosevic<sup>1</sup> Zoran Popovic<sup>1</sup> Milan Damnjanovic<sup>1</sup><sup>1</sup>Faculty of Physics, University of Belgrade, Belgrade

Experimental evidence [1] of regularly coiled carbon nanotubes (CNTs) have been reported in 1994. They are predicted to have excellent electro-magnetic properties, although their structure, formation mechanism and theoretical aspects are still subjects of scientific discussions [2]. We propose model of hexagonal, helically coiled single wall CNTs, determine their line group symmetry [3] and calculate optical response functions of the relaxed configurations of the armchair CNTs by means of fully symmetry adopted DFTB implemented into the POLSym code [4]. Comparison of conducting and optical properties of coiled and generic armchair carbon CNTs is presented.

[1] X. B. Zhang et al., Europhys. Lett. 27 (1994) 141.

[2] D. Fejes and K. Hernadi, Materials 3 (2010) 2618.

[3] M. Damnjanović and I. Milošević, *Line Groups in Physics* (Springer-Verlag, Berlin, 2010).[4] M. Damnjanović et al., in *Applied Physics of Nanotubes; Fundamentals of Theory, Optics and Transport Devices*, ed. S. V. Rotkin and S. Subramoney (Springer-Verlag, Berlin, 2005).

**THU 8****Inner and outer processes of the D-mode in graphene**

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<sup>2</sup> Department of Materials Science University of Patras

<sup>3</sup>J. Heyrovsky Institute of Physical Chemistry

The Raman 2D-band -important for the analysis of graphene- shows a splitting for uniaxial strain. This splitting depends on the strength and direction of the applied strain and on the polarization of the incident and outgoing light. We calculate the Raman spectra including the oscillator strength. The results emphasize a distinction between inner and outer processes in the double-resonant Raman mode. Based on ab-initio calculations of strain in graphene, we estimate the peak positions w.r.t. excitation energy, strain direction and polarization of light. Our prediction of the strain direction and polarization dependence agrees well with recent experiments [see poster by Otakar Frank *et al.*].

**THU 9****Using theoretical spectroscopy to assess the measured electronic structure of doped SWCNTs**

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Understanding the electronic structure is necessary for the design of nanoelectronics, chemical/bio-sensors, and electrocatalysts, using doped SWCNTs. In recent years experimentalists have been able to use spectroscopic techniques such as electron energy loss spectroscopy (EELS) and x-ray adsorption spectroscopy (XAS) to directly probe the electronic structure of these types of materials. At the same time, new computational methodologies and facilities have enabled theorists to model the spectroscopic properties of SWCNTs directly within density functional theory (DFT), including quasi-particle interactions ( $G_0W_0$ ), using both linear response within the random phase approximation (TDDFT-RPA) to describe the loss function  $-\Im\{\varepsilon^{-1}(q, \omega)\}$ , and core-hole calculations to include screening. In this work, we compare recent experimental EELS and XAS measurements on doped and undoped SWCNTs with ab initio calculations of the TDDFT-RPA loss function. These results provide a clear connection between the EELS and XAS measurements and the chirality, diameter, and electronic structure of the SWCNT samples.

**THU 10****Synthesis of Carbon Nanostructures by the High - Frequency Furnace Method**Andreas Müller<sup>1</sup> Karolin Ziegler<sup>1</sup> Konstantin Amsharov<sup>1</sup> Martin Jansen<sup>1</sup><sup>1</sup>Max Planck Institute for Solid State Research, Stuttgart, Germany

Traditionally the various forms of fullerenes and carbon nanotubes can be produced by direct evaporation of graphite by the arc-discharge or the laser ablation methods. The high – frequency furnace (HF-furnace) is an alternative synthesis approach which is based on the inductive heating of a graphite body as the carbon source. This approach provides better control over the synthesis parameters. The possibility of independantly co-evaporizing hetero-elements gives access to fullerene species, i.e. barium endohedral fullerenes and phosphor heterofullerenes which are not formed with the alternative methods. Vaporization of graphite in a chlorine containing atmosphere provides access to exohedrally chlorinated fullerene species including new members of the fullerene family not obeying the IPR-rule. Moreover, fullerenes derivatized with large per-chlorinated polycyclic aromatic hydro-carbons can be obtained. By co-evaporizing catalytic active elements, single-walled carbon nanotubes can be synthesized effectively using the HF-furnace while multi-walled carbon nanotubes can be grown from catalysts predeposited on substrates.

**THU 11****Confocal Raman spectroscopy on carbon nanotubes uniaxially loaded by micro actuators**Matthias Muoth<sup>1</sup> Jérôme Grimm<sup>1</sup> Christofer Hierold<sup>1</sup><sup>1</sup>Micro and Nanosystems, ETH Zurich, Zurich

We present Raman spectroscopy on single-walled carbon nanotubes grown suspended between actuated poly-Si tip pairs. By driving thermo-electromechanical micro actuators, tips were retracted and pristine nanotubes were strained. At a gap distance of  $2.9\mu\text{m}$  between the tips, a displacement of  $53\pm 10\text{nm}$  after pre-straining resulted in a downshift of the G-band frequency of  $-27\text{ rel. cm}^{-1}$ . A chirality dependent shift rate of  $-13\pm 2\text{ rel. cm}^{-1}\%$  of strain was extracted. Nanoscale displacement would be readily measurable by electron microscopy but to overcome the discrepancy in displacement output due to reduced thermal dissipation under vacuum conditions during electron microscopy, displacement needs to be characterized at the same ambient conditions of the Raman measurements. Therefore, displacement was recorded by a planar motion analyser relying on light microscopy image correlation. Compared to earlier work [1], displacement deduction is therewith achieved. Moreover, actuation inside a TEM was demonstrated [2] which enables discrimination between bundled and individual SWNTs.

[1] Jungen A. et al., Transd.&Euros., 1561 (2007).

[2] Muoth M. et al., IEEE MEMS 2011, accepted.

**THU 12****Thermal diffusivity of aligned multi-walled carbon nanotubes measured by flash method**

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Thermal diffusivity of freestanding, CCVD grown, multi-walled carbon nanotube (MWCNT) forests (height of 1.5 and 1.9 mm) was characterized in the temperature range between 25 and 200 °C. Copper and Al-alloy metal blocks were used as reference for validation of the experimental setup. The measurements were carried out along the MWCNT alignment direction with thermal properties analyzer that uses the flash method. The thermal diffusivities measured at room temperature for both as-grown and post-annealed (2h at 480 °C in open air) samples were found to be  $\sim 0.45$  cm<sup>2</sup>/s and  $\sim 0.2$  cm<sup>2</sup>/s, respectively. In both cases, the thermal diffusivity values were slightly decreasing in increasing temperature. The observed decrease in diffusivity after annealing is most probably due to an increased defect density in the nanotube walls resulting in a more pronounced phonon scattering in the lattice. The measured thermal diffusivities for as-grown samples agrees with data reported elsewhere for similar MWCNT materials [1, 2].

**THU 13****Photosynthetic reaction center protein in nano structures**

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Photosynthetic reaction center (RC) is one of the most important protein, because it is Nature's solar battery converting light energy into chemical potential in the photosynthetic membrane assuring conditions for carbon reduction in cells. Alt-

though it is developed in nanometer scale, and is working in nanoscopic power, this is the protein that assures the energy input practically for the whole biosphere on Earth. The extremely large quantum yield of the primary charge separation (close to 1) in the RC offers a big challenge to use it in nano-devices. It will be shown by AFM, EM that RC can be bound to different carrier matrices (like CNTs, ITO). The photochemical activity by optical and electro chemical investigations can be measured in this bio-nanocomposite system.

#### THU 14

##### **Influence of the Matrix Elements on the Dominant Phonon Wavevectors for the 2D Raman Mode in Graphene**

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We determine the dominant phonon wavevectors  $q$  contributing to the 2D mode in graphene using a full two dimensional calculation of the Raman matrix element  $K_{2f,10}(q)$  while including the variation of the optical and electron-phonon matrix elements. The dominant wavevectors are highly anisotropic and rotate with the polarizer:analyzer orientation. The associated dominant electronic transitions are no longer parallel to the high symmetry  $K - M$  direction, showing a small but significant component along  $K - \Gamma$  and connect the regions where the product of the ingoing and outgoing optical matrix elements is most intense. Our findings are crucial for the reliable interpretation of phonon mapping experiments on graphene and its allotropes especially in the context of symmetry breaking potentials such as uniaxial strain and we foresee an opportunity for phonon mapping experiments to accurately map the angular dependence of their phonon dispersions.

#### THU 15

##### **Revealing the grain structure of graphene grown by chemical vapor deposition**

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Graphene grown on metal surfaces (Ni, Cu) shows a patchwork of grains with varying shapes and sizes. Their size and crystallographic orientation relative to each other may influence the electronic properties of graphene nanoarchitectures. Visualizing and controlling this grain structure is important, because significant effects can be expected, in the electronic transport properties, in the case of graphene nanoarchitectures obtained by atomic scale lithography [1, 2, 3], particularly if grain boundaries cross graphene nanoribbons.

In this contribution we exploit the preferential oxidation and gasification of carbon at the grain boundaries by a mild annealing step. Using scanning probe techniques we explore the size distribution of the individual graphene flakes and map the misorientation angles of the grains. Our technique offers a quick and easy alternative to different electron microscopy and diffraction methods of visualizing the grain structure of graphene grown by CVD.

[1] L. Tapasztó et al., Nat. Nanotechnol. 3, (2008) 397

[2] P. Nemes-Incze et al., Nano Res. 3 (2010) 110

[3] L.P. Biró& Ph. Lambin, Carbon 48 (2010) 2677

#### THU 16

##### **Controllable synthesis and characterization of alumina/MWNT composites**

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Homogeneous alumina coating was successfully prepared on the surface of multi-walled carbon nanotubes (MWCNTs) by different methods using aluminium isopropoxide (AIIP), aluminium acetyl acetonate and aluminium nitrate, respectively, as precursors under solution conditions. Different solvents with various polarities (acetone, ethanol, toluene, isopropanol and chloroform) were investigated in the formation of alumina layer. The effect of the parameters of hydrolysis (such as speed and pH) was established on the evolving alumina coatings. The structure and morphology of alumina-MWNT nanocomposites were characterized using transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) techniques. In general it can be concluded that homogeneous alumina coating can be obtained in a controllable way.

**THU 17****Comparative study of bulk and interface transport in disordered fullerene films**

Almantas Pivrikas<sup>1</sup> Mujeeb Ullah<sup>2</sup> Helmut Sitter<sup>2</sup> Helmut Neugebauer<sup>1</sup> N. Serdar Sariciftci<sup>1</sup>

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The characterization of the charge carrier transport in disordered fullerene films, grown by physical vapor deposition, is highly interesting for organic electronics. In this contribution, the electron mobility in the bulk of the fullerene film and at the interface with dielectrics is compared. The bulk mobility is measured in diode structures using Charge Extraction by Linearly Increasing Voltage (CELIV) technique, which allows a simultaneous study of the electric field, concentration and temperature dependence. The interface mobility is determined using organic field effect transistor (OFET) geometry. Poole-Frenkel-type electric field dependence is observed in both types of devices, whereas the electron mobility values are lower and the dependence on carrier density, field and temperature are stronger in diodes compared to OFETs. In both structures, Meyer-Neldel rule (MNR) as well as Gill's law behavior is obtained, with good match between MNR and Gill energies. Furthermore, it is shown that the activation energy of electron transport is dependent on carrier density and electric field, and the relation between field and density dependent activation energy is shown.

**THU 18****A FEW LAYER GRAPHENE as a FAST and EFFICIENT SATURABLE ABSORBER for SOLID STATE LASERS**

Elena D. Obraztsova<sup>1</sup> Vladimir A. Shotniev<sup>2</sup> Anton V. Tausenev<sup>2</sup> Pavel S. Ruskov<sup>1</sup> Maxim G. Rybin<sup>1</sup>

<sup>1</sup>A.M. Prokhorov General Physics Institute of Russian Academy of Sciences, Moscow

<sup>2</sup>Avesta-Project Limited Liability Company, 142190 Troitsk, Moscow region, Russia

In this work we report the results on synthesis [1], characterization and application of a few graphene layer flakes as the saturable absorbers [2] for realization of a mode-locking regime with an output pulse duration of 355 fs in the Er fiber laser (working at 1.55  $\mu\text{m}$ ). A stable generation of individual pulses with a repetition rate of 34.2 MHz and a maximal pulse width of 7.2 nm has been demonstrated. In supposition of a spectrally limited pulses such width corresponded to the duration of 355 fs. An average power emitted was 2.3 mW. The graphene was grown by CVD technique from CH<sub>4</sub>:H<sub>2</sub> mixture [1] and was reprinted to the fiber cross section. A unique potential of graphene for formation of the saturable absorbers for a much

longer spectral range (up to 10  $\mu\text{m}$ ) is discussed [3]. The work was supported by RAS research programs and RFBR project-10-02-00792.

[1] M.G. Rybin, A.S. Pozharov and E.D. Obraztsova, Phys. Status Solidi C, 7(2010)2785.

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#### THU 19

##### **Transmission and reflection of terahertz radiation by anisotropic composite films from polystyrene and carbon nanotubes**

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Anisotropic composite materials have been prepared by repeated forge rolling of poly-styrene contained carbon nanotubes (CNTs) with a length of 63  $\mu\text{m}$ . The transmission and reflection spectra of the composites were recorded on a vacuum Fourier spectrometer IFS-66vs for two polarizations of electric field vector. We suggested that direction of the forge rolling coincides with a predominant orientation of CNTs in composite. Pyroelectrical detector and bolometer were respectively used for 100-700 and 15-100  $\text{cm}^{-1}$  region. Transmission contrast characterizing the polarization asymmetry reached 20 in the central part of sample. Reflection signal for parallel polarization was twice higher than the signal for perpendicular polarization. Anisotropic response of composites was measured on the Novosibirsk laser on free electrons at 130  $\mu\text{m}$  length of waves and the angular dependence of transmission was determined. Peculiarities of change of the spectrum were detected at the wave length corresponding to double length of CNTs. It was observed that contrast decreases beginning from the wave length 100  $\mu\text{m}$  that could be explain by different length of CNTs occurred in sample.

#### THU 20

##### **Coherent Conductance of Multi-Terminal Systems: Molecular Devices**

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The  $G_{pq}$  submatrices that enter Datta's formula for  $T_{pq}$  transmission functions of  $N$ -Terminal conductor (here, an arbitrary molecule)

$$T_{pq} = 4\text{Tr} [Im\Sigma_p G Im\Sigma_q G^*]$$

are represented in the form of a vector with  $p(\neq q) = 1, 2, \dots, N-1$  components  $G_{p,q}$ ,

given by the inversion of a set of  $L(q)$  matrices of reduced dimensionality

$$L(q)G_{p,q} = G_{p,q}^M.$$

Matrices  $L(q)$  are expressed in terms of free-molecule Green's function matrix elements  $G_{p,q}^M$  referring exclusively to molecular atoms perturbed by the lead-molecule interaction. The set of  $L(q)$  matrices is specified for a commonly used model of multi-terminal molecular devices, where the molecule is coupled with each of  $N$  leads via a single bond. For the connection of  $N$  molecular wires via a single atom, this gives an analytical expression that relates  $T_{pq}$  to the particle energy and dispersion relations within the leads. The I-V characteristics of such branched molecular wires are shown to be partly similar but partly strikingly different from that we know about branching resistors.

#### THU 21

##### **Confined and edge states on graphene nanoislands probed by scanning tunneling spectroscopy**

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Epitaxial graphene islands are prepared by ethylene deposition on Ir(111) at room temperature and subsequent annealing at 1050 °C. Using scanning tunneling spectroscopy (STS) at 5 K we were able to visualize confined states within the islands. The corresponding energies of the pattern are in good agreement with third nearest neighbor tight-binding calculations. The width of the confined state energy peaks has been used to determine the lifetime of the Dirac electrons, which is inversely proportional to the energy. Atomic resolution STM images show singly saturated zigzag edges which are predicted to feature a spin-polarized state. STS measurements at the graphene edge partly show a pronounced peak at the Fermi level. A similar peak with lower intensity at the Fermi level is measured on the iridium, which could be identified as a surface state. This suggests that the increase in intensity at the edge of the graphene is due to a coupling of the edge state to the iridium surface state which enhances strongly the intensity of the peak. Spin-polarized STS has been performed using an antiferromagnetic chrome tip in order to analyze the magnetic character of the edge state.

**THU 22****Monitoring the vibrational local character of single-walled carbon nanotubes by TERS**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

Tip-enhanced Raman spectroscopy (TERS) is used for studying the vibrational local character of single-walled carbon nanotubes (SWCNT) on the nanometer scale. Working in STM-mode with an Au-tip, we discuss the intensity changes and the frequencies shift of the Raman features of SWCNTs upon approaching the tip to the sample surface. The TERS amplitude of the G-mode is strongly dependent on the tip-sample distance and the used excitation energy plays a key role in matching the plasmon resonance. Moreover, the Raman intensity of the D mode and RBM are very sensitive to changes in the tip-sample distance in the first 1 nm contact region. Using the RBM and the G<sup>-</sup>-mode frequencies, an accurate chiral-index assignment is given, assuming that we observe predominantly tubes close to resonance.

**THU 23****Infrared active vibrations in carbon nanotubes**Aron Pekker<sup>1</sup> Katalin Kamaras<sup>1</sup><sup>1</sup>Research Institute for Solid State Physics and Optics, Budapest

Vibrational properties are usually studied with both infrared and Raman spectroscopy. However, in the case of nanotubes the method of choice is almost exclusively Raman spectroscopy. Theories predict the presence of infrared active vibrations in nanotubes but their intensities are faint and usually merged into the background. Due to the experimental difficulties only a few experimental studies have been published on this topic.

We performed infrared transmission measurements on various types of single- and double-walled carbon nanotubes. Experiments were done on self-supporting transparent films in order to avoid perturbation from substrates. We were able to detect the weak but reproducible vibrational peaks in the mid-infrared spectrum. Their frequency scales with the diameter of the tubes, indicating their intrinsic character. In double-walled nanotubes peaks typical of both outer and inner tubes can be distinguished. The vibrations of the inner tubes occur at the frequency as those of single-walled tubes with the same diameter.

**THU 24****Edge states and flat bands in graphene nanoribbons with arbitrary geometries**W. Jaskólski<sup>1</sup> M. Pelc<sup>1</sup> L. Chico<sup>2</sup> H. Santos<sup>2</sup> A. Ayuela<sup>3</sup><sup>1</sup>Institute of Physics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 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-UVP/EHU, Departamento de Física de Materiales (Facultad de Químicas), and Donostia International Physics Center (DIPC), 20080 Donostia, Spain

The subject of our study are the graphene nanoribbons (GNR) - stripes of nanometric widths cut from graphene. They exhibit edge-localized states that play an important role in transport and magnetic properties of GNR's. Their appearance and degeneracy depend on the edge shape. There are many theoretical [1,2] and experimental [3,4] works that show results for particular edges. Here we prescribe the general rules to predict the existence of edge states and zero-energy flat bands in GNR with any kind of edge. Without any calculations we are able to find out if the edge states appear, where exactly they localize and what is their degeneracy. For the so-called "minimal edge" they are determined only by the projection of the edge translation vector into the zigzag direction. While the edge bands of any other graphene edges can be found by applying hybridization rules of additional atoms, added to the minimal edge.

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[2] Y. W. Son et al., Phys. Rev. Lett. 97, 216803 (2006);

[3] Y. Kobayashi et al., Phys. Rev. B 73, 125415 (2006);

[4] Z. Liu et al., Phys. Rev. Lett. 102, 015501 (2009).

**THU 25****New Magnesium fullerene polymer for energy storage applications**Daniele Pontiroli<sup>1</sup> Mauro Riccò<sup>1</sup> Marcello Mazzani<sup>1</sup> Alessandra Gorreri<sup>1</sup><sup>1</sup>Dipartimento di Fisica, University of Parma, Parma

It is known that magnesium cannot be intercalated easily in graphite. On the contrary, solid fullerene can host up to 5 Mg atoms per C<sub>60</sub> in the lattice interstices, where C<sub>60</sub> molecules polymerise to form a 2D rhombohedral structure with metallic character and unexpected thermal stability. Recently, we also managed to isolate a new Mg fulleride Mg<sub>2</sub>C<sub>60</sub>, through a direct solid state reaction. Neutron powder diffraction (HRPT, PSI) proved that Mg<sub>2</sub>C<sub>60</sub> shares the same structure of the superionic conductor Li<sub>4</sub>C<sub>60</sub>, with a peculiar hybrid 2D bonding network. Diffraction scans on heating evidenced also an extraordinary thermal stability up to 800 K, while Li<sub>4</sub>C<sub>60</sub> undergoes a polymer-to-monomer transition at 600 K. The small Mg<sup>2+</sup> ions are expected to diffuse already at low temperature promoting even

in this system an efficient superionic conductivity and this opens to applications in future Mg-ion batteries. The well known ability of Mg to bind hydrogen makes this material also promising as a solid absorber of this gas.

## THU 26

### Helically deformed carbon nanotubes

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Helically coiled carbon nanotubes were firstly reported [1] in 1994. Several later papers [2] on their synthesis and properties did not include theoretical and numerical studies.

We consider a simple model: single wall nanotube pulled on a helix. The structure consists of hexagons only. After studying symmetry of such model [3], we use numerical POLSym code for full symmetry implementing DFTB calculations. Conclusions are also derived within a very simple analytical model, in order to show their geometry predetermination.

It is assumed that compression along the main axes of the nanotube can result in only two conformations: either homogeneously squeezed (preserving cylindrical shape, though with a reduced translational period), or helically coiled nanotube. Calculations indicate that the second relaxation channel is energetically favorable. A study of electro-optical properties show that most of these tubes are conducting, with significant density of states around Fermi level.

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## THU 27

### Electronic scattering at local defects in monolayer graphene

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We investigated the electronic scattering pattern appearing at different types of defects in monolayer graphene using scanning tunneling microscopy at 5 K. The graphene has been prepared by exfoliation on a SiO<sub>2</sub>-substrate and electrically contacted by indium microsoldering. First the scattering pattern appearing at a monolayer-bilayer step edge has been investigated. Using FFT-filtering a characteristic interference pattern could be separated from the atomically periodic corrugation, specific for the graphene intervalley scattering. The amplitude of the interference pattern decreases with increasing energy. This is caused by the growth

of the equipotential lines in k-space leading to the overlap of more wave vectors and partially to a destructive interference. Further we could identify different types of point defects and their characteristic local density of states. In addition to adsorbates on top of the graphene lattice and carbon vacancies we found defects located below the graphene flake at the SiO<sub>2</sub> substrate. The interference pattern caused by this type of defects could be suppressed by lifting up the graphene flake from the substrate using tip induced forces.

#### THU 28

##### **Photocatalytic measurements of TiO<sub>2</sub>/MWCNT catalysts having different surface coverage**

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Photocatalytic oxidation using TiO<sub>2</sub> is one way to deal with pollutant compounds. Due to literature data further improvement can be achieved by using MWCNT based composites as photocatalysts. TiO<sub>2</sub>/multiwall carbon nanotube composite photocatalysts were synthesized by sol-gel method with different bare carbon nanotube surface ratio. As-prepared catalysts were characterized with TEM, SEM and XRD. These investigations revealed that we could make MWCNT composite either homogenously, inhomogenously or barely coated with TiO<sub>2</sub>. XRD results showed that after annealing the amorphous titanium-oxide-hydroxide formed anatase phase titanium-dioxide which is photocatalytically more active than rutile phase TiO<sub>2</sub>. Catalysts were tested in both gas- and liquid-phase photocatalytic reactions using Aerioxide (Degussa) P25 as reference. The concentrations of the model compounds were measured by GC and HPLC techniques. As a result of catalytic tests we found correlation between bare MWCNT surface and photocatalytic activity. Interestingly we also found that pure MWCNT showed photocatalytic activity.

#### THU 29

##### **Surface-related 2D conductivity of nanocrystalline diamond in-plane nanowires**

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Diamond is an attractive material for nanoelectronics, biological interfaces and electrical transducers [Sensors 9(2009)3549; Biosens. Bioelectron. 26(2010)1307]. Small dimensions are highly demanded for higher sensitivity, parallelism, remote sensing and reduced costs. Recently we demonstrated directly grown functional diamond microwires [Sensor Lett. 8(2010)482]. Here we report on fabrication, structure, and

electronic properties of in-plane nanocrystalline diamond nanowires. By employing electron beam lithography, polymer wires are prepared on diamond seeding layer. After selective removing of diamond seeds outside the wires using BOE, diamond nanowires (140 to 500 nm wide, 2-5  $\mu\text{m}$  long) are grown by MW-CVD. We characterize their morphology by SEM and AFM, composition by micro-Raman, and present 3D growth model. Electronic conduction is measured using nanomanipulators with current probes. By comparing conduction of nanowires with as-grown, H- and O-terminated surface we demonstrate transfer p-doping of intrinsic nanowires which gives rise to surface-related 2D conduction. This proves high electronic quality of the nanowires and facilitates their use as nanosensors.

### THU 30

#### **Muons probe hydrogen interactions with defective graphene**

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Macroscopic quantities of graphene, prepared by different chemical methods, have been investigated by Muon Spin Rotation. The implanted muons capture an electron and form muonium (Mu), an isotope of hydrogen with similar chemical behaviour. A clear muon spin precession is observed in all the samples, while it is missing in graphite and nanostructured graphite where only a weak muon spin depolarization is observed. The comparison of different samples shows a clear correlation between the precession signal amplitude and the concentration of graphene in-plane defects assessed by SQUID and Raman spectroscopy. The observation of zero field precession signal is usually the fingerprint of the onset long-range magnetic ordering. In this case, however, the signal disappears if the samples are treated with deuterium. This indicates the dipolar (and not hyperfine) origin of the local field on the muon, which is consistent with the formation of a CHMu state. The persistence of the precession signal up to 800K testifies the great stability of the in-plane CH<sub>2</sub> (CHMu) groups, while the relatively large amplitude of the signal witnesses an extraordinary H-capture cross-section of CH units.

### THU 31

#### **Electronic and vibrational properties of edge-functionalized graphene nanoribbons**

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While graphene nanoribbons (GNRs) possess largely the remarkable features of graphene the confinement to one dimension leads to interesting additional effects.

The most obvious advantage of GNRs is their non-zero band-gap which depends strongly on the ribbon width and the edge structure. Apart from a simple passivation with hydrogen the presence of edges offers a wide range of possible functionalizations. Functional groups can either be a side product of the preparation process or they may be introduced in order to control certain properties of the GNRs.

In this study we present ab initio calculations of hydroxyl-functionalized armchair GNRs. For high degrees of functionalization which are expected from energetic considerations we find a substantial variation of the band-gap. The observed shift can only partially be ascribed to the small strain caused by repulsive forces between neighboring hydroxyl groups. The dependence of the main Raman-active eigenmodes on the number of functional groups allows to determine the degree of functionalization experimentally.

#### THU 32

##### **Controlling substitutional B-acceptors in purified doped SWCNTs**

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One of the advantages of SWCNTs is the possibility to functionalize them to control their electronic structure. Functionalization via substitutional doping with heteroatoms such as B, P and N, has significantly improved in the last years. However, accessing the electronic structure of these SWCNTs and its modification compared to pristine samples has been limited by the unavailability of clean material with a defined dopant concentration.

In this contribution, we mainly focus on probing the electronic structure of B doped SWCNTs. Our approach consists of performing in-situ doping during growth employing a high-vacuum CVD system. Pioneering results on the purification of the tubes with density gradient ultracentrifugation will be shown. Raman Spectroscopy, TEM and core level photoemission spectroscopy were used to monitor the sample quality regarding purity bonding environment and defect concentration.

In addition, the doping level was identified with utmost sensitivity by XAS, where we found a B atomic concentration of 0,01%, yielding a small shift in the vHs response of the valence band and a modified resonance Raman signal.

Work supported by FWF P21333-N20.

**THU 33****Extremely high density CNT growth by multi-step low temperature plasma CVD for LSI interconnect application**

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Carbon Nanotube (CNT) is expected as a new interconnect material for future LSI because of its large current carrying capacity, ballistic conductance and so on. In this study, we report extremely high density multi-wall CNT growth at low temperature suitable for LSI via application. We have achieved CNT density of 2E12 cm<sup>2</sup> at 450C by applying a multi-step plasma CVD method (1). In this method, at first, thin catalyst (Co) film layer is plasma treated to prepare high density catalyst particles. Then, the surfaces of particles are treated by carbon plasma to prevent aggregation. Finally, CNTs are grown at elevated temperature. The growth method was applied not only on blank substrates but also on bottoms of via-hole structures to fabricate fine (less than 100nm in diameter) CNT vias (2). We also report the electric characters of the CNT vias.

This work has been performed as a part of MIRAI Project supported by METI through NEDO Japan.

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(2) M. Katagiri et al., Abstract of ADMETA2010, p.10-11.

**THU 34****Theory of electron spin dynamics and electron spin resonance in graphene**

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A theory of spin relaxation in graphene including intrinsic, Bychkov-Rashba, and ripple spin-orbit coupling is presented. We find from spin relaxation data by Tombras et al. [Nature 448, 571 (2007).] that intrinsic spin-orbit coupling dominates over other contributions with a coupling constant of 3.7 meV. Although it is 1-3 orders of magnitude larger than those obtained from first principles, we show that comparable values are found for other honeycomb systems, MgB<sub>2</sub> and LiC<sub>6</sub>; the latter is studied herein by electron spin resonance (ESR). We assess the feasibility of bulk electron spin resonance spectroscopy on graphene and pinpoint experimental conditions where such experiments are realizable.

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**THU 35****Variation of electronic transport in CVD graphene grown under different conditions**

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Unlike highly ordered crystals of exfoliated graphene, graphene samples produced by the chemical vapour deposition (CVD) method on Ni substrate show an increase of the conductance with increasing temperature in a large range of carrier densities. This implies that, in contrast to exfoliated material, thermal assistance plays an important role in the conductivity of our CVD-graphene with more disordered structure. When CVD-graphene is modified by nitrogen, the main features of the temperature dependence of conductance stay quite similar to those of the pristine CVD-graphene, but the increase of conductance is much stronger as temperature rises from 50K to 300K. At low temperatures below 50 K, the conductance saturates to a constant non-zero value. The constant value of the conductivity implies that there are some metallic percolating path through the sample besides the disordered regions where the thermally assisted increase of conductance contributes at higher temperatures. However, graphene grown on Cu foil shows more similar behaviour to exfoliated graphene where, at high charge carrier densities, conductivity decreases with rising temperature due to phonon scattering.

**THU 36****Structural disorder in WS<sub>2</sub> nanotubes**

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Being a part of metal dichalcogenide nanostructures, tungsten disulfide nanotubes consist of rolled up triple layers {S-W-S} stacked in hexagonal 2H-order. In this work WS<sub>2</sub>-nanotubes with diameters between 38 and 134 nm were investigated by means of Resonance Raman spectroscopy. In addition, Raman measurements were done on agglomerated WS<sub>2</sub> nanotubes (average diameter 40 nm) under hydrostatic pressure.

We find that the second order Raman signal exhibits a distinct dependency on the nanotube diameter. One mode in particular is strongly gaining in intensity with decreasing diameter. Similarly to reducing the diameter of the nanotube, the intensity of the second order mode is sensitive to the amount of pressure applied.

We propose that the underlying mechanism for the intensity enhancement is the same in either case. Both, reducing the nanotube diameter and applying pressure lead to changes in the curvature of the WS<sub>2</sub> layers. The increase in curvature is accompanied by a growing number of intralayer defects and results in the emergence of the second order mode. Probing the nanotubes by Raman spectroscopy thus provides direct evidence of the amount of structural disorder.

#### THU 37

##### **Pd/MWCNTs catalytic activity in the formic acid electrooxidation dependent on catalyst surface treatment**

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The catalytic activity in the formic acid electrooxidation reaction of the Pd multi-wall carbon nanotubes (MWCNTs) supported catalyst, prepared by a microwave-assisted polyol method, treated under different gas atmospheres and temperatures (200 °C and 300 °C), was investigated. Their respective catalysts surface characterization proceeded in UHV using the electron spectroscopy methods. Content of constituents, i.e. Pd nanoparticles, C and O, was examined quantitatively. Content of chemical forms of Pd and C atoms was analyzed assuming respective binding energy (BE) values to Pd 3d and C 1s XPS spectra fitted to Gaussian-Lorentzian components. Surface structure was examined from the 3D nanostructure analysis by QUASES. Catalytic activity of Pd/MWCNTs after various surface treatments was attributed to different surface content and forms of Pd nanoparticles, and contaminations overlayer on Pd crystallites.

**THU 38****Graphene Nanoribbon memory Cell**

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The past few years have witnessed a surge of interest in graphene, a recently isolated single sheet of graphite. Due to the absence of a bandgap, graphene-based field-effect transistors cannot be turned off, thus limiting their application in conventional electronic circuits. The on/off ratio is increased for graphene nanoribbons (GNRs), wherein quantum confinement and edge effects open a bandgap. Here, we demonstrate a GNR memory cell based on a nondestructive storage mechanism. The devices are fabricated by patterning graphene into nanoribbons using V<sub>2</sub>O<sub>5</sub> nanofibers as etching masks. A pronounced memory effect is observed under ambient conditions, which is attributed to charge traps in the vicinity of the GNRs. Gate voltage pulses of opposite polarity are used to switch between the distinct on- and off-states of the device. Reliable switching is demonstrated for clock frequencies of up to 1 kHz and pulse durations as short as 500 ns for >10<sup>7</sup> cycles. The durable and stable memory cell can be rendered nonvolatile upon exclusion of oxygen and humidity. GNRs thus emerge as promising components of highly integrated memory arrays.

**THU 39****Nitrogen-doped SWCNT thin films show anomalously high sheet resistances**

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Directly deposited as-grown nitrogen-doped single-walled carbon nanotube films show unexpectedly high sheet resistances. To understand this effect, we developed a simple resistor network model, employing experimental bundle length and diameter distributions. Combining the model with data from similar undoped films, we disentangled the contribution of bundle-bundle contact resistances. The analysis indicates that the increased resistances are likely due to enhanced carrier scattering by defect sites in the nanotubes predicted theoretically (e.g. [1]).

This work represents the first experimental report on macroscopic N-SWCNT thin films, and stands in contrast to the widely studied N-MWCNT case, where decreased resistance has been achieved with N-doping [2].

Furthermore, the material was characterized by multi-frequency Raman and optical absorption spectroscopies and electron microscopy. To inspect the dopant concentration, distribution and bonding environments, X-ray photoelectron spectroscopy and STEM electron energy-loss spectroscopy were used.

[1] S. Latil et al., PRL 92 (2004) 256805

[2] J.D. Wiggins-Camacho and K.J. Stevenson, JPCC 113 (2009) 1908

#### THU 40

##### **Density of states in potassium doped carbon nanotubes; a model system of biased graphene**

Péter Szirmai<sup>1</sup> Gábor Fábián<sup>1</sup> Balázs Dóra<sup>1</sup> Ferenc Simon<sup>1</sup> János Koltai<sup>2</sup> Viktor Zólyomi<sup>3</sup> Jenő Kúrti<sup>2</sup>

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<sup>3</sup>Physics Department, Lancaster University, UK

We study the electron spin resonance (ESR) signal of pristine and potassium doped SWCNTs produced by a solid state reaction method. Resulting from the Ni:Y catalyst, a superparamagnetic background is observed. In doped samples, a narrow line of itinerant electrons is superimposed on the former wide one. On the basis of the contribution of conduction electrons to the ESR intensity, we determine the density of states (DOS) experimentally. Tight-binding and first-principles calculations yield the DOS as a function of the chemical potential. The latter changes upon doping due to the presence of additional electrons. We show that the DOS as a function of the chemical potential of a carbon nanotube ensemble mimics that of graphene.

#### THU 41

##### **Covalent Functionalization of Peapods**

Nikos Tagmatarchis<sup>1</sup> Nikolaos Karousis<sup>1</sup> S. P. Economopoulos<sup>1</sup> Yoko Iizumi<sup>2</sup> Toshiya Okazaki<sup>2</sup> Zheng Liu<sup>2</sup> Kazu Suenaga<sup>2</sup>

<sup>1</sup>Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece

<sup>2</sup>Nanotube Research Center, AIST, Tsukuba, Japan

Manipulation and processing of peapods is limited by their insolubility, similarly with pristine SWCNTs. In this context, functionalization and solubilization of peapods is a major issue that would allow to study properties in solution – especially when considering the rich electrochemistry of fullerenes – while enable better manipulation and handling, and therefore, practical applications.

Here, we report the covalent functionalization of the outer surface of C60@SWCNT peapods, by in-situ generated aryl diazonium salts, assisted by microwave irradiation.[1] The dissolution achieved for aryl modified C60@SWCNT peapods endows to perform a thorough spectroscopic as well as thermal and microscopy characterization. Moreover, electrochemistry revealed the three reversible reductions of encapsulated C60, however, shifted towards positive potentials when compared with intact C60, thus highlighting the importance of confinement in low-dimensional nanostructures.

[1] N. Karousis, S. P. Economopoulos, Y. Iizumi, T. Okazaki, Z. Liu, K. Suenaga, N. Tagmatarchis, *Chem. Commun.*, 2010, 46, 9110.

#### THU 42

##### **Temperature dependent structural breathing of graphite oxide immersed in excess H<sub>2</sub>O media.**

Alexandr V. Talyzin<sup>1</sup> Serhiy M. Luzan<sup>1</sup> Tamas Szabo<sup>2</sup> Dmitry Chernyshev<sup>3</sup> Vladimir Dmitriev<sup>3</sup>

<sup>1</sup>Department of Physics, Umeå University, Umeå, Sweden

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<sup>3</sup>SNBL, European Synchrotron Radiation Facility, ESRF, 38043 Grenoble, France

Hydration of graphite oxide by excess of water was studied in the temperature interval 295-230K using synchrotron X-ray diffraction. Expansion of hydrated graphite oxide structure due to insertion of additional water occurs upon cooling down from ambient temperature to the point of water media freezing. Continuous shift of (001) reflection, which corresponds to interlayer distance of graphite oxide structure, indicates interstratification of layers hydrated to various degree. Structural breathing is found around the freezing point of H<sub>2</sub>O and connected to insertion/expulsion of water to/from interlayer space. Cooling down below the point of water medium solidification results in stepwise contraction of graphite oxide interlayer distance by 25 percents due to partial withdrawal of water from the hydrated structure. Heating back from 230K to ambient temperature results in graphite oxide structure expansion due absorption of water from medium, thus making a reversible cycle. The effect of structure breathing is important for any chemical treatments performed with graphite oxide in solution, e.g. graphite oxide functionalization and conversion into graphene-related materials.

**THU 43****Surfactant Screening for Metal/Semiconductor Separation of Single-Wall Carbon Nanotubes**

Takeshi Tanaka<sup>1</sup> Yasuko Urabe<sup>2</sup> Daisuke Nishide<sup>2</sup> Hiromichi Kataura<sup>2</sup>

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

<sup>2</sup>NRI, AIST, and Japan Science and Technology Agency (JST), CREST, Japan

There are two electric types of single wall carbon nanotubes (SWCNTs), metallic (M) and semiconducting (S) ones. Among the M/S separation methods using surfactants in an aqueous solution, sodium dodecyl sulfate (SDS) plays a key role in density gradient ultracentrifugation (DGU) and agarose gel separation. In this study, we screened various surfactants for the M/S separation and newly found a few surfactants which can be used for DGU and agarose gel separation. Gel centrifugation method using agarose was applied for the high-throughput screening because the method was suitable for multiple and micro separation. From 96 kinds of amphiphiles in the first screening, two surfactants were found to show a slight M/S separation. From the common feature of these surfactants and SDS, i.e. straight alkyl tail and charged head group, several kinds of surfactants were selected and used for the second screening, resulting that three kinds of surfactants were newly discovered. Especially, the M/S purity after the separation using sodium dodecane-sulfonate was almost same with the case of SDS. Some of these surfactants could also be used for the M/S separation by DGU.

**THU 44****Electron-beam assisted local oxidation of carbon-based materials**

Cornelius Thiele<sup>1</sup> Ralph Krupke<sup>1</sup>

<sup>1</sup>Institute of Nanotechnology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen

A new technique to locally oxidize carbon-based materials at the nanometer scale is presented. In an oxygen atmosphere an electron beam is scanned across the material. Secondary electrons escaping from the surface ionize the oxygen, which then oxidizes material around the focal point of the electron beam. The formation of trenches in graphene sheets and cuts across carbon nanotubes is shown. In-situ electrical measurements are used to characterize the cutting process. In the future, these gaps could provide a reliable means for contacting nanometer-size objects.

**THU 45****Quantized conductance of a suspended graphene nanoconstriction**

Nikolaos Tombros<sup>1</sup> Alina Veligura<sup>2</sup> Juliane Junesch<sup>2</sup> Marcos H. D. Guimarães<sup>2</sup> Ivan J. Vera Marun<sup>2</sup> Harry T. Jonkman<sup>1</sup> Bart J. van Wees<sup>2</sup>

<sup>1</sup>Molecular Electronics, Groningen, The Netherlands

<sup>2</sup>Physics of Nanodevices, Groningen, The Netherlands

We present the experimental observation of quantized conductance at integer multiples of  $2e^2/h$  at zero magnetic field and 4.2 K temperature in a high mobility suspended graphene ballistic nanoconstriction [1]. High quality devices were prepared by a new technique on a polydimethylglutarimide based organic resist [2]. This quantization evolves into the typical quantum Hall effect for graphene at magnetic fields above 60 mT. Voltage bias spectroscopy reveals an energy spacing of 8 meV between the first two subbands corresponding to a constriction with a width of approximately 250 nm. A pronounced feature at  $0.6 \cdot 2e^2/h$  present at a magnetic field as low as 200 mT resembles the "0.7 anomaly" observed in quantum point contacts in a GaAs-AlGaAs two dimensional electron gas, having a possible origin in electron-electron interactions. Our work opens the way towards the verification and discovery of new quantum mechanical effects in the one-dimensional limit.

[1] N. Tombros *et al.* submitted to Nature

[2] N. Tombros *et al.* submitted to APL

**THU 46****Strain in CdSe-based heterostructure nanocrystals**

Norman Tschirner<sup>1</sup> Holger Lange<sup>1</sup> Karel Lambert<sup>2</sup> Zeger Hens<sup>2</sup> Christian Thomsen<sup>1</sup>

<sup>1</sup>Department for Solid State Physics, Berlin Institute of Technology, Germany

<sup>2</sup>Physics and Chemistry of Nanostructures, Ghent University, Belgium

Colloidal semiconducting spherical nanocrystals (NCs) are a promising material for future applications in nanotechnology. This is due to the possibility to tune the band gap energy very precisely by adjusting the diameter of the NC during the growth process. By an appropriate epitaxial coating using a second semiconducting material, parameters like the quantum yield or the lifetime of the crystal are improved significantly. The coating has several additional advantages, e.g., it protects the core chemically. However, a second semiconducting material also introduces strain into the system. The strain has a significant impact on the NC structure and can even be used to tune the electronic and optical properties of the NC.

In this study we investigate the evolution of strain in CdSe-based nanocrystals by means of Raman spectroscopy. As shell material CdS, ZnS and structures involving a CdZnS buffer layer are used. Using the Grüneisen parameter we are able to evaluate the strain quantitatively.

**THU 47****Application of CVD Graphene Film for FE Transistors**A.V. Tyurnina<sup>1</sup> A.N. Obraztsov<sup>1</sup> K. Tsukagoshi<sup>2</sup> H. Hiura<sup>2</sup><sup>1</sup>M.V.Lomonosov Moscow State University, Moscow, Russia<sup>2</sup>MANA, NIMS, Tsukuba, Japan

One of the most attractive applications of graphene is the production of a field effect (FE) transistor. To be compatible with usual microelectronic technologies, graphene films should be produced in a large scale with reproducible properties. The methods based on CVD potentially might provide graphene films with suitable characteristics. We report here about production and characterization of FE transistors based on a few layer graphene films obtained by using a plasma enhanced CVD method. The FE transistors were produced by the same lithography techniques using the PE CVD films and the graphene obtained by traditional micro-mechanical cleavage of different bulky graphite materials (single crystal graphite, kish graphite etc.). The materials quality and structural characteristics were evaluated using Raman spectroscopy and electron microscopy. Obtained results show that electrical characteristics (including carrier mobility) of the CVD graphene and produced FE transistors are quite similar to that of other types of graphene. Taking into account possible large area fabrication of the CVD graphene, this confirms its prospective applicability in industrial electronics production.

**THU 48****Wide range optical study of separated carbon nanotube films**Hajnalka-Mária Tóháti<sup>1</sup> Aron 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

Nowadays, transparent conducting films are one of the most promising applications of carbon-based systems. The substitution of ITO with an appropriate material is a quite important and pressing problem. Carbon nanotubes could be one of these substituents. We will report wide-range optical investigations on transparent conducting networks made from separated single-walled carbon nanotubes, complemented by transport measurements. We will focus on the problem how transparency and conductivity can be improved at the same time: is it necessary to separate the metallic nanotubes from the semiconducting ones to obtain a more conducting thin film or is it sufficient to expose the unseparated sample to doping? To this end, we compare different, arc discharge prepared – separated (semiconducting, metallic) and reference – materials in their pristine form and doped by nitric acid.

**THU 49****Photocatalytic activity of TiO<sub>2</sub>/SWCNT and TiO<sub>2</sub>/MWCNT composites with different carbon nanotube content**

Krisztina Vajda<sup>1</sup> Karoly Mogyoros<sup>1</sup> Andras Dombi<sup>1</sup> Klara Hernadi<sup>1</sup> Zoltan Nemeth<sup>1</sup>

<sup>1</sup>department of Inorganic and Analytical Chemistry, University of Szeged, Szeged

With different mass ratio, titanium dioxide/carbon nanotube ( 0,1-10 wt % CNTs ) composites were prepared with the aid of ultrasonication. The structures of the various TiO<sub>2</sub>/CNT composites were characterized by electron microscopy (SEM, TEM) and their photocatalytic activity was tested by the degradation of phenol in aqueous solution under near-UV irradiation. The concentrations of the model compound were measured by spectrophotometer and HPLC technique. In parallel experiments, SWCNTs and MWCNTs were treated in a reflux system with nitric acid to functionalize the nanotubes, subsequently preparing the composites in the same method. At higher CNT concentration ( 10 % ) used in the composites lower photocatalytic activity was observed compared to the samples with lower CNT concentration, probably because the higher CNT concentration reduces the light intensity on the surfaces of TiO<sub>2</sub> particles. Our aim was to find the optimal composition of the TiO<sub>2</sub>/CNT composites for phenol degradation under UV irradiation.

**THU 50****Three-terminal single-molecule junctions**

Herre S.J. van-der-Zant

Kavli Institute of Nanoscience, Delft University of Technology, Delft

With a self-breaking electromigration technique, we make nanogaps (Au and Pt) on an aluminum gate electrode in a planar geometry. Molecules are trapped in the gaps from solution at room temperature. Molecule-specific properties are observed as deduced from the interaction between electronic transport and vibrational modes, from singlet-triplet transitions or from high-spin states in the molecule. For example, in the robust Fe-4 molecular magnet we observe features that confirm the high-spin state and find Kondo behavior, spin blockade and a zero-field splitting that depends on the redox state. A central question is: "Where are the additional charges induced by the gate voltage located?". In conjugated systems these charges are likely to be found close to the metal electrodes leading to spin separation; in single-atom complexes charges are added to the organic ligands which may induce high-spin to low spin transitions and interesting spin-spin interactions. Finally, we propose a new design for an all-electric molecular motor which is set in motion by ac electric fields applied by the gate electrode.

**THU 51**

**Assembly, Characterization and Applications of Chirality-Sorted Carbon Nanotube Device Arrays**

Aravind Vijayaraghavan<sup>1</sup> Marc Ganzhorn<sup>2</sup> Ninette Stürzl<sup>2</sup> Simone Dehm<sup>2</sup> Frank Hennrich<sup>2</sup> Ralph Krupke<sup>2</sup>

<sup>1</sup>University of Manchester, Manchester

<sup>2</sup>Karlsruhe Institute of Technology, Karlsruhe

In order to fully realize the potential of CNTs for electronics-based applications, it is essential to overcome the poly-dispersity problem. Integrated circuits or sensor/resonator arrays should ideally consist of SWCNTs of the same chirality or electronic type. Here, we demonstrate how this can be achieved by a combination of solution-phase sorting and directed assembly by Dielectrophoresis (DEP).

SWCNTs are sorted into metallic and semiconducting species with 99% purity, using density-gradient ultracentrifugation, and to individual chirality using targeted polymer wrapping with purity up to 80%, resulting in solutions of SWCNTs in water and toluene respectively. DEP is used to deposit device arrays out of these sorted solutions, and characterized by Raman and PLE spectroscopy, electronic-transport and voltage-contrast SEM to confirm the chirality-sorted arrays. DEP is scalable to high integration densities. Devices can be assembled at any arbitrary location or orientations simultaneously.

We also demonstrate that Hydrogen sensing with SWCNT devices is strongly dependent on nanotube chirality, with an optimum band-gap of 1 eV for highest sensitivity and fastest response.

**THU 52****Carbon nanotube quantum dots with graphene leads**

Peter Weber<sup>1</sup> Stephan Engels<sup>1</sup> Karin Goß<sup>2</sup> Claus M. Schneider<sup>2</sup> Carola Meyer<sup>2</sup> Christoph Stampfer<sup>1</sup>

<sup>1</sup>JARA FIT and II. Physikalisches Institut B, RWTH Aachen/Germany, Aachen

<sup>2</sup>Institut für Festkörperforschung (IFF-9), Forschungszentrum Jülich/Germany, Jülich

Carbon nanomaterials, such as carbon nanotubes (CNTs) and graphene, both exhibiting unique electronic and mechanical properties are very promising materials for future nano- and quantum-electronic applications. The absence of the hyperfine field in <sup>12</sup>C enriched carbon materials make CNTs and graphene particularly interesting for quantum dot systems promising for hosting individual spin-qubits. Here we present the fabrication and electrical characterization of carbon hybrid devices and CNT quantum dots.

The CNTs are CVD grown either from Fe/Mo or Ferritin-based catalyst islands on a highly doped *Si/SiO<sub>2</sub>* substrate. Subsequently, graphene has been deposited by mechanical exfoliation on the 300 nm thick *SiO<sub>2</sub>* oxide with pre-grown nanotubes. Electron beam lithography and standard lift-off techniques are used to place metal

Finally, we show low-noise tunneling-spectroscopy transport measurements on an individual single-walled CNT quantum dot with graphene leads.

## Quantification of the metallic/semiconducting ratio of bulk SWCNT samples by cobalt porphyrin probe EPR spectroscopy

<sup>1</sup>University of Antwerp, Universiteitsplein 1, B-2610 Antwerp, Belgium

[2] S. Cambre, W. Wenseleers, E. Goovaerts, D.E. Resasco, ACS; Nano; 2010, 4, 6717

## Aberration-corrected in-situ TEM investigation under extreme heat: Atomically resolved adsorbates of gold and hydrocarbon on graphene

<sup>4</sup>Institute of Micro- and Nanomaterials, Ulm University, 89081 Ulm, Germany

167

allow applying in situ an electrical current to a freestanding graphene membrane. In this way the TEM sample reaches local temperatures exceeding 2000 K enabling to observe directly the transformation of adsorbed hydrocarbons into atomic layers of amorphous carbon and eventually into polycrystalline graphene. Moreover, we observed in real time the migration of gold nanoparticles and their self-organized alignment along parallel straight lines along the negative temperature gradient. Furthermore, we investigated the periodical arrangement of individual gold atoms into rectangularly shaped atomic mono- and bilayers as well as entire cuboids of many atomic layers. We found, that their lattice parameter is significantly larger than the value for pure gold particles, which might be caused by the incorporation of excess carbon into the gaps of the cubic (fcc) gold lattice. DFT calculations suggest that an gold-carbon compound has been developed.

**THU 55****Theory of carrier multiplication in graphene**

Torben Winzer<sup>1</sup> Andreas Knorr<sup>1</sup> Ermin Malic<sup>1</sup>

<sup>1</sup>Technische Universität Berlin, Berlin

The unique band structure of graphene allows Auger-type relaxation channels, which are inefficient in conventional semiconductors. In contrast to other Coulomb-induced scattering processes, these channels do not conserve the total carrier density. Here, we present microscopic calculations of the coupled time dynamics of the carrier population, the optical coherence, and the phonon population after an ultrashort optical excitation. Our calculations include carrier-carrier as well as carrier-phonon scattering and enable a resolution in time and momentum. We observe an asymmetry between processes increasing (impact ionization) and decreasing (Auger recombination) the carrier density, leading to a significant multiplication of the optical excited carriers during the relaxation process. The asymmetry is caused by the non-equilibrium carrier distribution immediately after the excitation, where Pauli blocking terms in the scattering rates cause a much higher probability for the impact ionization. The efficiency of the carrier multiplication depends on the strength of excitation, where the factor of carrier multiplication increases with decreasing pump fluence.

**THU 56****Spin/pseudo-spin degeneracy effects on the transport properties of suspended carbon nanotube quantum dots.**

Abdullah Yar<sup>1</sup> Andrea Donarini<sup>1</sup> Sonja Koller<sup>1</sup> Milena Grifoni<sup>1</sup>

<sup>1</sup>Physics Department, University of Regensburg, Germany

A low energy theory of suspended carbon nanotube quantum dots is presented. At low energies transport is dominated by electron-vibron processes where transfer of an electron through the dot is accompanied by the excitation/emission of quanta

(vibrons) of the involved longitudinal stretching modes. Because the frequency of the  $n$ th mode is an  $n$ th multiple of the frequency of the fundamental mode, several energetically degenerate or quasi-degenerate vibronic configurations can contribute to transport. We investigate the consequences of strong electron-vibron coupling, typical of small diameter nanotubes, in a fully symmetric set-up. Several striking features are predicted. In particular, a gate-asymmetry and pronounced negative differential conductance features are observed. We attribute the latter to the presence of slow channels originating from the interplay of Franck-Condon suppression of transport channels and spin/pseudo-spin degeneracies.

#### THU 57

##### **Structure evolution of DWCNTs of different morphology under high non-hydrostatic pressure**

Shujie You<sup>1</sup> Mattias Mases<sup>1</sup> Alexander A. Green<sup>2</sup> Mark C. Hersam<sup>2</sup> Alexander V. Soldatov<sup>1</sup>

<sup>1</sup>Department of Engineering Sciences and Mathematics, Luleå University of Technology, SE - 97187 Luleå, Sweden

<sup>2</sup>Department of Materials Science and Engineering, Department of Chemistry, Northwestern University, Illinois 60208-3108, USA

We report on Raman study of highly enriched double wall carbon nanotubes (DWCNTs) inhomogeneously dispersed in water solution of sodium cholate at high pressure in a diamond anvil cell. Pressure evolution of the Raman spectra of lightly bundled CNTs differs considerably from that of heavily bundled ones: the G band evolves into a very broad feature at P above 4.5 GPa and has a weaker pressure dependence; the RBM signals disappear at lower pressure. Specifically, the inner tubes of heavily bundled CNTs excited with 532nm laser collapse above 30 GPa whereas that occurs already at 17 GPa for lightly bundled nanotubes. On p release we observed strong hysteresis in the recovery of the RBM spectra from the outer tubes and the G-band shape of lightly- and heavily bundled CNTs becomes nearly identical below 8.6 GPa, in contrary to the upstroke p spectra. Remarkably, both RBMs and G-band fully recovered at ambient p after the sample exposure to 35 GPa whereas the D-band intensity has increased. Our results indicate that theoretical calculations [1] highly underestimate the pressure stability of DWCNTs. [1] V. Gadagkar, P. K. Matit, Y. Lansac, et al., Phys. Rev. B 2006, 73, 085402.

**THU 58****Hyperfine enhancement at lattice defects in single-walled carbon nanotubes**Viktor Zólyomi<sup>1</sup> Ádám Gali<sup>2</sup><sup>1</sup>Department of Physics, Lancaster University, Lancaster<sup>2</sup>Res. Inst. for Solid State Physics and Optics of Hung. Acad. Sci.

We present a first principles study of the hyperfine interaction in  $^{13}\text{C}$  enriched achiral single-walled carbon nanotubes (SWCNTs). We show that while the hyperfine coupling is extremely small in pristine nanotubes, it is significantly enhanced near lattice defects such as vacancies and Stone-Wales pairs. We argue that this hyperfine enhancement is due to electron localization at the defect sites. Using this argument we give a qualitative explanation of recent measurements on the hyperfine coupling in SWCNT-based double quantum dots which showed a larger than expected hyperfine coupling.









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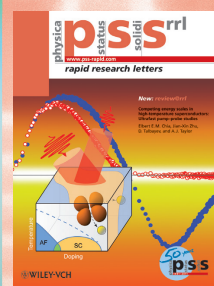


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Friday, March 4

## Carbon nanomaterials growth and spin properties

- 8:30 – 9:00      G. T. Kim, KR  
—
- 9:00 – 9:30      S. Arepalli, KR  
*Selective Growth of Single Wall Carbon Nanotubes and Type Separation Experiments*
- 9:30 – 10:00    A. Balandin, US  
*Thermal Properties of Graphene and Low-Dimensional Carbon Materials*
- 10:00 – 10:30    Coffee break
- 10:30 – 11:00    H.-M. Cheng, CN  
*Graphene Foam: A Three-Dimensional Interconnected Graphene Network*
- 11:00 – 11:30    R. Schlögl, DE  
*Nanostructured Carbon in Catalysis*
- 11:30 – 12:00    Ewa Borowiak-Palen, PL  
*Carbon Nanotubes Based Stimuli Responsive Controlled-Release System*
- 12:00 – 17:00    Mini Workshops
- 17:00 – 17:30    N. Pascual, DE  
*Kondo ground state of organic charge-transfer salts on a metal surface*
- 17:30 – 18:00    Y. Kubozono, JP  
*New type of carbon-based superconductors: metal intercalated hydrocarbons*
- 18:00 – 18:30    T. Pichler, AT  
*IWEPNM 2011 - Conference Summary*
- 18:30 – 20:00    Break
- 20:00      Bauernbuffet - Farewell

Friday, March 4

Carbon nanomaterials growth and spin properties

Friday, March 4

**8:30**

Gyu Tae Kim  
Korea University

**9:00****Selective Growth of Single Wall Carbon Nanotubes and Type Separation Experiments**

Sivaram Arepalli

Department of Energy Science, Sungkyunkwan University, Suwon

Some of the practical applications of single wall carbon nanotubes (SWCNTs) require "type specific" and "chiral specific" materials. Our group at NASA Johnson Space Center focused on controlled growth of SWCNTs using a modified double pulse laser oven method [1,2]. Increased arm chair tube populations are observed by the use of a "warm up" laser to prolong the nucleation process. Similar results are noticed by changing the production conditions and by using different metal catalysts (Pt/Rh instead of Co/Ni). The talk will also discuss some of the results from our recent "type separation" experiments carried out at Sungkyunkwan University using agarose gel and ultracentrifugation.

## References:

- (1) P. Nikolaev, W. Holmes, E. Sosa, S. Arepalli and L. Yowell, Effect of Vaporization Temperature on the Diameter and Chiral Angle Distributions of Single Wall Carbon Nanotubes, *J. Nanoscience and Nanotechnology*, Vol. 10, 3780-3789 (2010).
- (2) P. Nikolaev, W. Holmes, E. Sosa, P. Boul, and S. Arepalli, Effect of the Laser Heating of Nanotube Nuclei on the Nanotube Type Population, *Nano Research* Vol. 2, pp. 818-827 (2009).

**9:30****Thermal Properties of Graphene and Low-Dimensional Carbon Materials**Alexander Balandin

Department of Electrical Engineering, University of California - Riverside, Riverside

Recent years witnessed a rapid growth of interest of the scientific and engineering communities to thermal properties of materials. This is explained both by practical needs, e.g. heat removal is now a crucial issue for continuing progress in electronic industry, as well as the fundamental science: material's ability to conduct heat is rooted deeply in its atomic and electronic structure and the knowledge of thermal properties can shed light on many other material characteristics. Carbon allotropes and derivatives occupy a unique place in terms of their ability to conduct heat. The room-temperature thermal conductivity of carbon materials span an extraordinary large range - of over five orders of magnitude - from the lowest in amorphous carbons to the highest in graphene and carbon nanotubes. I will review thermal and thermoelectric properties of carbon materials focusing on recent results for graphene, carbon nanotubes and nanostructured carbons. A special attention will be given to the exotic size dependence of heat conduction in 2D crystal lattices and, more specifically, in graphene. Thermal management applications of graphene and graphene composites will also be discussed.

**10:30****Graphene Foam: A Three-Dimensional Interconnected Graphene Network**Hui-Ming Cheng<sup>1</sup> Zongping Chen<sup>1</sup> Wencai Ren<sup>1</sup><sup>1</sup>Shenyang National Laboratory for Materials Science, Institute of Metal Research, CAS, Shenyang 110016, China

Integration of individual 2D graphene into macroscopic structures is essentially important for the application of graphene. A series of graphene-based composites have been recently fabricated using chemically derived graphene sheets. However, these composites and structures suffer from poor electrical conductivity because of the low quality and/or high inter-sheet junction contact resistance of chemically derived graphene sheets. We report the direct synthesis of 3D foam-like graphene macrostructures by template-directed CVD, which we call graphene foams (GFs). A GF consists of an interconnected network of graphene, which is flexible and has fast transport channel of charge carriers for high electrical conductivity. Even with a GF loading as low as 0.5 weight percent, GF/poly (dimethyl siloxane) (PDMS) composites show a very high electrical conductivity of 10 S/cm, which is 6 orders of magnitude higher than chemically derived graphene-based composites. Using this unique network structure and the outstanding electrical and mechanical properties of GFs, as an example, we demonstrate the possibility of GF/PDMS composites for flexible, foldable and stretchable conductors.

**11:00****Nanostructured Carbon in Catalysis**Robert Schlögl

Abt. Anorganische Chemie, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

Elemental carbon is usually a detrimental inhibitor or site blocker in heterogeneous catalysis. In selected cases it is used as support for noble metal catalysts frequently applied in hydrogenation reactions.

The use of elemental carbon as catalyst is new in catalysis. It will be shown that the whole class of selective activations of alkanes can be performed with nanostructured carbon. Functional groups and the curvature of active surfaces as well as the inertness of graphene-type structural motifs combine to a unique mix of properties that can be utilized for metal-free catalysis.

Supported systems with Pd and metal carbides can be used for hydrogenation of oxygen and for dehydrogenation of ammonia both being reactions with relevance to the storage of regenerative energy.

The basis of these potentially attractive applications of nano-carbons is the control of electronic and chemical structure that is executed by fundamentally understood synthesis procedures.

[1] E. M. Vass, M. Hävecker, S. Zafeirotos, D. Teschner, A. Knop-Gericke, R. Schlögl, *Journal of Physics-Condensed Matter* 2008, 20.

[2] D. S. Su, J. Zhang, A. Thomas, X. Wang, J. Paraknowitsch, R. Schlögl, *ChemSusChem* 2010, 3, 169-180.

[3] S. Hofmann, R. Blume, C. T. Wirth, M. Cantoro, R. Sharma, C. Ducati, M. Hävecker, S. Zafeirotos, P. Schnörch, A. Oestereich, D. Teschner, M. Albrecht, A. Knop-Gericke, R. Schlögl, J. Robertson, *J. Phys. Chem. C* 2009, 113, 1648-1656.

**11:30****Carbon Nanotubes Based Stimuli Responsive Controlled-Release System**

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A recent study on stimuli-responsive controlled-release delivery system based on carbon nanotubes will be presented [1]. Functional groups attached to the tubes open ends enable functionalized silica spheres to preferentially attach to the ends, in essence, plugging the ends of the tube. Reducing agents or elevated temperature allow for the controlled release of encapsulated material within the tubes. The efficiency of the process is illustrated through fluorescein filled carbon nanotubes. The biocompatibility of the presented molecular hybrid with mouse fibroblast (cell line L929) will be also shown.

[1] X. Chen, H. Chen, C. Tripisciano, A. Jedrzejewska, M. H. Rümmeli, R. Klingeler, R. J. Kalenczuk, P. K. Chu and E. Borowiak-Palen, Carbon Nanotubes Based Stimuli Responsive Controlled-Release System, Chemistry - A European Journal, accepted 2011

**17:00****Kondo ground state of organic charge-transfer salts on a metal surface**Isabel Fernandez Torrente<sup>1</sup> Dagmar Kreikemeyer<sup>1</sup> Anna Strozecka<sup>1</sup> Katharina Franke<sup>1</sup> Nacho Pascual<sup>1</sup><sup>1</sup>Inst. Experimentalphysik, Freie Universität Berlin, Berlin

Magnetism in single molecules usually occurs due to unpaired electron spins in transition metal cores of metal-organic complexes. Here, we show that the localization of a single spin also can occur in a self-assembled molecular layer of the pure organic charge transfer complex tetrathiafulvalene (TTF) - tetracyanoquinodimethane (TCNQ) on a Au(111) surface. In these structures, the localisation of an unpaired electron in the LUMO of TCNQ leads to a free radical state, which can be demonstrated by the observation of the Kondo effect in low-temperature scanning tunnelling spectroscopy. The unpaired spin is coupled to vibrations, thus leading to a splitting of the Kondo resonance into vibrational sidebands of different intensity across the TCNQ molecule. The anionic ground state of TCNQ molecules is robust and survives for various functionalisation of the organic donor or when alkali atoms are used instead.

**17:30****New type of carbon-based superconductors: metal intercalated hydrocarbons**Yoshihiro Kubozono

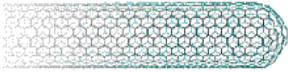
Okayama University, Okayama

We have recently discovered new high-T<sub>c</sub> organic superconductors by intercalating alkali and alkali earth atoms into hydrocarbon solids, which take pseudo two-dimensional (2D) crystal structure [1]. The crystal structure is similar to graphite. Intercalation of K, Rb and Ca into solids of phenacene-type hydrocarbon, picene, produced superconductors with T<sub>c</sub> of either 7 or 18 K. The filling of three electrons to unoccupied pi-orbitals of picene molecule is important for superconducting transition, i.e., the intercalation of 3 K (or Rb) or 1.5 Ca metal atoms produces the superconductors. The Raman scattering shows that three electrons transfer exactly from metal atoms to picene molecule. Furthermore, the K or Rb intercalation into solids of 2D expanded hydrocarbon, coronene, also showed the superconducting transition with three different T<sub>c</sub>s of 3.5, 7 and 11 K. It has been found from the variation of lattice constants by intercalation of metal atoms that the metal atoms are not intercalated into the inter-layer space but into the layer, in contrary to the graphite intercalation compounds.

[1] R. Mitsuhashi et al. Nature 464, 76 (2010)

**18:00****Summary**Thomas Pichler

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# Index

- Abiad, A. , **36**  
Abouelsayed, A. , 101  
Ahn, J. , **22**  
Aksenov, V. L. , **36**  
Alem, N. , 57  
Almadori, Y. , 37  
Alvarez, L. , **37**, 49  
Amara, H. , 80  
Amsharov, K. , 90, 143  
Andrei, E. Y. , **16**  
Anufienko, V. , 104  
Ansaldò, A. , **38**  
Arenal, R. , 37, 159  
Arepalli, S. , **178**  
Avdeev, M. V. , 36  
Awano, Y. , 156  
Ayala, P. , **38**, 99, 142, 159  
Ayuela, A. , 151  
Aznar, R. , 49
- Babaa, R. , 37  
Babchenko, O. , **39**, 100, 153  
Bachmatiuk, A. , 88  
Baetz, C. , 85  
Baer, S. , 129  
Balandin, A. , **179**  
Balogh, Z. , 84  
Bantignies, J. , 37  
Bantignies, J. L. , 49  
Bao, W. , 119  
Battie, y. , **39**  
Baudalet, F. , 34  
Baumgartner, A. , 134
- Bayer, B. C. , 47, 58, 60, 85  
Bazarnik, M. , **40**  
Belle, B. D. , 45  
Bencsik, G. , 144  
Bendjemil, B. , 87  
Benner, G. , 91, 95  
Berseneva, N. , **40**  
Bégin, D. , 81  
Bignardi, L. , **41**  
Biró, L. P. , 145  
Biskupek, J. , 91  
Biso, M. , 38  
Blake, P. , 45  
Blinc, R. , **41**  
Blume, R. , 85  
Blüher, J. , 88  
Bluemmel, P. , **42**, 79  
Bobkin, E. , **42**  
Bockrath, M. , **119**  
Boden, A. , 59  
Bognani, L. , 48  
Bolusheva, L. , 51  
Bonifazi, D. , 44  
Bonini, N. , 145  
Borodzinski, A. , **43**, 94 , 106 , 158  
Borowiak-Palen, E. , 108, **182**  
Bostwick, A. , 50, **131**  
Botka, B. , **44**, 97  
Botos, ; 101  
Boukhzar, S. , 81  
Bousige, C. , **44**  
Börrnert, F. , 88  
Branscheid, R. , 87

## Index

- Brar, V. W. , 124  
Brillet, J. , 86  
Britnell, L. , **45**  
Brose, K. , **46**  
Broz, A. , 93  
Bulusheva, E. G. , 98  
Bulusheva, L. G. , 98 , **47**, 110 , 148  
Bungener, S. , 86  
Burgdörfer, J. , 132  
Burgdörfer, J. , 146  
Burghard, M. , 48, 159  
Burke, S. A. , 124  
Busse, C. , 149  
Büchner, B. , 81 , 88
- Cai, N. , 86  
Cambedouzou, J. , 49  
Cambré, S. , 32 , 167  
Campbell, E. , 83  
Campos-Delgado, J. , 38  
Capaz, R. B. , 124  
Casiraghi, C. , **74**  
Castellarin-Cudia, C. , **47**  
Cavalieri, E. , 48  
Cendrowski, K. , 182  
Cepek, C. , 47, **48**  
Cervetti, C. , **48**  
Chacón-Torres, J. , **49**  
Chan, K. T. , 124  
Chandra, B. , 119  
Charlier, J. , **133**  
Chekhova, G. N. , 110  
Chen, C. , 135  
Chen, X. , 47, 182  
Chen, Y. , 124  
Chen, Z. , 180  
Cheng, H. , **180**  
Chernyshev, D. , 161  
Chico, L. , 151  
Chikkadi, K. , 83  
Choi, A. , 20  
Chorro, M. , **49**  
Choucair, M. , 154  
ChristianThomsen, , 94
- Chuvilin, A. , 55, 91  
Cohen, M. L. , 124  
Collins, G. , 97  
Crassee, I. , **50**  
Crommie, M. F. , **124**  
Cuniberti, G. , 88  
Czajka, R. , 40
- D'Souza, F. , 102  
Dabrowska, A. , **55**  
Dabrowski, J. , 106  
Dai, H. , 124  
Damnjanovic, M. , **50**, 52, 141, 152  
Das, S. K. , 102  
Dauber, J. , 62  
Decker, R. , 124  
Dehm, S. , 166  
Delhalle, J. , 81  
Deshpande, V. , **135** , 119  
Detriche, S. , 81  
Dettlaff-Weglikowska, U. , **51**, 95  
Dmitriev, V. , 161  
Dobardzic, E. , **52**  
Dobrik, G. , 145  
Dobrowska, A. , 87  
Dombi, A. , 110, 165  
Donarini, A. , 168  
Dora, B. , 81, 156  
Dossot, M. , **52** , 138 , 139  
Dotzer, C. , 57  
Döring, V. , **54**  
Dóra, B. , **54**, 160  
Dröscher, S. , 129  
Dressel, M. , 48  
Dresselhaus, M. S. , 92  
Drndic, M. , **136**  
Drnovsek, A. , 64  
Drozdik, M. , 182  
Ducastelle, F. , 80  
Duesberg, G. S. , **23**  
Dulic, D. , **53**  
Dumlich, H. , **53**
- Economopoulos, S. P. , 160

- Eder, F. , **55**  
 Eelkema, R. , 53  
 Elkaim, E. , 34  
 Elumeeva, K. , **56**  
 Elumeeva, K. V. , 104  
 Engels, S. , 62, 166  
 Englert, J. M. , **57**  
 Ensslin, K. , **129**  
 Erickson, K. , **57**  
 Erni, R. , 57  
 Esch, J. v. , 53  
 Esconjauregui, S. , 47, **58**, 60  
  
 Fanetti, M. , 48  
 Farhat, H. , 92  
 Farjam, M. , 81  
 Fábíán, G. , **64**, 160  
 Fedorovskaya, E. O. , 47  
 Fejes, D. , **58**  
 Feng, J. , 124  
 Ferrari, A. C. , **18**  
 Ferrer-Anglada, N. , 36, **59**  
 Figueras, J. , 59  
 Firkowska, I. , **59**  
 Flensberg, K. , 89  
 Forró, L. , 56, **60** , 58, 110, 144  
 Fort, Y. , 139  
 Fouquet, M. , 58, **60**  
 Francis, E. A. , **61**  
 Frank, O. , **61**, 142  
 Franke, K. , 183  
 Freitag, F. , 134  
 Friedrich, A. , 64, 99  
 Frielinghaus, R. , **62**  
 Fringes, S. , **62**  
 Fuhrer, M. S. , **122**  
 Fujii, S. , 27, **63**  
 Fujisawa, T. , 89  
 Futaba, D. N. , 38  
  
 Gaal, R. , 60  
 Gadermaier, C. , **64**  
 Gali, Á. , 170  
 Galiotis, C. , 61  
  
 Ganin, A. Y. , 138  
 Gannett, W. , 57  
 Ganzhorn, M. , 166  
 Garcia, R. , 83  
 Gavioli, L. , 48  
 Gavrilenko, A. , 107  
 Gavrilenko, V. , 107  
 Gebhardt, B. , **65**, 78, 84  
 Geim, A. K. , 45  
 Gemming, S. , 99  
 Georgi, A. , **65**, 152  
 Geringer, V. , 65, 149, 152  
 Ghandour, A. J. , **66**  
 Gillen, R. , **66**  
 Gimenez-Lopez, M. d. C. , 91  
 Girit, C. , 124  
 Giusca, C. , 81  
 Goß, K. , 62, **67**, 166  
 Golberg, D. , 85, 109  
 Goldoni, A. , 47  
 Goovaerts, E. , 32, 167  
 Gorbachev, R. V. , 45  
 Gorreri, A. , 151  
 Gottfried, J. M. , 57  
 Grätzel, M. , 86  
 Green, A. A. , 169  
 Grifoni, M. , 168  
 Grimm, J. , 143  
 Grinoni, M. , 89  
 Groß, A. , 167  
 Grove-Rasmussen, K. , 89  
 Grüneis, A. , 49 , 81 , **130**  
 Guellati, O. , **81**  
 Guerioume, M. , 81  
 Guimarães, M. H. D. , 163  
 Guinea, F. , **123**, 124  
 Guldi, D. M. , 111  
 Guloy, A. , 107  
 Güttinger, J. , 129  
  
 Haag, R. , 42, 79  
 Haarlammert, T. , 41  
 Haberer, D. , **81**  
 Hackl, R. , 44

## Index

- Haider, M. , 91  
Hajdu, K. , 110, 144  
Hakonen, P. J. , 109  
Halonen, N. , **82**, 144  
Haluska, M. , **83**  
Harutyunyan, A. R. , **30**  
Hata, K. , 38  
Hauke, F. , 57, 65, 78, 84  
Havlicek, M. , 103  
Hecht, S. , 79  
Heeg, S. , **83**  
Heimel, G. , 137  
Heinz, D. , 135  
Heinz, T. F. , **15**  
Hennrich, F. , 105, 166  
Henrard, L. , 80  
Hens, Z. , 163  
Hermet, P. , 37  
Hernádi, K. , 58,**84**, 110, 144 , 153, 165  
Hersam, M. C. , **28**, 169  
Herziger, F. , 139  
Hierold, C. , 54, 83, 143  
Hill, E. W. , 45  
Hirsch, A. , 57, 65, 78, 84  
Hiura, H. , 164  
Hof, F. , 65, 78, **84**  
Hoffman, M. , 92  
Hoffmann, P. , 99  
Hofmann, S. , 47, **85**, 94  
Holmes, J. D. , 97  
Hone, J. , 119, 135  
Hong, S. J. , 20  
Horváth, E. , 58, **86**, 110  
Horváth, L. , **85**  
Hoshyargar, F. , **87**  
Houben, L. , 62  
Huczko, A. , 55, **87**  
Hulman, M. , **88**  
Humbert, B. , 52  
Hwang, C. , 145  
  
Ibrahim, I. , **88**  
Ihn, T. , 129  
  
Iizumi, Y. , 160  
Incze, P. N. - , **145**  
Irle, S. , 81  
Ischenko, A. , 56  
  
Jafari, S. A. , 81  
Jalil, R. , 45, 61  
Janowska, I. , 81  
Jansen, M. , 90, 143  
Jantsch, W. , 103  
Jargalan, N. , 36  
Jaskólski, W. , 151  
Jespersen, T. S. , **89**  
Jégou, P. , 37  
Jhang, S. , **89**  
Jiang, H. , 159  
Jiao, L. , 124  
Jiguet, S. , 60  
Jiricek, P. , 43, 106, 158  
Jonkman, H. T. , 163  
Jorio, A. , **75**  
Jousselme, B. , 37  
Juarez, B. H. , 105  
Judelewicz, M. , 60  
Junesch, J. , 163  
  
Kaarour, M. N. , **90**  
Kabdulov, M. A. , **90**  
Kadir, A. , 90  
Kaiser, A. B. , **91**  
Kaiser, U. , 55,**91**, 95, 102, 167  
Kalbac, M. , **92**, 93  
Kalbacova, M. , **93**  
Kalenczuk, R. J. , 108, 182  
Kamarás, K. , 97, 101  
Kamarás, K. , 44, **93** , 138,150, 164  
Kanygin, M. , 148  
Kappes, M. , 105  
Kaptás, D. , 97  
Karousis, N. , 160  
Kaskela, A. , 159  
Katagiri, M. , 156  
Kataura, H. , **27**, 44, 63, 99, 103, 107, 155, 162

- Kauppinen, E. , 159  
 Kavan, L. , 61, 92  
 Kedzierzawski, P. , 43, **94**, 158  
 Kern, J. , 46  
 Kern, K. , 48, 159  
 Khachadorian, S. , **94**  
 Khlobystov, A. N. , 91  
 Kholmanov, I. , 48  
 Kim, D. , **95**  
 Kim, G. , 51  
 Kim, G. T., **177**  
 Kim, H. , 23  
 Kim, K. H. , 20  
 Kim, P. , 135  
 Kim, Y. , 95  
 Kinyanjui, M. K. , **95**  
 Kleshch, V. I. , **96**  
 Klupp, G. , 138  
 Knorr, A. , 42, 168  
 Knupfer, M. , 81  
 Knyazev, A. , **96**  
 Koch, N. , **137**  
 Kocsis, D. , 44, **97**  
 Koerdel, C. , 79  
 Kolb, U. , 87  
 Kolesnik, M. M. , **97**  
 Koller, S. , 168  
 Koltai, J. , 104, 160  
 Kong, J. , 92  
 Kong, Q. , 34  
 Konya, Z. , **98**  
 Kordás, K. , 82, 98, 101, 144  
 Korobov, M. V. , 36  
 Koroteev, V., **98**  
 Kotakoski, J. , 55  
 Kövér, L. , 106  
 Kónya, Z. , 82, 101, 144  
 Kramberger, C. , 64, 95, **99**  
 Krasheninnikov, A. , 40, 55  
 Kratka, M. , 100  
 Krause, M. , **99**  
 Kreikemeyer, D. , 183  
 Krill, C. , 167  
 Kromka, A. , 39, **100**, 153  
 Krstic, V. , 97  
 Krupke, R. , 162, 166  
 Kubarev, V. , 148  
 Kubozono, Y. , **184**  
 Kukkola, J. , 82  
 Kukovecz, Á. , 82, 144  
 Kukovecz, A. , 98, **101**  
 Kumar, S. , 23  
 Kuntscher, C. , **101**  
 Kuntscher, C. A. , 61  
 Kurasch, S. , 55, **102**, 167  
 Kurzewski, M. , 182  
 Kurzydowski, K. J. , 94 ,111  
 Kutner, W. , **102**  
 Kuzmany, H. , **103**, 108  
 Kuzmenko, A. , 50  
 Kuznetsov, V. L. ,56, **104**  
 Kürti, J. , **104**, 160  
 Laiho, P. , 159  
 Lambert, K. , 163  
 Landois, P. , 34  
 Lange, H. , **105**, 163  
 Lapczuk, J. , 182  
 Larina, T. A. , 104  
 Lau, C. N. , 119  
 Laudénbach, J. , **105**  
 Launois, P. , **34**, 44, 49  
 Lauret, J. , 80  
 Lazzeri, M. , 73  
 Ledinský, M. , 153  
 Lee, H. , 124  
 Lee, J. , 95  
 Lee, K. , 23  
 Lee, Z. , 57  
 Leijnse, M. , 67  
 Leino, A. , 82  
 Lemme, M. , 106  
 Leon, A. B. , **45**  
 Leschner, J. , 91  
 Lesiak, B. , 43, **106**, 158  
 Levallois, J. , 50  
 Levy, N. , 124  
 Li, Y. , 149

## Index

- Libisch, F. , **132**, 146, 149  
Liebmann, M. , 65, 149, 152  
Lin, H. , 80  
Lin, X. , 167  
Lippert, G. , **106**  
Litvinchuk, A. , **107**  
Liu, H. , 27, **107**  
Liu, X. , 45, 99, **108**  
Liu, Z. , 160  
Lloveras, V. , 36  
Loiseau, A. , 39, **80**, 159  
Louie, S. G. , 124  
Lounis, B. , **77**  
López-Urías, F. , 49  
Lukaszczuk, P. , **108**  
Lupina, G. , 106  
Luzan, S. M. , 161  
Lyashenko, D. , **109**  
Lyashenko, S. A. , 96, **109**
- Maciejewski, M. , 83  
Maggini, L. , 44  
Magrez, A. , 56, 60, 85, 86, 96  
Magyar, M. , **110**, 144  
Maier, S. , 83  
Maity, C. , 79  
Makarova, T. L. , **110**  
Mal, S. , 44  
Malic, E. , 42, 168  
Malig, J. , **111**  
Malissa, H. , 103  
Malolepszy, A. , 43, 94, **111**, 158  
Malysheva, L. , 148  
Mamane, V. , 139  
Marel, D. v. d. , 50  
Marganska, M. , 89  
Maria-Vogt, A. , 59  
Martin, C. A. , 53  
Marun, I. J. V. , 163  
Marzari, N. , 145  
Maserati, L. , 124  
Mases, M. , 19, **138**, 139, 169  
Mashoff, T. , 65, 152  
Mattmann, M. , 83
- Matus, P. , **138**  
Maultzsch, J. , 46, 61, 67, 78, 105, 139, 142, 150, 154  
Mauri, F. , **73**  
May, P. , **139**, 142  
Mayne, M. , 34  
Mazurkiewicz, M. , 43, 94, 111, 158  
Mazzani, M. , 151, 154  
Mazzarello, R. , 149  
Mäklin, J. , 82, **144**  
McDonald, M. T. , 138  
McEvoy, N. , 23  
McLennan, A. , 138  
McRae, E. , 138, **139**  
Meaker, K. L. , 124  
Meinke, R. , 78  
Mekhalif, Z. , 81  
Mercier, G. , 139  
Meyer, C. , 62, 67, **140**, 166  
Meyer, J. , 55, 95, 102, 167  
Miata, Y. , 99  
Michel, K. H. , **141**  
Michel, T. , 37  
Michely, T. , 149  
Mihailovic, D. , 64  
Mikkola, J. , 82  
Mikolajczuk, A. , 43, 94, 158  
Milosevic, I. , 50, **141**, 152  
Mionic, M. , 60  
Miska, P. , 52  
Mleczko, L. , **31**  
Mocuta, C. , 34  
Moehl, T. , 86  
Moessner, R. , 54  
Mogyorosi, K. , 153, 165  
Mohr, M. , 61, 139, **142**  
Molenkamp, L. W. , **117**  
Molitor, F. , 129  
Moore, J. E. , **118**  
Morgan, C. , 140  
Morgenstern, K. , 40  
Morgenstern, M. , **17**, 65, 149, 152  
Morley, G. W. , **121**  
Moseenkov, S. I. , 104

- Mowbray, D. , 38, **142**  
 Mukhopadhyay, B. , 139  
 Muoth, M. , 54, **143**  
 Muraki, K. , 89  
 Muranyi, F. , 156  
 Müller, A. , 90, **143**  
 Müller, M. , 62, 65, **78**
- Nagy, K. , **144**  
 Nagy, L. , 110, 144  
 Nair, R. R. , 45  
 Narula, R. , **145**  
 Nasibulin, A. , 159  
 Németh, K. , 84  
 Németh, Z. , 84, 144, **146**, 165  
 Neto, A. H. C. , 124  
 Neugebauer, H. , **147**  
 Neuville, A. , 19  
 Nichele, F. , 159  
 Nieminen, R. , 40  
 Nishide, D. , 27, 107, 162  
 Nitze, F. , 94  
 Noël, M. , 138, 139  
 Nolan, H. , 23  
 Novikov, D. S. , 119  
 Novoselov, K. , **21**  
 Novoselov, K. S. , 19, 45, 61  
 Nygård, J. , 89
- Obraztsov, A. , 96, 109, 164  
 Obraztsov, I. , 102  
 Obraztsova, E. D. , **147**  
 Okazaki, T. , 160  
 Okotrub, A. , 47, 98, **148**  
 Oksanen, M. , 109  
 Omerzu, A. , 64  
 Onipko, A. , **148**  
 Ostler, M. , 50
- Paaske, J. , 89  
 Palacin, S. , 37  
 Panlasigui, M. , 124  
 Panthöfer, M. , 87  
 Papagelis, K. , 61, 94, 142
- Papp, C. , 57  
 Parc, R. L. , 37  
 Park, H. J. , 55  
 Park, Y. W. , **20**  
 Parthenios, J. , 61  
 Pascual, N. , **183**  
 Pauly, C. , 65, **149**, 152  
 Peica, N. , 67, **150**  
 Pekker, Á., 44, 93, 101, **150** , 164  
 Pelc, M. , **151**  
 Pelech, I. , 182  
 Peltekis, N. , 23  
 Perrin, M. L. , 53  
 Pérez-Puigdemont, J. , 59  
 Pham-Huu, C. , 81  
 Pichler, T. , 38, 45, 49, 64, 81, 95, 99,  
 108, 142, 155, 159, **184**  
 Pieta, P. , 102  
 Pietraszkiewicz, M. , 44  
 Pietraszkiewicz, O. , 44  
 Pinakov, D. V. , 110  
 Pinault, M. , 34  
 Pivrikas, A. , 147  
 Plocke, T. , 65  
 Pontiroli, D. , **151**, 154  
 Popeney, C. S. , 42, 79  
 Popovic, Z. P. , 141, **152**  
 Porterat, D. , 34  
 Prassides, K. , 138  
 Pratzer, M. , 65, 149, **152**
- Radovsky, G. , 157  
 Rafailov, P. , 157  
 Raffai, M. , 58  
 Reich, S. , 42, 53, 59, 79, 83, 145  
 Reiter, R. , 149  
 Remškar, M. , 99  
 Remes, Z. , 39  
 Ren, W. , 180  
 Repain, V. , 80  
 Reti, B. , **153**  
 Rezek, B. , 39, 100, **153**  
 Riaz, I. , 45, 61  
 Riccò, M. , 151, **154**

## Index

- Ricci, D. , 38  
Rinnert, H. , 52  
Robertson, J. , **33**, 47, 58, 60, 66  
Rodríguez-Macías, F. , 49  
Rols, S. , 37, 44  
Romammenko, A. I. , 104  
Roman, C. , 83  
Rosenkranz, N. , **154**  
Rosseinsky, M. J. , 138  
Rotenberg, E. , 50  
Roth, S. , 36, 55, 102  
Rotter, S. , 132, 146  
Roulleau, P. , 129  
Rousset, S. , 80  
Rouzière, S. , 34  
Rubio, A. , 38, 142  
Rudolf, P. , 41  
Ruitenbeek, J. M. v. , 53  
Ruiz-Soria, G. , 38  
Rusakov, P. S. , 147  
Rusznayák, Á. , 104  
Rümmeli, M. H. , 88,99,103,182  
Rybin, M. G. , 147
- Sachdev, H. , 81  
Sahoo, J. K. , 87  
Sakai, T. , **156**  
Sakuma, N. , 156  
Salzmann, I. , 137  
Santos, H. , 151  
Sariciftci, N. S. , 147  
Sauvajol, J. , 37  
Sápi, A. , 101  
Schliwa, A. , 94, 105  
Schlögl, R. ,85, **181**  
Schmidt, M. , 57  
Schneider, C. M. , 62, 67, 140, 166  
Schoenfelder, R. , 103  
Scholz, F. , 167  
Schönenberger, C. , **134**  
Schukarev, A. , 82  
Schwaller, B. , 85  
Seifarth, O. , 106  
Seifert, G. , 99
- Setaro, A. , 42, **79**  
Seyller, T. , 50  
Shaikh, A. , 53  
Shames, A. I. , 110  
Shiozawa, H. , 99  
Shotniev, V. A. , 147  
Sillanpää, M. A. , 109  
Silva, S. , 81  
Simon, F. , 64, 99, **156**, 160  
Sitter, H. , 147  
Skákalová, V. ,55, 91,102, **157**  
Skourski, Y. , 89  
Smajda, R. , 56, 58, 86, 96  
Smerat, S. , 67  
Smet, J. , 157  
Soldatov, A. V. , **19**, 138, 139, 169  
Solowan, H. M. , 124  
Song, H. , 47  
Song, X. , 109  
Sordan, R. , 159  
Soszynski, M. , 55  
Spiecker, E. , 57  
Spina, M. , 56  
Spudat, C. , 62  
Srenseck-Nazzal, J. , 182  
Srivastava, A. , 102  
Stürzl, N. , 166  
Stüttzel, E. U. , 48, **159**  
Staiger, M. , **157**  
Stampfer, C. , 62, 166  
Steinrück, H. , 57  
Stephan, O. , 159  
Stobinski, L. , 43, 94, 106, 111, **158**  
Stojchevska, L. , 64  
Strain, K. , 83  
Strano, M. S. , **35**  
Stride, J. A. , 154  
Strle, J. , 64  
Strojnič, M. , 64  
Strozecka, A. , 183  
Strunk, C. , 89  
Subramaniam, D. , 65, 149, 152  
Suenaga, K. , 160  
Susi, T. , **159**

- Suzuki, M. , 156  
 Swan, A. K. , **76**  
 Szabó, T. , 110, 144, 161  
 Szabó, M. , 98  
 Szirmai, P. , **160**  
  
 Tagmatarchis, N. , **160**  
 Tahir, M. N. , 87  
 Taioli, S. , 81  
 Takabayashi, Y. , 138  
 Talyzin, A. V. , **161**  
 Tanaka, T. , 27, 63, 107, **162**  
 Tang, Z. , 107  
 Taniguchi, T. , 45  
 Tao, C. , 124  
 Tapasztó, L. , 145  
 Tausenev, A. V. , 147  
 Tenne, R. , 99  
 Terres, B. , 62  
 Terrones, M. , 38  
 Tétreault, N. , 86  
 Thiele, C. , **162**  
 Thomsen, C. , 61, 62, 65, 67, 78, 105, 142, 150, 154, 157, 163  
 Tian, Y. , 159  
 Till, C. , 154  
 Tombros, N. , **163**  
 Topolovsek, P. , 64  
 Torrente, I. F. , 183  
 Tóháti, G. , 82, 98, 101, 144  
 Tóháti, H. , **164**  
 Tóháti, J. , 106  
 Tour, J. M. , 124  
 Traversi, F. , 159  
 Trbovic, J. , 134  
 Trellenkamp, S. , 62  
 Tremel, W. , 87  
 Tropin, T. V. , 36  
 Tschirner, N. , **163**  
 Tsoukleri, G. , 61  
 Tsukagoshi, K. , 164  
 Turnina, A. V. , 96  
 Tyurnina, A. , **164**  
  
 Ullah, M. , 147  
 Urabe, Y. , 162  
 Usachov, D. , 81  
  
 Vajda, K. , **165**  
 van-der-Zant, H. S. , **165**  
 Vasilyeva, E. A. , 96  
 Váró, G. , 144  
 Vega-Cantú, Y. , 49  
 Veligura, A. , 163  
 Venezuela, P. , 73  
 Vengust, D. , 64  
 Verberck, B. , 141  
 Vergnat, M. , 52  
 Vetushka, A. , 153  
 Vidal-Gancedo, J. , 36  
 Vigolo, B. , 139  
 Vijayaraghavan, A. , **166**  
 Viršek, M. , 99  
 Volk, C. , 62  
 Vretenár, V. , 88  
  
 Wachsmuth, P. , 95  
 Wajda, A. , 182  
 Walter, A. , 50  
 Wang, P. , 86  
 Wang, Y. , 81, 124  
 Watanabe, K. , 45  
 Weatherup, R. , 85  
 Wågberg, T. , 94  
 Weber, P. , 62, **166**  
 Wees, B. J. v. , 163  
 Wegewijs, M. R. , 67  
 Weiss, M. , 134  
 Wenseleers, W. , **32, 167**  
 Westenfelder, B. , **167**  
 Wichmann, U. , 62  
 Winter, C. , 41  
 Winzer, T. , **168**  
 Wirtz, L. , 49, 65  
 Wolff, U. , 88  
 Wosnitza, J. , 89  
 Wrachtrup, J. , **120**  
  
 Xu, Y. , 135

## Index

Yamazaki, Y. , 156  
Yanagi, K. , 103, 155  
Yang, G. , 57  
Yar, A. , **168**  
Yazyev, O. V. , 124, 154  
Yella, A. , 87  
Yeremin, R. A. , 36  
Yoo, K. J. , 145  
You, S. , 19, **169**  
Yudanov, N. F. , 110  
  
Zacharias, H. , 41  
Zak, A. , 157  
Zakeeruddin, S. M. , 86  
Zant, H. S. J. v. d. , 53  
Zemek, J. , 43, 106, 158  
Zettl, A. , 57, 124  
Zhang, H. , 119  
Zhang, J. , **29**  
Zhang, X. , 124  
Zhu, Z. , 159  
Zitouni, K. , 90  
Ziegler, K. , 143  
Zouni, A. , 46  
Zólyomi, V. , 104, 160, **170**