XXVIIIth
International Winterschool
on Electronic Properties
of Novel Materials

Molecular Nanostructures

Program

Hotel Sonnalp
Kirchberg/Tirol
Austria

08-15 March, 2013
SUPPORTERS
Verein zur Durchführung der International Winterschool on Electronic Properties of Novel Materials
Verein zur Förderung der Internationalen Winterschulen in Kirchberg Austria

PATRONAGE
Helmut Berger
Major of Kirchberg

LAYOUT
María Machón, Felix Herziger
Logo designed by Kazuhiro Yanagi and Asmus Vierck
The logo shows colour changes in thin films of metallic carbon nanotubes, induced by electrochemical doping.

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Financial assistance from the sponsors and supporters is greatly acknowledged.
Dear Friend:

Welcome to the 28th International Winterschool on:

**Electronic Properties of Novel Materials: "Molecular nanostructures"**

This Winterschool is a sequel of twenty-seven 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, Hans Tornatzky: accommodation
- Nils Scheuschner, Roland Gillen: technical assistance, video transfer
- Amelie Biermann: finances
- Asmus Vierck, Harald Scheel: website
- Reinhard Meinke: sponsoring, visa applications
- Sevak Khachadorian: announcements
- Harald Scheel, Emanuele Poliani: receipts, technical assistance
- Dirk Heinrich: technical assistance
- Felix Herziger: abstract booklet
- Anja Sandersfeld: general assistance

Also the managers of the hotel, Mrs. Mayer and Mr. Mayer, and their staff promised to help us wherever they can. We want to acknowledge their help.

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, Andreas, Hans, Stephanie, and Siegmar
Chairpersons

C. Thomsen (Berlin)
A. Hirsch (Erlangen)
H. Kuzmany (Vienna)
S. Reich (Berlin)
S. Roth (Munich)

Program Committee

E. Andrei (US)   Y. H. Lee (KR)   A. Rubio (ES)
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A. Jorio (BR)    S. Reich (DE)    C. Thomsen (DE)
H. Kataura (JP)  J. Robertson (UK) A. Zettl (US)
H. Kuzmany (AT)  S. Roth (DE)

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 nanographene
- Carbon nanotube / graphene optics and electronics
- Carbon nanotube / graphene growth and selection
- Novel two-dimensional materials
- Applications of molecular nanostructures
- Theory of molecular nanostructures
- Biomolecule physics and applications
- Nanostructure spintronics
- Single-molecule experiments
INFORMATION FOR PARTICIPANTS

Time and location
The IWEPNM 2014 starts on Saturday, 8 March, evening, at the hotel Sonnalp in Kirchberg/Tirol, Austria and extends to Saturday, 15 March, breakfast. There will be a reception party on 8 March, after dinner, and a farewell party including dinner on Friday, 14 March.

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

Addresses
The address of the Winterschool is:
IWEPNM 2014, Hotel Sonnalp, A-6365 Kirchberg/Tirol, Austria
e-mail: info@hotelsonnalp.info, web: www.hotelsonnalp.info

All questions concerning the IWEPNM 2014 should be directed to:
Prof. Dr. Christian Thomsen,
Institut für Festkörperphysik, Technische Universität Berlin
Hardenbergstr. 36, 10623 Berlin, Germany
Tel: 0049-(0)30-31423187, Fax: 0049-(0)30-31427705
e-mail: iwepnm-info@physik.tu-berlin.de, web: www.iwepnm.org

Participation
Participation at the IWEPNM 2014 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, Tel.: 0043-664-5225265). 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, 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 use.

Conference Publication
Invited and contributed presentations from IWEPNM 2014 are scheduled for publication in physica status solidi (pss). **Manuscript submission is due on April 15th.**
The publication is planned as a special issue with regular articles to be published in the journal pss (b) (Feature Articles/topical reviews, Original Papers) or pss (c). In selected cases articles are highlighted in pss (RRL) (Reviews@RRL, Rapid Research Letters). A hardcover edition will be distributed to the participants.
Accepted manuscripts will fulfill the standards and requirements of the journal and are peer-reviewed in the same way as regular submissions. Acceptance of a contribution for presentation at the winterschool does not automatically include acceptance for publication in the special issue. Detailed information will be provided at the winterschool.

Manuscript preparation and submission
Preparation instructions and templates are available at [http://www.pss-b.com](http://www.pss-b.com) → **Author guidelines**. Manuscripts of contributed presentations are limited to 6 pages (no page limit for invited presentations). We strongly recommend using the Word or Latex templates to get an accurate estimate of the article length. Do not modify any pre-settings in the style files such as font sizes, margins, and other formats, to avoid an incorrect layout of the publication.

Please **submit one complete PDF- or Word-file for review** (Word or Latex source files are required after acceptance for production).
The NEW submission system (may require new user registration) is here:


Select article type ‚‘Original Paper‘‘ and section ‚‘Electronic Properties of Novel Materials (IWEPNM 2014)‘‘. If you intend to submit a ‚‘Rapid Research Letter‘‘ or a ‚‘Feature Article‘‘ manuscript, please consult with the editors.
pss editorial office e-mail: pss@wiley-vch.de
The following participants are asked to support the program of the Winterschool by serving as chairperson:

Sunday, 09.03.
- morning
- morning, after coffee break
- evening

Monday, 10.03.
- morning
- morning, after coffee break
- evening

Tuesday, 11.03.
- morning
- morning, after coffee break
- evening

Wednesday, 12.03.
- morning
- morning, after coffee break
- evening

Thursday, 13.03.
- morning
- morning, after coffee break
- evening

Friday, 14.03.
- morning
- morning, after coffee break
- evening

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

Chairpersons please remember:
You have to ask for questions from the sideroom (bar)!

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
<table>
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<tr>
<th>Time</th>
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<th>Speaker</th>
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<td>10:00</td>
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<td>Real-space mapping of graphene plasmons</td>
<td>HILLENBRAND</td>
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<td>Mid-IR photodetection with graphene plasmonic superstructures</td>
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<td>Fabrication and applications of van der Waals-based heterostructures</td>
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<td>Topological insulators, applications, TMDs</td>
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<td>Charge manipulation in molecules inside single-walled carbon nanotubes</td>
<td>MOLENKAMP</td>
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<td>Mapping charge transport in carbon nanotubes by Raman microscopy</td>
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<td>Effect of various atomically flat substrates on graphene quality</td>
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<td>Transconductance fluctuations in graphene and bilayer</td>
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<td>Transport, in Structurally and Chemically Modified Graphene</td>
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<td>Observation of the valley Hall effect in MoS2 transistors</td>
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<td>Progress in Chemical Vapour Deposition of High Density Carbon</td>
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<td>Nanotube forests and Graphene, and their Applications</td>
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<td>Effect of anisotropic band curvature on carrier multiplication in</td>
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<td>Measurement of coherent length of optical phonons in graphene</td>
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<td>by near-field Raman scattering</td>
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<td>Flexible devices based on carbon nanotube thin films</td>
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<td>Carbon materials: design, growth and applications</td>
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PROGRAM

AND

ABSTRACTS
Fabricated using a dry transfer technique to ensure a clean and contamination-free interface between the graphene and hBN, our heterostructure devices are of the very highest quality. E-beam lithography is deployed throughout.

Get in touch with us to discuss your requirements and how graphene is helping to revolutionise many areas of technology.

**2-D Tech heterostructure devices**

Graphene is transferred to hBN and shaped into a hall bar. Au contacts are added as electrical connections.

For increased mobility and protection, the hall bar can be further encapsulated with another hBN layer.

Carrier mobilities from 50,000 to 150,000 cm²/Vs

**2-D Tech – helping the graphene revolution to happen**

**BUY GRAPHENE**
We supply the highest quality graphene and other 2-D materials internationally

**GRAPHENE CHARACTERISATION**
Send us your samples for a full analysis

**GRAPHENE CONSULTANCY**
We’ll work in partnership with you to develop groundbreaking new products

Contact us to discuss whatever graphene application you have in mind. We’re interested in hearing about your ideas and talking to you about how we could help you to realise them.
08:30 – 00:00 A. Loiseau, Chatillon  
Near-band edge optical properties of h-BN: from bulk to 1D and 2D structures

09:00 – 00:00 J. Kotakoski, Wien  
Atomic structure and electron-beam-driven dynamics of defects in graphene

09:30 – 10:00 A. Vazquez de Parga, Madrid  
Long range magnetic order in purely organic 2D layer adsorbed on epitaxial graphene

10:00 – 10:30 coffee break

10:30 – 11:00 T. Pichler, Vienna  
Charge transfer, local strain and hybridization in functionalized carbon nanotubes and graphite intercalation compounds

11:00 – 11:30 F. Ernst, New York  
Tailoring the optoelectronic properties of nanotube-chromophore complexes

11:30 – 12:00 C. Voisin, Paris  
Chirality dependence of the absorption cross-section of carbon nanotubes revealed by energy transfer in nanotube/porphyrin compounds.

12:00 – 17:00 mini workshops

17:00 – 18:30 Dinner

18:30 – 19:00 A. Hartschuh, München  
Near-field optical and ultrafast spectroscopy of single carbon nanotubes

19:00 – 19:30 F. Wang, Berkeley  
Optical Spectroscopy of Individual Carbon Nanotubes

19:30 – 20:00 J. Maultzsch, Berlin  
Raman spectroscopy and near-field Raman scattering in carbon nanotubes and semiconductor nanostructures

20:00 – 20:30 L. Cancado, Belo Horizonte  
Measurement of coherent length of optical phonons in graphene by near-field Raman scattering
Layered materials, CNT / graphene optics
Layered materials, CNT / graphene optics

08:30
Near-band edge optical properties of h-BN: from bulk to 1D and 2D structures
Annick Loiseau\textsuperscript{1}, Aurélie Pierret\textsuperscript{1}, Julien Barjon\textsuperscript{2}, Simona Moldovan\textsuperscript{3}, Ovidiu Erșen\textsuperscript{3}, Frédéric Fossard\textsuperscript{1}, François Ducastelle\textsuperscript{1}
\textsuperscript{1}LEM, CNRS-ONERA, Chatillon, France
\textsuperscript{2}GEMAC, Université Versailles St Quentin - CNRS, Versailles, France
\textsuperscript{3}IPCMS, CNRS - Université de Strasbourg, Strasbourg, France

h-BN is a wide band gap semiconductor (6.4 eV), which can be synthesized, as graphite, its carbon analog, as bulk crystallites, nanotubes and layers. These structures meet a growing interest for deep UV LED and graphene engineering. In this talk, we will review the interplay between the structure, defects and luminescence properties of different BN structures and how these properties can be further exploited for their characterization. By combining cathodoluminescence and TEM experiments, we will show that, whatever the structure, bulk or nanoscale, near band edge luminescence is governed by excitonic effects in the range 5.5 - 6 eV and consists of two series of lines called S and D \cite{1}. D lines being issued from defective areas, D/S ratio can therefore be used as a qualification parameter of the defect densities in this layers \cite{2}. Concerning nanotubes, we will show that exciton trapping on structural defects gives rise to a spectacular localization of the luminescence caused by a complex structure of these tubes, that we have analysed by combining different TEM techniques.

\begin{itemize}
\item[(1)] L. Museur et al., PSS rrl, 5 (2011)
\item[(2)] A. Pierret et al, Phys. Rev. B (2014) in press
\end{itemize}
Atomic structure and electron-beam-driven dynamics of defects in graphene

Jani Kotakoski\textsuperscript{1}, Toma Susi\textsuperscript{1}, Franz Eder\textsuperscript{1}, Clemens Mangler\textsuperscript{1}, Jannik Meyer\textsuperscript{1}

\textsuperscript{1}Universität Wien, Wien

Graphene, the poster child of the group of two-dimensional materials, is well known to contain ripples even when free-standing. Nevertheless, various defects have been assumed to be accommodated preserving a locally flat geometry in graphene. In this work, we combine high resolution transmission electron microscopy (TEM) and atomic-scale simulations to study the atomic structure of both beam-induced defects and intrinsic lattice imperfections. By constructing atomic structures from microscopy images, we show that continuous electron irradiation lattice turns graphene first into a vitreous matrix separating small crystallites and finally into a random network. Against the common assumption, even the smallest defects are found to cause local buckling in graphene. We further establish trends for formation energies and the buckling height as a function of the defect size. Finally, we present a careful analysis of beam-driven dynamics of defects (including point defects and impurity atoms), and show how the constant bombardment of the imaging electrons leads to atomic changes in such structures even at acceleration voltages as low as 60 kV.
09:30
Long range magnetic order in purely organic 2D layer adsorbed on epitaxial graphene
Amadeo Vazquez de Parga¹
¹Fisica Materia Condensada, Universidad Autonoma de Madrid, Madrid

Collective magnetic properties are usually associated to d or f electrons which carry the individual magnetic moments. Band magnetism in organic materials based on p electrons has remained an experimental challenge, in spite of rigorous predictions of a fully spin polarized ground state in half-filled flat band organic systems. Cryogenic Scanning Tunnelling Microscopy and Spectroscopy and accurate Density Functional Theory simulations show that isolated TCNQ molecules deposited on graphene epitaxially grown on Ru(0001) acquire charge from the substrate and develop a magnetic moment of 0.4 μB per molecule, which is revealed by a prominent Kondo resonance. The magnetic moment is preserved upon dimer and monolayer formation with a value of 0.18 μB per molecule for the monolayer. The self-assembled molecular monolayer develops spatially extended spin-split electronic bands whose predicted spin alignment in the ground state is visualized by spin-polarized STM. The observation of long range magnetic order in an organic layer adsorbed on graphene paves the way for incorporating magnetic functionalities to graphene.
10:30

*Charge transfer, local strain and hybridization in functionalized carbon nanotubes and graphite intercalation compounds*

Thomas Pichler

1Faculty of Physics, University of Vienna, Austria

In this contribution I will present our recent progress on unraveling the influence of charge transfer, local strain and hybridization on the electronic transport properties of functionalized single walled carbon nanotubes and graphite intercalation compounds using resonance Raman, photoemission and x-ray absorption spectroscopy as probes. I will first discuss our recent results on charged and strained graphene layers in highly staged graphite intercalation compounds, serving as a tool to identify local internal strain in graphene and nanotube based devices and composites. Then I will present a gas sensing model based on external functionalisation illustrating how reactive gases like nitric oxides are predominantly physisorbed, also depending on the metallicity of the SWCNT. Concomitantly, I will discuss recent progress in unravelling the charge transfer, strain and bonding environment in filled SWCNT and DWCNT with special emphasis on the influence of basic correlation effects on the two particle excitation and the nature of the metallic ground state.

Work supported by FWF and the EU.
Tailoring the optoelectronic properties of nanotube-chromophore complexes

Friederike Ernst, Timm Heek, Antonio Setaro, Rainer Haag, Zhenghong Gao, Laurent Cognet, Rodrigo Fernandez-Pacheco, Raul Arenal, Stephanie Reich

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2 Institute of Chemistry, Free University of Berlin
3 University of Bordeaux, France and CNRS, Talence, France
4 Laboratorio Microscopias Avanzadas (LMA), Inst Nanociencia Aragon (INA), University of Zaragoza, Spain
5 Fundacion ARAID, Zaragoza

The formation of nanotube-chromophore complexes is of great interest for a number of applications, in particular in optical transistors, light-to-energy conversion, and biological sensing. We create super robust van-der-Waals stacked nanotube-perylene complexes which exhibit ultra efficient energy transfer. Upon radiative excitation of the chromophore, energy is transferred into the nanotube through a Förster-type dipole-dipole coupling mechanism. We observe this energy transfer through the radiative recombination of the exciton in the nanotube at the nanotube’s characteristic $E_{11}$ energy after an excitation of the chromophore. The complexation with chromophores creates a single excitation band for all nanotube chiralities, making the costly and difficult sorting of nanotubes by chirality unnecessary for many applications. Furthermore we demonstrate that chromophores can be integrated into functional surfactants and provide a guideline for the successful design of these surfactants. Lastly we show that said surfactants suspend nanotubes in biological surroundings and demonstrate the bio-compatibility of the nanotube-surfactant energy transfer complexes.
11:30
Chirality dependence of the absorption cross-section of carbon nanotubes revealed by energy transfer in nanotube/porphyrin compounds.
Fabien Vialla\textsuperscript{1}, Cyrielle Roquelet\textsuperscript{2}, Jean-Sébastien Lauret\textsuperscript{2}, Christophe Voisin\textsuperscript{1}
\textsuperscript{1}Laboratoire Pierre Aigrain, Ecole Normale Supérieure, Paris
\textsuperscript{2}Laboratoire Aimé Cotton, Ecole Normale Supérieure de Cachan, Université Paris Sud

The variation of the optical absorption of carbon nanotubes with their geometry has been a long-standing issue for both metrology and applications, especially because optical spectroscopy is the primary tool for the assessment of the species abundance. Several theoretical studies pointed a possibly strong variation of this absorption cross-section not only with diameter but also with the chiral angle and the family type. The measurement of the absolute absorption cross-section through single nanotube spectroscopy was reported for two species only. Here, we present an original method to carry out a systematic experimental study of the variations of absorption of semiconducting nanotubes at their S22 transition for a broad range of chiral species. Porphyrin molecules stacked on the wall of the nanotubes allow to achieve efficient and uniform photo-excitation of the whole set of chiral species, revealing intrinsic properties of the nanotubes. We show that the absorption is larger for type I nanotubes and that it varies by up to a factor of 2.2 with the chiral angle. In contrast, the luminescence quantum yield remains almost constant \cite{1}.

\cite{1} Vialla et al., PRL 111, 137402 (2013)
Near-field optical and ultrafast spectroscopy of single carbon nanotubes
Achim Hartschuh¹, Nina Mauser¹, Julia Janik¹, Richard Ciesielski¹, Alberto Comin¹, Kevin Donkers¹, Matthias Handloser¹
¹Department Chemie and CeNS, LMU München, Germany

The physical properties of carbon nanotubes (CNTs) are known to vary from nanotube to nanotube due to their structural diversity. Even for CNTs of the same structural type, local defects and coupling to heterogeneous environments can result in a broad distribution of the observed characteristics that cannot be resolved in ensemble measurements. We report on our efforts to study the optical properties of single CNTs on nanometer length and femtosecond time-scales. Using tip-enhanced near-field microscopy we probed the optoelectronic properties along electrically contacted CNTs. In this approach a laser-illuminated metal tip acts as an optical antenna that locally enhances both excitation and spontaneous emission rates (1). We achieved photoluminescence, Raman scattering as well as photocurrent and electroluminescence images with a spatial resolution below 30 nm (2). We investigated the excited state dynamics of single CNTs by probing their photoluminescence response while varying the spectral phase and amplitude of broadband laser excitation pulses.
(1) N. Mauser and A. Hartschuh, Chem. Soc. Rev. 43, 1248 (2014),
(2) N. Rauhut et al. ACS Nano 6, 6416 (2012)
19:00
Optical Spectroscopy of Individual Carbon Nanotubes
Feng Wang\textsuperscript{1}
\textsuperscript{1}UC Berkeley, Berkeley

Electronic and optical properties of single-walled carbon nanotubes depend sensitively on the nanotube chirality. Single tube spectroscopy provides a powerful tool to probe the chirality-dependent physics in nanotubes. In the talk, I will discuss our recent progress on optical spectroscopy of individual carbon nanotubes. I will describe a high-throughput optical imaging and spectroscopy technique that enables in-situ characterization of single tubes on substrate and in functional devices. I will also show that systematic spectroscopy of individual double-wall nanotubes indicate strong electronic coupling between the inner- and outer-wall tubes that vary strongly with the nanotube chirality.
19:30
Raman spectroscopy and near-field Raman scattering in carbon nanotubes and semiconductor nanostructures
Janina Maultzsch

1Institut für Festkörperphysik, Technische Universität Berlin, Germany

We present resonant Raman spectroscopy of the double-resonant $D$ mode in carbon nanotube ensembles enriched with different $(n,m)$ structures. The $D$-mode dispersion is distinctly different between nanotube ensembles and single-$(n,m)$ enriched samples. We show that in nanotube ensembles the $D$-mode can be assigned to specific Kataura-plot branches, due to strong resonances [1]. This will support characterization of defective nanotubes, e.g., after selective functionalization. In the second part of the talk, recent results of tip-enhanced Raman spectroscopy on semiconductor nanostructures [2] will be presented, giving information with high spatial resolution and surface sensitivity.

20:00

**Measurement of coherent length of optical phonons in graphene by near-field Raman scattering**

Luiz Gustavo Cancado\(^1\), Ryan Beams\(^2\), Ado Jorio\(^1\), Lukas Novotny\(^3\)

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\(^3\)Photonics Laboratory, ETH Zurich, 8093 Zurich, Switzerland.

The Raman effect in crystals has been historically treated in the literature as an incoherent process in the spatial domain. This approach is justified by the early theory of coherence which stated that the field emitted by an incoherent thermal source at a given wavelength \(\lambda\) is spatially correlated over distances on the order of \(\lambda/2\). At the begging of the current century, the great interest on optical processes at the nano-scale, combined with the development of the near-field optics technology gave rise to several studies showing that the near-field components of a thermal emitter reveal correlation lengths much shorter than \(\lambda\). In this talk we show that the Raman scattering of a pristine graphene performed in the near-field regime can be used to measure the coherence length of optical phonons. The coherence properties of lattice vibrations is of great importance for the development of the fast-growing field of graphene-based electronics, since the scattering of optical phonons provide the main channel for relaxation of charge carriers and heat dissipation in this system.
Layered materials, CNT / graphene optics  
Sunday, March 9th
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08:30 – 09:30  E. Mele, Philadelphia
   Tutorial: IWEPNM and the winding road to topological insulators

09:30 – 10:00  L. Molenkamp, Wuerzburg
   HgTe as a topological insulator

10:00 – 10:30  coffee break

10:30 – 11:00  O. Frank, Prague
   Raman spectroscopy of graphene wrinkles

11:00 – 11:30  M. Fuhrer, Monash
   Graphene optoelectronics: sensitive photothermoelectric detectors, and the ultimate transparent conductors

11:30 – 12:00  D. Carroll, Winston-Salem
   Building Meta-Assemblies that are Simultaneously Piezoelectric and Thermoelectric

12:00 – 17:00  mini workshops

17:00 – 18:30  Dinner

18:30 – 19:00  K. Mak, Ithaca
   Observation of the valley Hall effect in MoS2 transistors

19:00 – 19:30  Y. Iwasa, Tokyo
   Valley-spin physics in tranistion metal dichalcogenides

19:30 – 20:00  A. Castellanos-Gomez, Delft
   Atomically thin MoS2: nanomechanics and optoelectronics

20:00  Poster I
Monday, March 10th

Topological insulators, applications, TMDs
08:30
IWEPNM and the winding road to topological insulators
Eugene Mele\textsuperscript{1}
\textsuperscript{1}Department of Physics, University of Pennsylvania, Philadelphia

This will be a tutorial lecture on topological insulators focusing on the main ideas as developed through many previous meetings of the IWEPNM.
HgTe as a topological insulator
Laurens Wigbolt Molenkamp
Physics Department, EP3, University of Wuerzburg, Wuerzburg

HgTe is a zincblende-type semiconductor with an inverted band structure. While
the bulk material is a semimetal, lowering the crystalline symmetry opens up a gap,
turning the compound into a topological insulator. The most straightforward way to
do so is by growing a quantum well with (Hg,Cd)Te barriers. Such structures 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, which now
is seen as the prime manifestation of a 2-dimensional topological insulator. To turn
the material into a 3-dimensional topological insulator, we utilize growth induced
strain in relatively thick (ca. 100 nm) HgTe epitaxial layers. The high electronic
quality of such layers allows a direct observation of the quantum Hall effect of the
2-dimensional topological surface states. These states appear to be decoupled from
the bulk. This allows us to induce a supercurrent is induced in the surface states by
contacting these structures with Nb electrodes.
10:30

Raman spectroscopy of graphene wrinkles

Otakar Frank¹, Jaroslava Rahova¹, Jana Vejpravová², Ladislav Kavan¹, Martin Kalbac¹

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Periodic wrinkles in graphene represent an interesting phenomenon, which can be potentially utilized in various applications, e.g. in the creation of nanoribbons. From a fundamental point of view, the formation of wrinkles has a straight connection to the mechanical properties of graphene. In the present study, we focused on wrinkles in graphene on SU8 photoresist. Wavelength, amplitude and orientation of the wrinkles are measured by optical and atomic force microscopies on graphene membranes with varying number of layers – ranging from one to approx. six, as determined by Raman spectroscopy. As expected, the wavelength and amplitude scale with the number of layers accordingly to the classical elasticity theory. MicroRaman spectroscopy cannot distinguish individual wrinkles in mono- and bilayer graphene, however, for thicker samples, variations in frequencies, widths and intensities of the Raman features can be traced in maps of the scanned wrinkled regions. Most of the changes can be explained by differences in doping levels, where wrinkle valleys touch the underlying substrate. Behavior of the wrinkles is further tested in-situ during uniaxial bending.
I will discuss two optoelectronic applications of graphene. First, gapless graphene allows photoabsorption across a wide spectral range, which we exploit to realize an extremely broadband detector. We accomplish ultrafast, sensitive detection via the hot electron photothermoelectric effect at room temperature. We demonstrate room-temperature detection of THz radiation with sensitivity $>700$ V/W and noise equivalent power of $<20$ pW/\text{sqrt}(Hz), competitive with the best commercial room temperature THz detectors. However our device is $\sim7$ orders of magnitude faster, with characteristic timescales $<100$ ps. Second, we measure the electrical conductivity and optical transmission spectra of ultrathin graphite during lithium intercalation. The high doping upon lithium intercalation increases the conductivity to near the phonon-limited value at room-temperature, and also increases the transmission in the visible range, due to Pauli blocking of optical transitions. Transmission as high as 91.7 % for sheet resistance of 3.0 $\Omega$ is achieved for 19 layer LiC$_6$, better performance than any other continuous-film electrode.
Building Meta-Assemblies that are Simultaneously Piezoelectric and Thermoelectric
David Carroll¹, Corey Hewitt¹, David Montgomery¹
¹Physics, Wake Forest University, Winston-Salem

We introduce a layered organic material assembly that combines both thermoelectric effects with piezoelectric effects, yielding a strikingly useful amount of power. Surprisingly, however, the power output is not the linear addition of the two effects. When examined closely, the structures intrinsic thermoelectric properties are modified by the local fields of its piezoelectric components. The modification depends on several factors including interlayer spacing, in-plane heterogeneity of the conductor and mechanical stress/strain. The coupling of mechanical and thermoelectric properties to length scales of the assembly suggests that this system might more properly be viewed as a mechanical-thermal meta-material. Taking this approach we describe the power generated by such assemblies by presenting temperature dependent thermoelectric and piezoelectric characterizations as a function of the dynamical stress/strain state. We discuss how the resulting nonlinearities might play a role in observed pyroelectric and electrocaloric effects. From this, a simple thermodynamic model will be introduced that connects intrinsic length scales of the system to the fundamental constants S and p. Such assemblies may offer a competitive alternative approach to waste energy scavenging.
Observation of the valley Hall effect in MoS2 transistors

Kin Fai Mak

Kavli Institute at Cornell for Nanoscale Science, Cornell University

Two-dimensional (2D) atomic layers of molybdenum disulfide (MoS2) have attracted much recent attention due to their unique electronic properties. In addition to charge and spin, electrons in MoS2 monolayers possess a new valley degree of freedom (DOF) that has finite Berry curvatures. As a result, not only optical control of the valley DOF is allowed, but each valley is also predicted to exhibit a Hall effect in the absence of a magnetic field whose sign depends on the valley index. In this talk, we will discuss our recent observation of this new valley Hall effect (VHE) in monolayer MoS2 transistors. Experimentally, this is manifested as a finite anomalous Hall effect when circularly polarized light is used to preferentially excite electrons into a specific valley. We will describe the dependence of the anomalous Hall conductivity on photon helicity, photon energy, doping levels and crystal symmetry, and will compare these observations with theoretical predictions. Finally, possibilities of using the valley DOF as an information carrier in next-generation electronics and optoelectronics will also be discussed.
Valley-spin physics in transition metal dichalcogenides

Yoshi Iwasa

1University of Tokyo, Tokyo
2RIKEN CEMS, Wako

Transition metal dichalcogenide (TMD) is a beyond-graphene two dimensional crystals. Of particular importance is an optoelectronic properties based on valleytronics, which originates from the noncentrosymmetric structure of monolayer TMDs. Also, TMD has a relatively large spin-orbit interactions, which is missing in graphene and thus makes TMD system quite unique. Here we review our latest achievements on spin-valley physics and functionalities in TMD materials. We provide the first proof of spin/valley polarization using spin- and angle-resolved photoemission spectroscopy on bulk single crystals. This valley dependent spin polarization was predicted in monolayers, but became observable in bulk by choosing noncentrosymmetric single crystals. Photoluminescence circular dichroism proved that the valley polarization is not dependent on layer numbers when they are made from the noncentrosymmetric crystals, whereas the valley polarization quickly decreases with increasing the layer number when they are fabricated from the normal centrosymmetric crystals. Furthermore, we demonstrate electrically switchable circular polarized light source, based on novel valleytronics.
Single-layer MoS2 is an attractive two-dimensional material that combines the mechanical flexibility of graphene with a large direct bandgap. While graphene is very interesting as a transparent electrode, its lack of a bandgap limits its usefulness in semiconducting and optoelectronic devices. Atomically thin MoS2, on the other hand, has a large intrinsic bandgap. Our work on MoS2 has been focused on the intrinsic mechanical (1) and optical (2) of this atomically thin material. Here, I will show an overview of our last results paying special attention to our studies on the photocurrent generation in single layer MoS2 (2), the strain engineering in atomically thin MoS2 (3) and MoS2 based mechanical resonators (4).

References
MON 1
Photocurrent Imaging of Carbon Nanotube Devices with Local Mirrors
Asiful Alam\textsuperscript{1,2}, Benjamin S. Flavel\textsuperscript{1}, Simone Dehm\textsuperscript{1}, Uli Lemmer\textsuperscript{3,4}, Ralph Krupke\textsuperscript{1,2,3}
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Schottky barriers in carbon nanotube-metal contacts can be imaged successfully using scanning photocurrent microscopy. For long channel devices with similar metallic electrodes, the photocurrent image is ambipolar in nature. However, diffraction-limited laser spots can cause simultaneous excitations of both contacts in short-channel devices (<1\,\mu m), leading to partial cancellation of the photocurrent. We present a device geometry involving the fabrication of an isolated metallic mirror over one of the barriers in order to avoid simultaneous excitation of both contacts. Chirally-sorted (6,5) nanotubes were dielectrophoretically deposited across electrodes embedded into the substrate. Isolated chromium mirrors were then fabricated at one end of the nanotubes. Results show that photocurrent images of such devices are unipolar, displaying only one of the SBs. Furthermore the photocurrent spectrum shows a resonant peak near the $E_{22}$ interband transition of (6,5) nanotubes, with a good correlation to the absorption spectrum of the (6,5) dispersion.

MON 2
Enhanced electrical and mechanical properties of nanographite electrodes for supercapacitors by addition of nanofibrillated cellulose
Britta Andres\textsuperscript{1}, Sven Forsberg\textsuperscript{1}, Håkan Olin\textsuperscript{1}
\textsuperscript{1}Department of Natural Sciences, Mid Sweden University, Sundsvall, Sweden

Graphene and other porous carbon materials are widely used as electrodes in supercapacitors. In order to form mechanically stable electrodes, binders can be added to the conducting electrode material. However, most binders degrade the electrical performance of the electrodes. Here we show that by using nanofibrillated cellulose (NFC) as binder the electrical properties, such as sheet-resistance, were enhanced. NFC is a good ion conductor and improves the access of ions to the electrodes. Thus electrodes made of a mixture of nanographite and NFC achieved larger capacitances in supercapacitors than electrodes with nanographite only. The lowest sheet-resistance and the highest capacitance were measured at NFC contents of 10–15\% in ratio to the total amount of active material. Furthermore, NFC formed a network that improved the mechanical stability of the electrodes significantly. Beside the mechanical stability, NFC stabilized the aqueous nanographite dispersion that was used to prepare the electrodes. NFC avoids the restacking of the delaminated graphene flakes by forming a fiber network between the graphene layers.
**MON 3**

Dark Field TEM imaging of grains in graphene flakes

Giacomo Argentero\(^1\), Viera Skakalova\(^1\), Clemens Mangler\(^1\), Jannik C. Meyer\(^1\)

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The increasing interest for graphene and its applications have raised the crucial problem on how to fabricate large area, single crystal and defect-free monolayers of graphene. Among other synthesis methods, chemical vapor deposition (CVD) seems to be the most promising approach, because of its scalability, availability of raw materials and relatively simple growth technique. Despite recent progress, important questions are still open, especially regarding the kinetics involved in the growth. Here, we present a transmission electron microscopy (TEM) study of CVD graphene flakes that exhibit a characteristic holey four-pointed star shape. Dark field (DF) TEM images reveal multiple crystal domains arranged around the central hole and spreading radially towards the edges of the flake. Interestingly, grains located at opposite sides with respect to the hole show the same crystalline orientation, in spite of being completely separated. Although an unambiguous explanation for the observed structure is still to be found, this study shows how DF imaging in TEM can be efficiently employed to uncover the crystal structure of graphene that, in turn, might elucidate its growth mechanism.

**MON 4**

Quasi Self-consistent Monte Carlo Particle Simulations of Local Heating Properties in Graphene Nano-channel FETs

Taichi Misawa\(^1\), Shusuke Oki\(^1\), Aizuddin Mohamad\(^1\), Yuji Awano\(^1\)

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Owing to high density integration of LSIs and high power applications, thermal management becomes more and more important. In this paper, we report a new algorithm for Monte Carlo quasi self-consistent particle simulations of both electron and phonon transport in nanometer-channel FETs, based on computer time saving considerations. We simulate local heating properties of a single layer graphene (SLG) FETs for the first time (1), comparing with that of conventional GaAs and GaN devices. We developed two simulation algorithms: (1) the algorithm to estimate a local temperature from phonon spatial distribution, and (2) the algorithm, which made it possible to calculate long time phonon transport by introducing different time steps for Monte Carlo electron and phonon transport simulations. The local heating in the SLG channel is much smaller than that of GaAs channel. It is probably due to high speed optical and acoustic phonon transport in SLG, even though the heat generation rate in SLG is much higher than that of GaAs. This research is supported by JSPS through its FIRST Program of Japan.

(1) S. Oki, et al., IEEE IWCE (2013)
MON 5
Adsorption of NOx on SWCNTs: Physisorption vs. Desorption Induced by X-ray Radiation

Georgina Ruiz-Soria¹, Paola Ayala¹, Markus Sauer¹, Paolo Lacovig², Matteo Dalmiglio², Silvano Lizzit², Kazuhiro Yanagi³, Andrea Goldoni², Thomas Pichler¹
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²Sincrotrone ELETTRA, Trieste, Italy
³Tokyo Metropolitan University, Tokyo, Japan

A way to use single-walled carbon nanotubes (SWCNTs) as gas sensors is studying the changes in their electric response while interacting with gas molecules. With this perspective, several papers can be found in the literature but a large percentage corresponds to studies that use nanotube-material that is either highly defective or nonpurified, which obliges us to rethink the established sensing principles, or at least how to describe the sensing mechanism addressed to a specific nanotube-based sensor. Using photoemission and X-ray absorption, which are highly surface sensitive techniques, we have observed that physisorption governs the adsorption mechanisms of these molecules on the ultrapure metallicity sorted nanotubes. Additionally, we have observed that the reaction of the NOx molecules are governed by photoinduced effects.

¹ G.Ruiz-Soria et al. ACS Nano, 10.1021/nn405114z

MON 6
Optically transparent diamond-PDMS microfluidic system for electronic monitoring of cells

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Diamond thin films exhibit unique combination of electronic and material properties that is suitable for biological applications. Atomic and molecular diamond surface modifications can affect adhesion of cells, proteins or DNA molecules to diamond as well as diamond electrical conductivity [Sensors 9 (2009) 3549]. Here we report on the fabrication, and characterization of microfluidic system for in vivo-like monitoring of living cells. The system combines polydimethylsiloxane microfluidic channel(s) with the diamond thin film acting as optically transparent conductive electrode(s) and cell support at the same time. The fully transparent and re-sealable system can provide impedance (TEER) and solution-gated FET characteristics of cell culture medium,
cell insertion and cell incubation under perfusion conditions. The proposed system is thus suitable for simultaneous optical and electrical monitoring of cell motion, adhesion and proliferation.

We acknowledge the support of LNSM infrastructure and GACR project P108/12/0996.

MON 7
Influence of Sample Dimensionality on Near-Field Raman Enhancement
Ryan Beams\textsuperscript{1}, Luiz Gustavo Cancado\textsuperscript{2}, Ado Jorio\textsuperscript{2}, Lukas Novotny\textsuperscript{3}
\textsuperscript{1}Institute of Optics, University of Rochester, USA
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\textsuperscript{3}Photonics Laboratory, ETH Zurich, Switzerland

Tip-enhanced Raman spectroscopy (TERS) is a powerful technique for characterizing low dimensional samples such as organic molecules and carbon nanotubes. However, TERS has had limited success in studying graphene despite due to the confocal background overwhelming the near-field signal. We use the Raman modes in graphene to explore the influence of sample dimensionality on the TERS enhancement. Graphene is the ideal material for this study due to the presence of two-dimensional (2-D) Raman bands, such as the G and G\textsuperscript{′} bands as well as the 1-D disorder induced D band localized at the edges of a flake. We present TERS images of a graphene flake and find that the enhancement for the totally symmetric G\textsuperscript{′} band is larger than the G band enhancement, which was previously predicted and provides evidence that the TERS process is coherent (1). Finally the distance dependence of the TERS enhancement was studied and we found that the TERS signal for 2-D bands scales with the 8th power of the tip-sample separation, whereas 1-D bands scale with the 10th power in agreement with a previous study on carbon nanotubes (2).

(1) PRB 85, 235434(2012).
(2) PRL 103, 186101 (2009).

MON 8
Distance scaling of the energy transfer rate between a single semiconductor quantum dot and graphene
François Federspiel\textsuperscript{1}, Guillaume Froehlicher\textsuperscript{1}, Michel Nasilowski\textsuperscript{2}, Benoît Dubertret\textsuperscript{2}, Ather Mahmood\textsuperscript{1}, Bernard Doudin\textsuperscript{1}, Serin Park\textsuperscript{3}, Jeong-O Lee\textsuperscript{3}, David Halley\textsuperscript{1}, Pierre Gilliot\textsuperscript{1}, Stéphane Berciaud\textsuperscript{1}
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Graphene, as an atomically thin semi-metal, may be viewed as an ultimate quasi-
transparent electrode, while Colloidal semiconductor quantum dots (QDs) exhibit excellent light emission and light harvesting properties. It is thus natural to combine these two model systems into novel optoelectronic devices. In such conditions, the photophysical properties of QDs are expected to be dramatically affected by the neighboring graphene layer. In particular, energy and/or charge transfer may occur and govern the performance of the QD-graphene hybrid device. Here, we make use of time correlated single photon counting to investigate the photophysics of individual CdSe/CdS core/shell QDs physisorbed onto a graphene monolayer. We observe highly efficient Förster energy transfer, resulting in a shortening of the luminescence decay and subsequent luminescence quenching. The energy transfer rate is further monitored as a function of the distance $d$ between the QDs and the graphene layer. We obtain a quantitative agreement with a $1/d^4$ scaling, as expected for the Förster energy transfer rate between a "0-dimensional" emitter and an atomically thin acceptor surface.

**MON 9**

**Raman study of spherical colloidal CdSe/CdS nanocrystals**

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Colloidal nanocrystals (NC) have attracted a lot of interest because they show fascinating properties such as two-photon absorption, multiple exciton generation and narrow photoluminescence. The possibility to synthesize NCs with a precise control over their size, stoichiometry and crystal structure enables the use in systems like biological sensors, LEDs, lasers and solar cells. For those applications a high quantum yield and a long lifetime are of utmost importance. These properties all strongly depend on the electronic states on the surface of the NC. A coating with a suitable material has been shown to drastically improve these properties through surface passivation, resulting in a chemically more stable structure. However, for epitaxial grown shells, the lattice mismatch between the core and the shell material results in a strained crystal lattice, which in turn influences the optical and electronic properties. Thus, a detailed knowledge on the composition is required. In our study we analyze CdSe/CdS NCs with varying size and shell thickness. We employ Raman spectroscopy to analyze the structural properties of the crystal such as strain and the interface lattice.
MON 10
Raman Optical Activity of Carbon Nanotubes

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It is well known that Raman spectroscopy is a very useful tool for studying carbon nanostructures, especially nanotubes. To the contrary much less is known about Raman Optical Activity (ROA) of carbon nanotubes. We investigated theoretically the ROA spectra of single walled carbon nanotubes. Spectral intensities were calculated using standard time dependent linear response theory. Tight binding calculations were carried out to obtain the matrix elements of the necessary electromagnetic multipoles. Reliability of the method was tested on several chiral fullerene molecules (1). Vibrational properties (phonon dispersion and normal modes) were calculated on the density functional theory level exploiting the helical symmetry of the tubes. We show calculated Raman and ROA spectra of some selected carbon nanotubes as a function of laser excitation energy.

(1) P. R. Nagy, P. R. Surján, Á. Szabados, accepted by JCP

MON 11
Impurity-induced valley relaxation in graphene

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Valley polarization, as a non-equilibrium population of one valley, is the key to using valley degree of freedom as an information carrier. Experimental realization of valley polarization has been proposed in graphene but its applicability in electronics depends on the lifetime of valley polarization.

In this work, we determined the relaxation time of a valley-polarized state due to charged impurities in the substrate. The valley relaxation time is calculated from Boltzmann equation taking into account screening. We find that the valley relaxation time is inversely proportional to Fermi-energy, and it grows exponentially as the distance between the graphene plane and the impurities is increased. Unlike transport lifetime, the valley relaxation time depends on the atomic structure of the wavefunction due to large momentum transfer in intervalley scattering.
MON 12
Ultrafast measurment of charge carriers dynamics in few-layers of MoS$_2$

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The novel families of atomic-thick 2D materials become popular because of their unique electronic, mechanical and optical properties (1). It was showed that 2D materials such as layered metal dichalcogenides could be exfoliated into one and few layers (2). The primary photoexcitations in MoS$_2$ are excitons (2) with a binding energy close to 0.5 eV or even higher in single flakes. Their relaxation behavior has been described as the interplay of trapping, phonon-assisted interband transitions and radiative recombination (3). On the other hand, the observation of photocurrents and a photovoltaic effect suggests that photoexcitation of MoS$_2$ also generate charge carriers (4). Using method of ultrafast spectroscopy we show the photogeneration of long-lived charge carriers few-layers flakes of MoS$_2$ dispersed in an inert PMMA matrix. Charges are formed from both the A and B excitons with a time constant of approximately 1 ps during the fastest observed exciton relaxation process.

Reference
(3) Shi et al., ACS Nano (2013)

MON 13
Field effect and charging in layered 2D materials

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Recently, layered 2D materials have attracted a lot of attention because of their interesting physical properties. Particularly challenging is the possibility of doping these systems by using an ionic-liquid based field-effect transistor (ILFET). In ILFETs the charging of the nanolayers is substantial allowing for the investigation of the transition from a band insulator, to a metal and, eventually, to a superconductor (1,2). Despite the extensive use of such ILFETs many questions remain open, e.g., what changes are induced by the large electric field and how is the induced charge distributed? We develop a first-principles framework to describe nanolayers in ILFET configuration (3) with full inclusion of the external electric field and the charging of the system. We apply the method to ZrNCl and show that the doping profile is very different from what has been proposed in previous studies, questioning assumptions made so far. Our work shows that the phase diagram of ILFET doped ZrNCl should
be substantially revised (1) and points out crucial differences with Li intercalated bulk ZrNCl.
(1) Nat. Mater. 9, 125(2010)
(2) Science 338, 1193(2012)
(3) submitted to PRB

MON 14
Effect of annealing temperature on the electronic state of nitrogen incorporated into mesoporous carbon

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Nitrogen-doped carbon materials have been synthesized by deposition of acetonitrile vapor on CaO nanoparticles, prepared by thermolysis of calcium tartrate in an inert atmosphere. Transmission electron microscopy (TEM) revealed that removing of CaO nanoparticles from the products using diluted hydrochloric acid produces mesopores in graphitic network. We found that layer graphitization and chemical state of incorporated nitrogen are varied with the synthesis temperature. The samples were annealed in vacuum chamber of X-ray spectrometer at the temperatures 800°C and 1100°C. A change in the electronic structure of nitrogen-doped mesoporous carbon was monitored by X-ray photoelectron and near-edge X-ray absorption fine structure spectroscopy at BESSY II. The rest nitrogen concentration and nitrogen transformation were shown to depend both on the temperature of material synthesis and material annealing.

The work was supported by RFBR grant No.13-03-00884.

MON 15
Dislocations in Bilayer Graphene - Materials Science meets Physics

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Tailoring the band structure of bilayer graphene can be realized by, e.g., elastic straining or the variation of the local stacking. Dislocations, as fundamental defects of 3D-materials, combine both and are therefore promising to induce appropriate modifications. In graphene, dislocation movement is restricted to the basal plane, which enables the confinement in between only two layers. Besides plastic deformation, dislocations are induced due to misfit during growth, e.g., of epitaxial graphene on SiC. Accordingly, we used this material to prepare bilayer graphene membranes.
This study is about the structure of dislocations in such membranes and their impact on the graphene’s properties. Burgers vector analysis revealed that all dislocations are partial dislocations, each leading to a change of the stacking from AB to BA. The equidistant alignment of the dislocations owes the absence of stacking fault energy. Each dislocation induces pronounced buckling as result of strain accommodation. From atomistic simulations we learned that the buckling completely redistributes the usual strain concentration at the dislocations cores resulting in a surprising strain state of the material.

MON 16
Probing weak interactions and charge transfer at the interfaces between organic molecules and graphene field effect transistors

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Graphene exhibits many fascinating physical properties which make it very attractive for use in electronic and sensing applications. Since graphene has a two-dimensional structure and every atom is exposed on the surface, the electrical properties of graphene are highly sensitive to the smallest change of charge on its surface. Recent experiments have demonstrated that these charge changes induced by adsorption of molecules can be monitored by measuring electrical conductivity in graphene field-effect transistors (FETs). Although graphene sensors have proven to be extremely sensitive, their selectivity remains a major problem for their practical use. Here we present a combined experimental and theoretical study of small organic molecules adsorbed on graphene FETs by investigating their role on the electronic structure modification of graphene. In particular, we explore the mechanism of charge transfer doping and the existence of molecular specific signatures in FET electrical conductivity measurements for selective chemical sensing. Electron transport data are compared to synchrotron-based X-ray photoelectron spectroscopy measurements and density functional theory calculations.
MON 17
Single-walled carbon nanotubes as a template for growth of graphene nanoribbons and polyaromatic chains

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Single-walled carbon nanotubes (SWCNTs) can serve as nanoscale chemical reactors. Molecules placed inside SWCNTs are well protected from the external environment and can form one dimensional structures which are thermodynamically unstable in the absence of encapsulating template. We demonstrate that the filling of SWCNTs with different average diameter and the change of the synthesis thermal parameters results in formation of various structures inside. The experimental results are in good agreement with the performed calculations. Optical properties of the encapsulated graphene nanoribbons (1) and polyaromatic chains have been studied via photoluminescence (PL), absorption and Raman spectroscopies (2). The PL mapping showed the new features corresponding to the inner structures in the visible spectral range. We have investigated the response from the encapsulated compounds and side products, which were formed outside of the nanotubes.

Funding by RFBR grants 13-02-01354, 14-02-00777 and MESRF grants 14.513.12.003, SP-7362.2013.3 is acknowledged.
(1) A.V. Talyzin et al., Nano Lett. 11, 4352 (2011)
(2) A.I. Chernov et al., ACS Nano 7, 6346 (2013)

MON 18
Graphene nanostructures on boron nitride: superlattice effects in a magnetic field

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We study the density of states (DOS) and individual eigenstates of graphene flakes placed on a hexagonal boron nitride substrate in a perpendicular magnetic field using the tight-binding approach. We approximate the substrate by a periodic, hexagonal moiré potential. The largest geometrically possible periodicity is 13.8 nm (1). In this case, secondary Dirac cones emerge close to the original Dirac point due to zone folding caused by the supercell periodicity. The resulting band structure gives rise to a rich structure in the magnetic-field dependent DOS, e.g., at the zeroth Landau level, a Hofstadter butterfly emerges. Additionally, the band gaps induced by the moiré result in the simultaneous appearance of relativistic (square-root) and non-
relativistic (linear) Landau level structures. Quantitative comparison of the emerging fine structure to analytic solutions of the Dirac equation offers a means for extracting details of the substrate potential from experiment. We find several avoided crossings with secondary Landau levels similar to the case of pristine graphene quantum flakes (2).

(1) M. Yankowitz et al., Nat Phys 8 (2012) 382
(2) F. Libisch et al., PRB 81 (2010) 245411

MON 19

Synthesis conditions of carbon nanotubes with the Chemical Vapour Deposition method

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The paper describes a synthesis of carbon nanotubes obtained with the chemical vapour deposition method (CVD) and the impact of the process parameters on its efficiency and quality of carbon nanotubes. Carbon nanotubes were synthesised on a silicone substrate containing a catalyst in the form of a thin film (2 nm Fe, 20 nm Al\textsubscript{2}O\textsubscript{3} and 500 nm SiO\textsubscript{2}) by using methane (CH\textsubscript{4}) and ethylene (C\textsubscript{2}H\textsubscript{4}) as a source of carbon, argon (Ar) as a carrier gas and hydrogen (H\textsubscript{2}) to regulate a chemical reaction of hydrocarbons decomposition. The influence of temperature, process time and a hydrocarbon gas flow rate on the quality of synthesised carbon nanotubes was examined. A Raman spectrometer, high-resolution electron microscope and high-resolution transmission electron microscope were used to examine the structure and geometric characteristics of the nanomaterials produced. The optimum conditions of the synthesis process were characterised in order to obtain high quality carbon nanotubes containing small amounts of contaminations.

MON 20

Raman spectroscopy of two-phonon processes on isotopically labelled turbostratic and Bernal stacked bilayer graphene

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Raman spectroscopy is a key tool to characterise carbon nanomaterials, such as graphene. This work is focused on the stacking of the layers in bilayer graphene. The stacking order can usually be determined according to the shape of the 2D band. However, it can be difficult to study the individual layers in a bilayer structure since they yield very similar signals. Isotopic labelling can solve this issue as the mass difference between the two isotopes yields Raman signals with phonon frequencies shifted from one another, allowing studies of each layer individually. In an attempt to clarify the mechanism of two-phonon Raman processes, such as 2D and 2D\textsuperscript{+} bands, turbostratic and Bernal stacked grains were investigated on isotopically labelled bilayer graphene. It was found that for Bernal stacked layers, the Raman...
features originated by two phonons have 3 different components assigned to 13C, 12C or 13C/12C. For turbostratic layers the behaviour is different, as each layer yields a signal similar to single layer graphene. This study represents a step forward in understanding the contribution of each layer, for both Bernal and turbostratic bilayer graphene.

**MON 21**

**Control and optimization of Chemical Vapor Deposition of Graphene on thin Cu film at low temperaure**

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Among the various methods for graphene large scale production, Chemical Vapor Deposition (CVD) is considered as very promising. Dealing with Cu thin films instead of foils leads to a family of problems related to the stability of the film at high temperatures. Incidentally, critical temperatures for the stability of thin Cu films are close to the temperatures needed for CVD (around 1000 °C).

By monitoring in-situ the thin film dewetting dynamics, the conditions at which film rupture and agglomeration is prevented can be found even for films $\sim$100 nm thick. By using a C precursor (ethanol) that catalyses at temperatures lower with respect to methane we were able to perform Low Pressure CVD (LPCVD) of graphene, e.g. on 200 nm Cu thin films. The same recipe applied on Cu foils leads to worse results suggesting a higher catalysis activity in films instead of foils.

In this work we report improvements of previous results by means of a better control of the process and by studying the influence of hydrogen in the deposition step.

**MON 22**

**Single-walled carbon nanotube assemblies for solar cells**

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The unique nanoscale physical and chemical properties make single-walled carbon nanotubes (SWNTs) stand out as promising building blocks for the next generation energy and electronic devices. However, the much inferior micro/macroscale properties have been hindering their real-world application. In this study, we discuss two different SWNT assemblies at the micro/macroscale, the random-oriented network and microhoneycomb network, using SWNT-Si solar cells as a benchmark. The random-oriented network possesses both high transparency and conductivity, leading
to a 11% efficiency; while the microhoneycomb network organizes charge transfer in an effective way, resulting in a record-high 72% fill factor. Both of the results are stable after months, which is attributed to the high-purity pristine SWNTs. The detailed mechanisms are also discussed.

2. K. Cui et al, submitted

MON 23
Stable doping of graphene with MoO$_3$ and WO$_3$

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Graphene has a great potential to replace indium tin oxide (ITO) as transparent, flexible conductor. Although pristine graphene has a high mobility, its intrinsic charge carrier density is close to zero so that doping is necessary to obtain sheet resistances useful for industrial applications. The deposition of an oxide layer is the most promising strategy to obtain a stable doping. In this report, we study the doping mechanism and the stability of two adsorbed oxides with high working functions: MoO$_3$ and WO$_3$. By in-situ ultra-violet photoemission spectroscopy and in-situ electrical conductive measurements, we observe the injection of holes into the graphene layer, hence increasing its conductivity. We evaluate the stability over a range of temperatures and pressures. The results allow us to establish a direct comparison between the two oxides and to determine advantages over less stable dopants (e.g. I$_2$). The materials studied in this report are microelectronic-compatible and liable to be employed at a large scale production, thus representing a step towards ITO replacement by a transparent and flexible material.

MON 24
Nanocomposites graphene/exfoliated graphite/epoxy resin: synthesis, electrical properties and electromagnetic shielding

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Nanocomposites are nowadays one of the most promising materials. Among different fillers (CNTs, silicon carbide nanowires NWSiC) already used with epoxy resin matrices, graphene and exfoliated graphite (EG) have some characteristics that makes them unique for electromagnetic shielding materials. However, there is still an unresolved problem of proper dispersion to ensure samples homogeneity. To overcome this drawback, the inorganic fibers were proposed. 0.25 phr NWSiC, added to the EG 1 phr/epoxy resin sample, efficiently prevents filler agglomeration. Within this
study the following nanocomposites samples have been produced (fillers content in phr): NWSiC/epoxy: 0.25, 0.5, 1, 6; NWSiC/MWCNTs/epoxy: 0.25/1, 0.5/1, 1/1; NWSiC/EG/epoxy: 0.25/1, 0.5/1, 1/1; EG/epoxy: 0.25, 0.5, 0.75, 1, 1.5, 2; MWCNTs/epoxy: 0.25, 0.5, 0.75, 1, 1.5, 2. NWSiC were obtained in combustion synthesis and EG was produced from intercalated graphite using microwaves. Samples mechanical, dynamical, electrical and magneto-electrical properties have been characterized, revealing significant improvement of pure resin features.

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**MON 25**

*Fabry-Perot interference patterns in a carbon nanotube with highly transparent contact*

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Carbon nanotubes with highly transparent metallic contacts constitute prime examples of ballistic electron waveguides. We present a theoretical analysis of Fabry-Perot interference patterns in the conductance using both a scattering matrix calculation where the reflection at the contacts is treated as a perturbation and a numerical calculation obtained from a real-space microcopical model. The data are compared to low-temperature measurements of an ultra clean suspended carbon nanotube, exhibiting strikingly high conductance and low reflection at the interfaces between tube and metal where a complex oscillatory behavior is observed, varying across the measured gate voltage region.

**MON 26**

*Analytical TEM investigation of high-quality GO*

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The ongoing interest in graphene and related carbon-based allotropes is accompanied by two important challenges. First, the large scale production of well-defined high-quality systems as well as the thorough analytical investigation of the obtained compounds. One up-scalable route to graphene flakes is the oxidation of graphite with subsequent exfoliation, yielding graphene oxide (GO). After reduction, GO can be converted to graphene, generally with plenty of defects within 1-2 nm. Here, we present a TEM study of GO with an almost intact carbon framework (ai-GO), synthesized by the authors, and reduced ai-GO using aberration corrected HRTEM with an analytical insight into the chemical peculiarities of ai-GO and reduced ai-GO by EELS and EDX. TEM samples are prepared by Langmuir-Blodgett technique, giving
high yields of freestanding membranes spanned over substrate holes. Upon in-situ thermal treatment under vacuum conditions we are able to follow the reduction of GO to graphene. For the first time, we can visualize a significantly higher integrity of the carbon framework in ai-GO compared to conventional graphene derived from GO.

**MON 27**

**Graphene-molecule interactions and the potential for selective chemical sensing by graphene FETs**

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Graphenes two dimensional nature, highly sensitive unique electrical properties and low intrinsic noise characteristics make it a prime candidate for the creation of a new generation of molecular sensors. Sensors that could provide single molecule sensitivity and selective determination of the sensed molecules. DNA sequencing technology is an area that stands to benefit greatly from such advances in sensing technology. In order to explore the suitability of graphene for such devices we have studied the electrical conductivity changes induced in graphene field effect transistors from the absorption of DNA nucleobase. He we report on the potential of single layer CVD graphene devices for single molecule selective sensing. We consider the current theory, and its limitations for more complex molecular structures and the effects of defects in the graphene and supporting substrate on device operation.

**MON 28**

**Toward Sensitive Graphene Nanoribbon-Nanopore Devices by Preventing Electron Beam Induced Damage**

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Graphene-based nanopore devices are promising candidates for next-generation DNA sequencing. Here we fabricated graphene nanoribbon-nanopore (GNR-NP) sensors for DNA detection. Nanopores with diameters in the range 2-10 nm were formed at the edge or in the center of graphene nanoribbons (GNRs), with widths between 20 and 250 nm on silicon nitride membranes. GNR conductance was monitored in situ during nanopore formation inside a transmission electron microscope (TEM). GNR resistance increases linearly with electron dose and GNR conductance and mobility decrease by a factor of 10 or more when GNRs are imaged at relatively high magnification with a broad beam prior to making a nanopore. By operating the TEM in scanning TEM (STEM) mode, in which the position of the converged electron beam can be controlled with high spatial precision via automated feedback, we prevent electron beam-induced damage and make nanopores in highly conducting GNR sensors. This method minimizes the exposure of the GNRs to the beam resulting

MON 29

Novel fabrication method of lateral spin valve devices based on graphene on hexagonal boron nitride

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Despite tremendous efforts in improving graphene-based spin transport devices the measured spin lifetimes are still orders of magnitude less than theoretically predicted. Contact-induced spin dephasing has recently been identified as the bottleneck for spin transport through Co/MgO spin injection and detection electrodes. It can, however, significantly be suppressed for devices with large contact resistance area products (1). Simultaneously, a strong reduction of the charge carrier mobility is usually observed. We present a new method to fabricate graphene-based non-local spin valves on hexagonal boron nitride yielding spin lifetimes above 2 ns, spin diffusion length above 10 μm and large charge carrier mobilities above 20.000 cm²/Vs.


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MON 30

Fast synthesis and characterization of ultrathin graphite foil

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Graphene is a two-dimensional (2D) atomic crystal consisting of carbon atoms arranged in a hexagonal lattice. This single layer of carbon atoms may be the most amazing and versatile substance available to mankind. The growing number of potential applications generates an extremely high interest in searching for an easy method of graphene large-scale production. In this paper we present a very simple and low cost method for bulk synthesis of ultrathin graphite foil. The process is a fast, one-step and autothermic reaction within different mixtures of a strong metal
MON 31
In situ Raman spectroscopy of heat treated isotopically labeled turbostratic and Bernal stacked bilayer graphene

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One of the greatest issues of nanoelectronics today is how to control the heating of the components. Graphene is a promising material in this area and it is therefore essential to study its thermal properties. In this work, the effect of heating a bilayer structure has been investigated using in situ Raman spectroscopy. It is difficult to study the individual layers in a bilayer structure since they yield very similar signals. Here, this is solved by studying a bilayer where the two layers are composed of different isotopes of carbon. The different mass results in different phonon frequencies from the two layers, allowing information about the individual layers to be obtained. Therefore, this technique allows characterization of the effects of heating on each individual layer of the bilayer.

This technique was used to investigate the influence of different stacking order. It was found that in bilayer graphene grown by chemical vapor deposition (CVD) the two layers behave very similarly, for both Bernal stacking and randomly oriented structures, while for transferred samples the layers act more independently. This highlights a significant dependence on sample preparation procedure.

MON 32
Dimensionally confined superconductors as probes for absolute spin-polarization

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In their pioneering work on spin-polarized tunneling Robert Meservey and Paul Tedrow employed superconducting electrodes in standard thin film sandwich junctions to probe the spin-polarization of ferromagnetic materials (1). In order to create a local probe for absolute spin-polarization we transfer this concept of superconducting detector electrodes to scanning tunneling microscopy (STM). Studying superconducting vanadium STM tips on normal conducting samples in high magnetic fields at 10 mK we found that the superconducting properties of those tips are deter-
mined by the confinement due to the specific tip geometry. These superconducting vanadium STM tips have been employed to probe local variations in the absolute spin-polarization of Co nanoislands on Cu(111). We find good qualitative agreement with experiments carried out by SP-STM (2). In addition, the absolute values of the measured spin-polarization allow for further analysis of the orbital wave functions involved in the tunneling process.

(2) H. Oka et al., Science 327, 843 (2010).

MON 33
Gate-tunable phase coherence time in encapsulated bilayer graphene
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Bilayer graphene (BLG) combines high carrier mobilities with a gate-tunable band gap, making this material an interesting platform for mesoscopic devices. Charge carriers in BLG mimic massive Dirac fermions leading to an unconventional sequence of Landau levels and fully broken symmetry states are accessible at magnetic fields of a few Teslas. Here, we show transport measurements of two terminal contacted bilayer graphene encapsulated in hexagonal boron nitride. The investigated devices exhibit carrier mobilities ranging from 40.000 to 80.000 V s/cm² at temperatures around 300mK. We show quantum Hall effect measurements exhibiting a full degeneracy breaking of the zero Landau level above B=6T. From weak localization measurements we extract the phase coherence time \(\tau_\Phi\) as function of charge carrier density and temperature. We observe a gate-tunable phase coherence time with values ranging from \(\tau_\Phi \approx 20\)ps at the charge neutrality point to \(\tau_\Phi \approx 240\)ps for \(n=0.8 \times 10^{12} cm^{-2}\). Most interestingly, we find that \(\tau_\Phi\) is limited by electron-electron interaction which is confirmed by a qualitative agreement with the results from Altshuler et al.

MON 34
Theoretical investigation of the new type of nanodisplacement devices based on C/BN joined nanotubes
Aleksandr S. Fedorov1,2,3, Aleksandr A. Kuzubov2,3, Lyudmila V. Tikhonova3
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It is proposed and theoretically investigated the new type of the nanodisplacement
devices. Now such devices contain piezodrives which have large dimensions and therefore can not be used in future nanodevices.

Here we offer a new type of the device. It consists of a single-layer boron-nitride nanotube (BNNT) which is grown around the conductive carbon nanotubes (CNT). Applying to the CNT of the electrostatic potential of $10 \div 100$ volts creates an electrical field acts on the positive and negative B and N ions of the BNNT. As a result, these ions move along the NT surface normal in opposite directions.

Our calculations show that for given electrical potential the forces acting on B and N ions would be $\approx 1 \text{ eV/Å}$. This leads to the normal displacements of the ions of $\approx 0.1 \text{ Å}$. It leads to a shortening of the BNNT length of the order of several percents. Attaching to the BNNT holder leads to holder’s substantial longitudinal displacement when the CNT electrostatic potential is changed.

Carried out detailed ab initio calculations using the VASP software show the possibility of technical realization of such nanodevices.

**MON 35**

**Electronic structure of fluorinated graphite intercalation compounds with acetonitrile**

Yuliya Fedoseeva¹, A.V. Okotrub¹, L.G. Bulusheva¹, I.P. Asanov¹, D.V. Pinakov¹, G.N. Chekhova¹

¹Siberian Branch of the Russian Academy of Sciences, Nikolaev Institute of Inorganic Chemistry, Novosibirsk

The electronic structure of fluorinated graphite compounds C2Fx (x=0.49-1.05) intercalated with acetonitrile yCH3CN (y=0.084-0.136) have been studied by X-ray photoelectron spectroscopy (XPS) and Near edge X-ray absorption fine structure (NEXAFS) spectroscopy. It was demonstrated that matrix of fluorinated graphites consists of both fluorinated carbon and graphite-like areas. The size of these areas depends on the fluorine content. The features of electronic interaction between guest molecules acetonitrile and fluorinated graphite layers were found. The thermal stability of the fluorinated graphite intercalation compounds at 250 C in UHV was studied by in situ XPS and NEXAFS methods. It was found that under high temperature fluorinated graphite compounds partially lost fluorine atoms, but electronic states of acetonitrile molecules did not change.

The reported study was supported by RFBR, research project No. 14-03-31359.

**MON 36**

**Optical Properties of Single-Walled Carbon Nanotubes filled with CuCl by Gas-Phase technique**

Pavel V. Fedotov¹, Alexander A. Tonkikh¹, Elena D. Obraztsova¹

¹A.M. Prokhorov General Physics Institute, RAS, Moscow

Properties of single-walled carbon nanotubes (SWNTs) can be modified by filling their internal cavity with various materials. We demonstrate that the encapsulation
of SWNTs with CuCl molecules through gas phase under certain conditions can lead to substantial transformations of their optical absorption and Raman spectra. As in case of iodine filling (1), this may happen due to formation of various CuCl 1D crystals inside nanotubes. Such encapsulation leads to a significant charge transfer between 1D crystal and nanotube surface. Due to a high p-type doping, nanotubes in this CuCl@SWNT composite become much more conductive, while their optical transparency coefficient is highly improved comparing with undoped nanotubes. (1) A. A. Tonkikh, E.D. Obraztsova, et al., Physica Status Solidi B 249 (2012), 2454-2459. The work is supported by RFBR projects 14-02-31829, 14-02-31818 and 13-02-01354.

MON 37
The effect of titania precursor on the morphology of the prepared TiO2/MWCNT nanocomposite materials
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Since material science is of great importance the application of composite materials based on carbon nanotubes is widely investigated. Current work aimed at preparing nanocomposites of TiO2/MWCNT using an impregnation method combined with slow hydrolysis. Different titanium alkoxide compounds [Ti(OEt)4, Ti(OiPr)4 and Ti(OBu)4] were used as precursor materials to cover the surface of carbon nanotubes in ethanolic solution. In our samples the mass ratio was 10:1 (TiO2:MWCNT). The produced composite materials were characterized by X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), Raman microscopy, transmission (TEM) and scanning electron microscopy (SEM) techniques, and the analysis of the specific surface area (BET) was also executed. The morphology of the amorphous layer was somewhat different, however all precursors were suitable for the preparation of homogenous coverage TiO2-layer on the surface of MWNT using the above-mentioned synthesis method. With heat treatment the covering amorphous titana layer was converted into crystalline anatase phase TiO2. These new MWNT-based composite materials are very promising candidates for gas sensors or photocatalysts.
**MON 38**  
**High Frequency Impedance of Single-Walled Carbon Nanotube Networks on Transparent Flexible Substrate**  
M. Zahir Iqbal$^{1,2}$, Jordi Pérez-Puigdemont$^1$, Jonghwa Eom$^2$, Núria Ferrer-Anglada$^1$  
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Transparent and flexible networks with randomly distributed single-walled carbon nanotubes, SWCNTs, are emerging as novel materials for various applications, particularly as electronic materials. The carbon nanotube networks are also expected to be used in the development of logic circuits such as radio-frequency identification tags and flexible e-papers. For such applications, the use of SWCNT networks on flexible plastic substrate has various advantages including fast deposition process, low-temperature and non-vacuum process, which help to reduce the cost of devices.

We investigate the frequency dependent impedance measurements up to 20 GHz, of SWCNT networks on transparent and flexible substrates, by using two different techniques: two probe and Corbino reflectometry setups. The thickness and roughness of the thin film are examined by AFM. The impedance measurements show the onset frequency decreases with increasing the density of SWCNT. High frequency impedance as a function of the onset frequency shows the same slope in both measuring techniques. The onset frequencies observed by Corbino technique are three orders of magnitude higher than those observed by two probe.

**MON 39**  
**Electron-phonon coupling in doped graphene**  
Jörg H. Fink$^1$, A. Fedorov$^{1,2}$, A. Grüneis$^{1,3}$, D. Haberer$^1$, N. Verbitskiy$^{3,4}$, O. Vilkov$^2$, D. Vyalikh$^{2,5}$, C. Struzzi$^6$, S. Fabris$^6$, L. Petaccia$^6$, D. Usachov$^2$, M. Knupfer$^1$, B. Büchner$^{1,5}$  
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$^5$TU Dresden  
$^6$Elettra Sincrotrone Trieste

Angle-resolved photoemission spectroscopy (ARPES) was carried out to perform a search for an electron donor for graphene, capable of inducing high electron-phonon coupling (EPC) and superconductivity. We examined the widespread electron donors Cs, Rb, K, Na, Li, and Ca and determined for each dopant the full electronic band structure, the Eliashberg function and the superconducting critical temperature $T_c$ from the spectral function measured by ARPES. The Eliashberg function has high-energy peaks related to the well-known graphene derived optical phonons. Unexpectedly, a new low-energy peak appears for all dopants with an energy and intensity that
depends on the dopant atom. By investigating the dopant dependence of this peak we show that it must come from a dopant related vibration. The low energy and high intensity of this peak is crucially important for achieving high EPC and hence also for superconductivity. The case of Ca doped graphene yields the highest EPC which is expected to sustain values of Tc=1.5 K which provides strong experimental support for the possibility to achieve superconductivity in graphene.

**MON 40**

**Excitons and disorder in CH3NH3PbI3 perovskite**

Ana Akrap², Jaćim Jaćimović², Andrea Pisoni¹, Csaba Forró¹, Dirk van der Marel², László Forró¹, Endre Horváth¹

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The lead-halide octahedra in organic-inorganic hybrid compounds can form 0, 2 and 3D structures. Recently, a 3D member of this family, the methylammonium lead iodide (CH3NH3PbI3) perovskite turned out to be extremely efficient material in photovoltaic cells, with a light conversion efficiency up to 15% (M.M. Lee et al., Science 338, 644 (2012). The investigation of the basic physical properties of this material is primordial for improving its performance in solar cells. We have grown large single crystals with mirror-like surfaces which allowed to address the exciton dynamics by ellipsometry. We have evaluated the exciton binding energy (Eb), the lifetime and its interaction with the continuum through the Fano lineshape. The d.c electrical resistivity shows a low-lying impurity level which ionization by the incident light might influence Eb.

**MON 41**

**MoS₂ thin films in electronic devices**

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2D molybdenum disulfide (MoS₂) is an exciting material for future nanoscale (opto)-electronics. Thus far, the low throughput of high quality MoS₂ thin films has hindered the development of devices, and so a scalable method is required to fully exploit its exceptional properties. We present a facile route to the manufacture of devices from MoS₂. Highly homogeneous thin films are produced, over large areas, by thermally assisted sulfurisation of metalised substrates. Fine control over the film thickness is achieved by modifying the thickness of the sputtered metal layers. Alternatively MBE produced metal layers are used to create very high quality films, nano-ribbons and layered structures. The thinnest films exhibit photoluminescence, as predicted for monolayer MoS₂. Gas sensors were produced, displaying sensitivity to NH₃ down to 400 ppb. Our versatile device production method is adaptable for future electronic devices. An advantage of our sputtered process is that it creates nano-crystalline films, with an abundance of catalytically active edge states. Thus leading to applica-
tions as a potential replacement for precious metals in hydrogen evolution reactions.

**MON 42**

**Origin of apparent sublattice symmetry breaking in scanning tunneling microscopy images of monolayer graphene on SiO2.**

Alexander Georgi¹, Christian Saunus¹, Marco Pratzer¹, Marcus Liebmann¹, Markus Morgenstern¹

¹2nd Institut of Physics B, RWTH Aachen University and JARA-FIT, Aachen, Germany

We probe natural nanomembranes appearing in monolayer graphene on a SiO2 substrate by a scanning tunnelling microscope (1). The membrane can be lifted up to 0.1 nm with pm precision induced by the electrostatic and van der Waals forces between tip and membrane (2), depending on the tip-sample distance. The atomic appearance of the nanomembrane changes during the lifting process. At small and large lifting heights, we measure a hexagonal symmetry, whereas at an intermediate lifting height a triangularly arranged symmetry is observed, especially the atoms of one sublattice appear 3 pm higher than the other sublattice. This effect can be explained neither by an atomic buckling nor by a strain induced Peierls transition. It can be explained by an imaging effect probably caused by a small change of the van der Waals forces between the last triangular arranged tip atoms and the relative tip position with respect to the carbon lattice.


**MON 43**

**Indirect doping effects from impurities in MoS2-BN heterostructures**

Roland Gillen¹,², John Robertson², Janina Maultzsch¹

¹Institut für Festkörperphysik, TU Berlin, Germany
²Department of Engineering, University of Cambridge, UK

Two-dimensional semiconductors from layered dichalcogenides MX₂ (M= Mo,W,...; X= S,Se...) attracted tremendous interest over the past couple of years for their promising electronical and optical properties (1). An important factor for the usability of such materials in applications is their behaviour in compounds with other materials, such as BN or graphene, to form novel materials (2).

Motivated by a recent study (3) of MoS₂ on SiO₂, we performed density functional theory calculations on heterostructures of single layers of hexagonal BN and MoS₂ to assess the effect of doping in the BN sheet and of interstitial atoms on the electronic properties in the adjacent MoS₂ layer. We find that n-doping of the boron nitride subsystem by O, C and S impurities should cause noticeable charge transfer into the conduction band of the MoS₂ sheet and a distinct change of band offsets, while p-doping leaves the MoS₂ layer unaffected. Intercalated Na atoms also lead to
a metallic ground state of the MoS$_2$ subsystem.

(1) Mak et al., PRL 105, 136802 (2010)
(3) Dolui et al., PRB 87, 165402 (2013)

**MON 44**  
**Modelling PFO-BPy-SWCNT Heterojunctions**  
Livia Noemi Glanzmann$^1$, Duncan J. Mowbray$^1$, Angel Rubio$^1$

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Single walled carbon nanotubes (SWCNT) are promising candidates for photovoltaic (PV) active layers in organic solar cells. To obtain high on/off current ratios, enriched semiconducting SWCNT solutions not containing metallic SWCNT are favourable. Solubilizers are found to selectively disperse SWCNTs. The copolymer of 9,9-di-octylfluorenyl-2,7-diyl and bipyridine (PFO-BPy) delivers dispersions containing 97% (6,5)-SWNT. The first part of our theoretical investigations is focused on modelling the PFO-BPy-SWCNT hybrid system to gain information about the geometries and interactions. We hope to find explanations for the selective adsorption of the polymer on the chiral (6,5)-SWCNT. In a second step we are focused on the absorbance and electron-hole dynamics to understand the heterojunction and tune its optical absorption.

**MON 45**  
**Exploiting the micelle-swelling technique to enhance the nanotube-molecular switch interaction**  
Mareen Glaeske$^1$, Pascal Bluemmel$^1$, Antonio Setaro$^1$, Stephanie Reich$^1$

$^1$Department of Physics, Freie Universität Berlin, Berlin

The optical properties of carbon nanotubes can be altered by functionalization with molecular switches. In particular, the interaction of the tubes with molecular dipole switches is supposed to influence their optoelectronic response. A promising candidate is spiropyran: In its closed form it possesses a small dipole moment, whereas the ring opened form merocyanine exhibits a strong dipole moment. We present spiropyran-carbon nanotubes complexes obtained by micelle swelling. In the micelle swelling technique the molecules enter the micelle stabilizing the carbon nanotube, which results in a minimum molecule-tube distance. Our adaptation of the technique showed to be successful in altering the optical response of carbon nanotubes. The merocyanine form changed the optical properties of the nanotubes, whereas spiropyran showed no significant effect. We observe shifts in the excitation and emission energies of the merocyanine-carbon nanotubes complexes. This effect is strongly dependent
on the coverage of the molecular moiety. We compare our experimental findings to recent calculations of changes in the optical transition energies in the vicinity of a dipole switch.

MON 46
CVD synthesis and MW plasma etching of carbon nanotube arrays
D.V. Gorodetsky\textsuperscript{1}, O.V. Polyakov\textsuperscript{1}, M.A. Kanygin\textsuperscript{1}, L.G. Bulusheva\textsuperscript{1}, A.V. Okotrub\textsuperscript{1}
\textsuperscript{1}Nikolaev Institute of Inorganic Chemistry, Novosibirsk

Arrays of aligned CNTs were produced by the CVD method. After that the CNTs arrays on Si substrate were treated in the microwave (MW) hydrogen plasma discharge with an operating frequency 2.45 GHz and maximum input MW power of 5 kW. The obtained samples were examined by scanning electron microscopy, transmission electron microscopy and Raman spectroscopy. It was shown that the CNTs ends are etching and outer edges were destructed. The correlation between the etching rate and the power of MW discharge was found. The parameters for synthesis of diamond microcrystals on CNT surface by plasma treatment were determined. The field emission (FE) properties of these modified structures were measured. As a result, the FE threshold of plasma-treated samples is significantly decreased compared to initial CNTs arrays.

MON 47
Fabrication and electrical characterisation of graphene resonators
Eldad Grady\textsuperscript{1}, Enrico Mastropaolo\textsuperscript{1}, Tao Chen\textsuperscript{1}, Andrew Bunting\textsuperscript{1}, Rebecca Cheung\textsuperscript{1}
\textsuperscript{1}Institute for Integrated Micro and Nano Systems, University of Edinburgh, Edinburgh

Single layer graphene resonators with up to 7 mm in length are presented. Research of graphene resonators has been focused so far on the high frequency regime. The goal of this work is the development of a sensitive sensor for the low frequency regime, specifically for acoustic waves.

To fabricate these devices, trenches have been patterned in silicon followed by silicon dioxide growth around the trenches. After depositing electrical contacts, a single layer graphene sheet was transferred onto the chips.

The quality of graphene was confirmed by Raman spectroscopy to be pristine single layer. Electrical characterisation of the samples will be taken and a comparison with different metal contacts will be presented. Optimal graphene-metal contacts will be discussed.
MON 48
Introducing Cellulose Polymers for Graphene handling
Toby Hallam\textsuperscript{1}, Alan Bell\textsuperscript{1}, Nina C. Berner\textsuperscript{1}, Georg S. Duesberg\textsuperscript{1}
\textsuperscript{1}CRANN, Trinity College Dublin, Dublin

With 10 years since the contemporary isolation of graphene, an increasing industrial and commercial emphasis is now being placed on two dimensional materials. As such we must inspect the validity of some common graphene processing techniques. For many applications, in particular in electronics, where CVD grown graphene is used, it needs to be transferred, generally employing a polymer as a support layer. This process step is crucial for the overall integrity and electronic performance of the graphene. In this work we will introduce cellulose polymers for use in graphene handling and compare them with the more common PMMA and Polycarbonate alternatives. Microscopy techniques such as AFM, Raman, He-Ion and SEM microscopy will be combined with XPS and GFET transport measurements to build up a complete picture regarding the morphology, structural integrity and electrical performance of CVD graphene when transferred using traditional and cellulose-based polymers.

MON 49
Differences in the Intensity Behavior of RBM, G, and 2D Raman Modes in Carbon Nanotubes under Electrochemical Gating
Benjamin Hatting\textsuperscript{1}, Friederike Ernst\textsuperscript{2}, Stephanie Reich\textsuperscript{1}
\textsuperscript{1}Institut für Experimentalphysik, Freie Universität Berlin, Berlin
\textsuperscript{2}Department of Physics, Columbia University, New York

The Raman intensity of carbon nanotubes under electrochemical gating decreases when applying a gate voltage, which has previously been explained in terms of a decrease in absorption oscillator strength due to screening\textsuperscript{(1)}. This decrease in intensity occurs as soon as any gate voltage is applied in metallic tubes, whereas semiconducting tubes exhibit a plateau of constant intensity around zero gate voltage. We present results of electrochemical Raman measurements of the relative intensities of the RBM, G, and 2D modes in carbon nanotube ensembles. Unexpectedly, we observe that the RBM intensity decreases up to two times faster than the 2D and G intensities, which cannot be due to changes in the absorption strength. To interpret our findings, we consider the different resonance mechanisms and widths of the resonant windows. We also present results of measurements of the electrochemical Raman intensity behavior in enriched samples to study the influence of polychirality. (1) Steiner, M. et al., Nano Letters, 2009, 9, 3477-3481
MON 50
Common Concepts in Carbon Allotrope Functionalization

Frank Hauke\textsuperscript{1}, Andreas Hirsch\textsuperscript{2}
\textsuperscript{1}ZMP - Institute of Advanced Materials and Processes, Friedrich-Alexander Universität Erlangen-Nürnberg (FAU), Fürth
\textsuperscript{2}Department of Chemistry and Pharmacy, Friedrich-Alexander Universität Erlangen-Nürnberg (FAU), Erlangen

The knowledge of the element carbon has inflationary been expanded with the advent of the fullerenes, carbon nanotubes and graphene. All three molecular allotropes share one common blueprint: their pi-framework is based on trigonally bound carbon atoms and the remaining electron is located in a more or less delocalized pi-system, responsible for the physical properties and chemical reactivity of these systems. Due to the inherently stored strain energy fullerenes exhibit the highest reactivity in endohedral addition reactions in contrast to the less curved carbon nanotubes and planar graphene. Nevertheless, the direct covalent framework derivatizations of these pi-allotropes has flourished within the past decade and common functionalization sequences suitable for all three allotropes have been identified. The direct nucleophilic addition of organmetallic reagents and the reductive functionalization with suitable electrophiles are two complementary derivatization reactions.

MON 51
Plasmon-enhanced Raman scattering by carbon nanotubes optically coupled with near-field cavities

Sebastian Heeg\textsuperscript{1,2,3}, Antonios Oikonomou\textsuperscript{2,4}, Roberto Fernandez Garcia\textsuperscript{5}, Christian Lehmann\textsuperscript{3}, Stefan A. Maier\textsuperscript{5}, Aravind Vijayaraghavan\textsuperscript{1,2}, Stephanie Reich\textsuperscript{3}
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\textsuperscript{3}Freie Universität Berlin, Germany
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Plasmon-enhanced Raman scattering combines the generation of highly localized light fields at metal-dielectric interfaces with the variety of properties that can be obtained by Raman spectroscopy. Here we realize the coupling of carbon nanotubes as a one-dimensional model system to plasmonic hotspots on a single device level. Carbon nanotubes are placed in a plasmonic cavity between two gold nanodisks by directed dielectrophoretic deposition. The near-fields in the cavity enhance the Raman signals of the nanotube thousandfold. The enhanced signal arises exclusively from tube segments within the cavity as we confirm by spatially resolved Raman measurements. Through the energy and polarization of the excitation we address the extrinsic plasmonic and the intrinsic nanotube optical response independently. For all incident light polarizations, the nanotube Raman features arise from fully symmetric vibrations only. We find strong evidence that the magnitude of the signal...
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enhancement depends on the orientation of the carbon nanotube relative to the cavity axis.


MON 52
Chemical challenges during the synthesis of MWNT based inorganic nanocomposite materials

Zoltan Németh¹, Balazs Reti¹, Zoltan Pallai¹, Peter Berki¹, Judit Major¹, Endre Horváth², Arnaud Magrez², László Forró², Klara Hernadi¹
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Multi-walled carbon nanotubes (MWNT) were successfully covered with various metal oxide - such as TiO₂, ZnO, Al₂O₃, SnO₂ and In₂O₃ - nanoparticles with different preparation methods under solvent conditions. The applied synthesis techniques were impregnation, hydrothermal process and ball milling method. As-prepared inorganic coverage layers were characterized by TEM, HRTEM, SEM, SEM-EDX and X-ray diffraction techniques. Results revealed that the choice of synthesis technique affects the quality and the layer structure of deposited inorganic particles on the surface of carbon nanotubes. For each inorganic chemical and for each synthesis method as well individual procedure has to be developed to grow layers of required quality. Consequently, there is no uniform recipe for the fabrication of MWNT-containing nanocomposite materials. These materials might be suitable candidates for further nanotechnology applications.

MON 53
Coffee stains and self-organized nanotube films

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¹Institute of Physical and Theoretical Chemistry, Wuerzburg

The development of versatile thin film technologies is essential for the implementation of SWNTs in numerous future device applications. We have studied the formation of self-organized SWNT films on solid substrates from colloidal suspensions. Film formation is facilitated by adsorption of SWNTs on a substrate at the solid-air-liquid contact line of a receding meniscus. Previously this phenomenon has been utilized for the fabrication of field-effect transistors using striped films of highly oriented SWNTs (coffee-stains) (1) but the parameters and mechanism controlling film structure and formation have remained elusive.

We present a detailed study of film and stripe formation from (6,5) SWNT suspensions. The study highlights the importance of controlling surfactant and SWNT concentrations, surface impurities, bundling and contact line velocity. Most strik-
ingly we find that the formation of striped coffee stains is not due to the generally implied simple stick-slip motion of the contact line.


MON 54
Full two-dimensional calculation of the double-resonant 2D-mode Raman scattering cross-section in bilayer graphene

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Since the beginning of investigating single- and few-layer graphene by Raman spectroscopy, the origin of the complex lineshape of the 2D mode in bilayer graphene is under discussion. Different explanations concerning so-called inner and outer processes, as well as symmetric and anti-symmetric processes were proposed. However, none of the discussed models could describe the 2D-mode lineshape in its full complexity. Moreover, most of the models concentrated on processes along just one high-symmetry line in the Brillouin zone of bilayer graphene, i.e., the Γ-K-M direction.

Using a full two-dimensional approach to calculate the Raman cross section of the 2D mode in bilayer graphene, we investigate the dominant contributions to the 2D-mode lineshape. Our approach covers all matrix elements and all possible scattering paths for electrons and holes. We show that so-called inner scattering events are by far the most dominant processes, as in single-layer graphene. Furthermore, we show that the TO phonon splitting cannot be neglected for a thorough analysis of the 2D mode in bilayer graphene. Additionally, we will investigate which TO phonons contribute to the symmetric and anti-symmetric scattering processes. Our results answer the long-standing question regarding the different contributions to the 2D-mode lineshape in bilayer graphene.

MON 55
Observing graphene grow: Catalyst-graphene interactions during scalable graphene growth on polycrystalline copper

Stephan Hofmann¹, Piran R. Kidambi¹, Bernhard C. Bayer¹, Raoul Blume², Zhu-Jun Wang³, Carsten Baehtz⁴, Robert S. Weatherup¹, Marc-Georg Willinger³, Robert Schloegl³
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The application potential of graphene hinges entirely on the development of growth and integration techniques that are scalable and allow an adequate level of structural control. We use a combination of complementary in-situ environmental SEM, in-situ XPS and in-situ XRD to fingerprint the entire graphene growth on technologically important polycrystalline catalysts, in particular Cu, to address the current lack of understanding of the underlying fundamental growth mechanisms and catalyst interactions.[1-4]

Graphene forms directly on metallic Cu whereby an upshift in the binding energies of the corresponding C1s XPS core level signatures is indicative of coupling between the Cu catalyst and the growing graphene. Post-growth, ambient air exposure even at room temperature decouples the graphene from Cu by reversible oxygen intercalation. The importance of these dynamic interactions is discussed for graphene growth, processing and device integration.

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08:30 – 09:30  K. Ensslin, Zurich  
*Tutorial: Graphene quantum dots: localized states, edges and bilayer systems*

09:30 – 10:00  L. Ponomarenko, Lancaster  
*Graphene Double-Layer Structures*

10:00 – 10:30  coffee break

10:30 – 11:00  C. Stampfer, Aachen  
*Ballistic transport in graphene nanostructures*

11:00 – 11:30  R. Gorbachev, Manchester  
*Effect of various atomically flat substrates on electronic quality of graphene*

11:30 – 12:00  D. Lee, Jeonbuk  
*Transconductance fluctuations in graphene and bilayer graphene*

12:00 – 17:00  mini workshops

17:00 – 18:30  Dinner

18:30 – 19:00  M. Strano, Cambridge  
*New Concepts in Biosensing using Single Walled Carbon Nanotubes and Graphene*

19:00 – 19:30  A. Vijayaraghavan, Manchester  
*Covalent and non-covalent functionalization of graphene by dip-pen nanolithography*

19:30 – 20:00  V. Krstic, Dublin  
*Optical and electrical properties of metal nano-helices*

20:00  Poster II
Tuesday, March 11th

Graphene transport, functionalization
Graphene quantum dots: localized states, edges and bilayer systems
Klaus Ensslin

Physics, ETH Zurich, Switzerland

Graphene quantum dots show Coulomb blockade, excited states and their orbital and spin properties have been investigated in high magnetic fields. Most quantum dots fabricated to date are fabricated with electron beam lithography and dry etching which generally leads to uncontrolled and probably rough edges. We demonstrate that devices with reduced bulk disorder fabricated on BN substrates display similar localized states as those fabricated on the more standard SiO$_2$ substrates. For a highly symmetric quantum dot with short tunnel barriers the experimentally detected transport features can be explained by 3 localized states, 1 in the dot and 2 in the constrictions. A way to overcome edge roughness and the localized states related to this are bilayer devices where a band gap can be induced by suitable top and back gate voltages. By placing bilayer graphene between two BN layers high electronic quality can be achieved as documented by the observation of broken symmetry states in the quantum Hall regime. This can be exploited to achieve smoother and better tunable graphene quantum devices. Work done in collaboration with D. Bischoff, P. Simonet, A. Varlet, Y. Tian, and T. Ihn.
Recent advances in the fabrication of heterostructures based on 2D atomic crystals have opened up several new directions in graphene research. The fabrication process usually involves mechanical exfoliation and transfer of one material on top of another. Simple heterostructures require only two transfers. However, fabrication of more complex devices is also possible and has been successfully demonstrated in the last couple of years. In this talk I will focus on electronic properties of graphene double-layer devices, which consist of two layers of graphene separated by a few-atom-thick layer of hexagonal boron nitride (hBN). The whole structure is then encapsulated with thicker hBN layers on both sides to achieve the highest possible mobility of graphene. The double-layer devices are the analogues of double quantum wells studied for the last 30 years in GaAs structures, yet have a number of advantages. The most crucial one is the possibility to reduce the separation between conducting layers by more than one order of magnitude compared to traditional devices, thus increasing interlayer Coulomb interactions and opening a new avenue for studying strongly correlated systems.
Ballistic transport in graphene nanostructures

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Graphene nanodevices, such as for example constrictions, nanoribbons, or quantum dots are interesting for a number of applications in the field of future nanoelectronics and quantum information technology. Up to date the quality of graphene nanodevices has been severely limited by disorder and imperfections. However, recent developments in the fabrication of graphene devices on different substrates have revealed a significant increase in carrier mobility bringing the mean free path in the order of the device dimensions of nanostructured graphene. This allows investigating different transport regimes, including ballistic transport in top-down nanostructured graphene. Here, we report ballistic transport in graphene nanostructures and the observation of quasi one-dimensional transport in graphene nanoconstrictions. The graphene nanoconstrictions have widths ranging from 100 to 500 nm and they are encapsulated in hexagonal boron nitride sheets. We discuss the width-dependency and the temperature-dependency of the overall conductance both a zero and finite magnetic field. A detailed overview of the electronic properties of these encapsulated graphene nanostructures will be provided.
11:00

**Effect of various atomically flat substrates on electronic quality of graphene**

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Hexagonal boron nitride remains the only substrate that allows graphene devices with consistently high carrier mobilities $\mu$ of above 20,000 cm²V⁻¹s⁻¹. We report on our search for alternative atomically-flat substrates. Graphene fabricated on top of molybdenum and tungsten disulphides (MoS₂ and WS₂) exhibits consistently high $\mu$ up to 60,000 cm²V⁻¹s⁻¹, somewhat lower but comparable to the quality usually achieved for hBN-supported devices. In contrast, the use of atomically flat substrates made from layered oxides such as mica, bismuth strontium calcium copper oxide (BSCCO) and vanadium pentoxide (V₂O₅) results in exceptionally low quality ($\mu \sim 1,000$ cm²V⁻¹s⁻¹). We attribute the difference to the self-cleansing process that takes place at graphene-dichalcogenide and hBN interfaces and allows heterostructures with atomically clean interfaces.
11:30
**Transconductance fluctuations in graphene and bilayer graphene**
Dong Su Lee$^1$

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The charge localization in quantum Hall regime can be captured by a simple measurement of transconductance. Transport measurements normally provide a macroscopic, averaged view of the sample, so that disorder frequently prevents the observation of fragile interaction induced states in the conductance. Here, we note that graphene magnetotransport traces are frequently cluttered with fluctuations and demonstrate that these fluctuations reflect processes that occur very locally. They are a manifestation of charge localization and are more pronounced in the transconductance. A systematic study allows observing higher order fractional quantum Hall states. The fluctuations appear when conduction channels are influenced by the compressible quantum dots which form near incompressible quantum states. Fractional quantum Hall states observed in Bernal-stacked bilayer graphene using the transconductance fluctuation measurement will also be presented.
18:30
New Concepts in Biosensing using Single Walled Carbon Nanotubes and Graphene

Michael S. Strano

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge

Our lab at MIT has been interested in how the 1D and 2D electronic structures of carbon nanotubes and graphene respectively can be utilized to advance new concepts in molecular detection. We introduce CoPhMoRe or corona phase molecular recognition as a method of discovering synthetic antibodies, or nanotube-templated recognition sites from a heteropolymer library. We show that certain synthetic heteropolymers, once constrained onto a single-walled carbon nanotube by chemical adsorption, also form a new corona phase that exhibits highly selective recognition for specific molecules. To prove the generality of this phenomenon, we report three examples of heteropolymers–nanotube recognition complexes for riboflavin, L-thyroxine and estradiol. The platform opens new opportunities to create synthetic recognition sites for molecular detection. We have also extended this molecular recognition technique to neurotransmitters, producing the first fluorescent sensor for dopamine. Another area of advancement in biosensor development is the use of near infrared fluorescent carbon nanotube sensors for in-vivo detection. Here, we show that PEG-ligated d(AAAT)_7 DNA wrapped SWNT are selective for nitric oxide, a vasodilator of blood vessels, and can be tail vein injected into mice and localized within the viable mouse liver. We use an SJL mouse model to study liver inflammation in vivo using the spatially and spectrally resolved nIR signature of the localized SWNT sensors. Lastly, we discuss graphene as an interfacial optical biosensor, showing that it possesses two pKa values in alkaline and basic ranges. We use this response to measure dopamine in real time, spatially resolved at the interface with living PC12 cells which efflux dopamine, indicating graphene’s promise as an interfacial sensor in biology.

1. Zhang, JQ et al., Nature Nanotechnology, 8, 12, 2013, 959-968
2. Iverson, NM, et al., Nature Nanotechnology, 8, 11, 2013, 873-880

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Covalent and non-covalent functionalization of graphene by dip-pen nanolithography

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The integration and patterning of biomolecules and biomimetic membranes on graphene has significant implications in biosensing, drug delivery and toxicology. We demonstrate the assembly of biomolecules on graphene and graphene oxide using dip-pen nanolithography, a direct-write technique with sub-100 nm resolution. In the case of non-covalent assembly, self-assembled biotinated lipid membranes can be assembled on graphene. For the covalent case, the graphene is functionalised with biotin using click-chemistry under the dip-pen tip. In either case, the biotin functional groups remains active towards streptavidin binding. The functionalization, spreading and binding is imaged using AFM in liquid and air. We also show that there is charge transfer interaction between the biomolecules and graphene, through fluorescence quenching, Raman spectroscopy and electronic transport measurements.
19:30
Optical and electrical properties of metal nano-helices
Vojislav Krstic\textsuperscript{1,2}
\textsuperscript{1}School of Physics, Trinity College Dublin, Dublin
\textsuperscript{2}Dept. of Physics, Friedrich-Alexander-University Erlangen-Nuremberg

Metallic helical structures and their arrays are widely used in many applications including radio-frequency and microwave-transceivers and as circular polarisers in the mid-infrared, parts of rectenna-circuits in the radio-frequency and microwave ranges as well as electrical applications such as position or contact-less current sensors. However, due to the lack of structurally well-defined metallic helical objects of nanometre size such chiral structures have not yet been exploited in the visible spectrum, nor has the impact of their chiral shape been investigated in terms of magneto-induced anisotropy effects on electrical transport.

In the present work the production of large area arrays of regularly-shaped, nano-sized, aligned, freestanding helices from elemental metal and some of their optical and electrical properties will be discussed. This includes their operation as plasmonic helical antenna, source of field-enhancement for Raman microscopy exemplified on carbon-structures such as graphene as well as the magneto-induced anisotropy in electrical transport.
**TUE 1**

Local hydrogenation of graphene by impact of highly charged ions

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The manipulation of the properties of graphene for applications as electronic devices has been a challenging task since the last years. For this purpose different methods have been investigated, i.e. doping, application of strain or chemical modification. We present a gentle method for local modification of graphene layers by ion irradiation. Highly charged ions may carry several keV of (internal) potential energy, which corresponds to their charge state. When an ion approaches a surface, its potential energy is deposited via a cascade of electronic processes, which leads to a strong electronic excitation localized in a nm region of the surface. In the case of graphene, the strong localized excitation leads to weakening and breaking of bonds, which may act as attractive adsorption sites. In this work, chemically modified graphene, created by single impacts of highly charged ions, could be observed by Friction Force Microscopy. By obtaining Raman Microscopy and Sum Frequency Spectroscopy, these localized areas could be identified as hydrogenated graphene. The size of hydrogenated areas can be tuned by impact parameters, i.e. potential and kinetic energies.

**TUE 2**

Low temperature solution processed crystallization of lead-methylamine iodide (CH\(_3\)NH\(_3\)PbI\(_3\)) micro- and nanowires for photovoltaics

Endre Horváth\(^1\), Massimo Spina\(^1\), Ana Akrap\(^2\), László Forró\(^1\)

\(^1\)EPFL, Lausanne

\(^2\)Uni Geneva

Solid-state hybrid organic-inorganic perovskite sensitized mesostructured solar cells have recently demonstrated remarkable power conversion efficiencies of 15 % at laboratory scale. Despite the rapid progress in boosting up the devices’ efficiency, there is a lack of knowledge regarding some fundamental physical and chemical properties of this re-discovered material. Here, we report on our recent findings related to low temperature solution processed crystallization properties of lead-methylamine iodide (CH\(_3\)NH\(_3\)PbI\(_3\)) micro- and nanoparticles. For the first time, the growth of photoconductive micro- and nanowire form will be introduced. The anisotropic particle shape may exhibit several advantages over the isotropic form in terms of charge transport and reduced charge recombination. These results provide a basis for tailoring structural morphologies as the crystallite size and their orientation in trihalide perovskite thin films, which once implemented into a device, may ultimately result in an enhanced charge carrier extraction.
TUE 3
Facile and fast combustion synthesis and characterization of novel carbon nanopowders

Andrzej Huczko¹, Agnieszka Dabrowska¹, Michał Soszyński¹, Olga Labedź¹, Michał Bystrzejewski¹, Piotr Baranowski¹, Sławomir Dyjak², Jakub Jurkowski³, Antoni Pietrzykowski³, Rita Bhatta⁴, Balram Pokhrel⁴, Bhim Prasad Kafle⁴, Swietłana Stelmakh⁵, Stanislaw Gierlotka⁵

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We present here a simple and fast method for synthesizing novel carbon nanostructures via one-step autogenous combustion synthesis in the mixtures of a strong reducer (Mg, Si, AlH₃, CaH₂ or BH₃NH₃) and a strong oxidizer (CₓF₂, TEFLON© (CF₂)n or C₂H₃Cl). The combustions were carried out both under neutral (Ar) and active atmosphere (CO₂) at the starting pressure equal to 1 MPa.

The wet chemistry processing of the raw product yielded various carbon products including exfoliated graphite with grain size well below 100 nm.

The solid products were chemically purified and the properties of the final product were characterized by TG/DTA, FTIR, XRD, SEM, BET and Raman spectroscopy. This synthesis route provides a potentially new approach to the efficient formation of novel nanocarbons.

Acknowledgement. The research has been supported by the NCN grant NCN UMO-2011/03/B/ST5/03256 and NCN grant No. 2012/05/B/ST5/00709.

TUE 4
Spectroscopic characterisation of the oxidation and reduction process of graphene

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Oxidation of graphene and its subsequent exfoliation is an alternative approach to obtain single- and few layer graphene flakes. However, fully oxidised graphene oxide (GO) is an insulator and therefore not suitable for electronic applications. On the other hand, the conductivity depends on the oxidation state of GO which, in turn, can be tuned either during the oxidation process or by subsequent reduction. Therefore, a full control over the oxidation/reduction process of graphene is highly desirable.
In our contribution, we focus mainly on spectroscopic characterisation of various stages of oxidation and reduction. A presence of oxygen containing groups is checked by infrared spectroscopy. UV-vis spectroscopy has been used for detecting the optical band-gap and its dependence on parameters of the oxidation/reduction process. A correlation with the electric conductivity of GO and reduced GO is demonstrated. Even though Raman response is rather insensitive to different stages of the oxidation/reduction process, attempts are in progress to detect low-energy mode of multi-layer graphene which we expect to be sensitive to inter-layer distance.

**TUE 5**

**Selective area deposition of CVD diamond films on AlGaN/GaN heterostructures**

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Diamond-on-GaN heterostructure is a promising material system with variety of applications such as heat spreaders, high-temperature and high-power devices. From the practical point of view, polycrystalline diamond is shown as an attractive solution to the limited use of the expensive monocrystalline diamond substrates. Here we present the selective area diamond deposition on AlGaN/GaN layers focusing on elimination of surface and metal contact (Ni or Ir) damaging and suppressing the spontaneous nucleation of diamond. Metal contacts are important for further applications such as diamond-coated c-HEMT devices. The growth of diamond films was performed by MWCVD in three different gas mixtures: standard CH₄/H₂, addition of CO₂ and addition of N₂ to CH₄/H₂. Adding of CO₂ resulted in high quality diamond, while adding of N₂ led to the formation of nanocrystalline diamond film. On the other hand, CO₂/CH₄/H₂ gas mixture damaged the surface of AlGaN/GaN layer. Raman spectroscopy was used to analyze the diamond films quality and to evaluate thermally-induced stress distribution. This work was supported by the grants P108/14/16549P and APVV-0455-12.
TUE 6
Conduction in CVD-grown Single-Wall Carbon Nanotube networks

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We compare and analyze electronic transport in single-wall carbon nanotube (SWCNT) networks prepared by chemical vapour deposition (CVD), examining how conductivity depends on network morphology. Denser networks tend to show metal-like behaviour, with a significant conductivity remaining in the zero-temperature limit. As temperature increases, their conductivity is augmented by thermally-assisted tunnelling through thin barriers between nanotubes (1).

In sparser, more disordered samples, conduction is limited by variable-range hopping (VRH) through disordered localized states. As the bias voltage is increased, we find that there is a changeover from field-assisted thermally-driven VRH towards purely field-driven VRH behaviour; this changeover follows the same model that we have proposed for the hopping changeover in other disordered carbon materials such as reduced graphene oxide (2).


TUE 7
Hybrid materials formed from coronene and carbon nanostructures

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We will report the results of an extensive study\textsuperscript{1} of hybrid materials formed by coronene and several carbon nanostructures: single-walled carbon nanotubes of different diameter, multiwalled nanotubes and graphite. Adsorption of coronene, predominantly in the dimeric form, dicoronylene, is observed in most hybrids. The presence of dicoronylene is proved by Raman and photoluminescence measurements.
We find that the green luminescence, attributed previously to coronene stacks inside nanotubes, originates from adsorbed dicroynylene that is dissolved by the surfactant solutions used to suspend carbon nanotubes.

Almost perfect stacks inside carbon nanotubes can be formed when the reaction is conducted at low temperature (by nanoextraction from supercritical carbon dioxide at 50 °C). Further treatment of these hybrids by annealing or electron irradiation results in the transformation of coronene molecules into an inner nanotube, including nanoribbon-like intermediate structures. This transformation was followed by transmission electron microscopy and Raman spectroscopy.

1B. Botka et al., Small, online, DOI: 10.1002/smll.201302613

TUE 8

Disorder and doping at the edges of graphene nanoribbons

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Lithographic monolayer graphene nanoribbons (GNR) with widths down to \(w = 30\) nm are studied by Raman spectroscopy in order to analyze the influence of the defects formed by the GNR edges. The intensity of the \(D\) mode is compared to the \(G\) mode intensity; their ratio is similar to the one of defective graphene. On the other hand we find the transition between the low and high defective regime at \(w \approx 50\) nm, indicating a different scaling than in graphene. We model the ratio attributing the \(D\) mode to a disordered region and the \(G\) mode to a pristine inner region of the GNR. The transition from the low to the high defect regime is interpreted in terms of an overlap of both edge regions for a GNR width below 50 nm. The Raman linewidths indicate an increasing amount of disorder below this width in agreement with the estimate from the model. We suggest \(p\)-type doping of the edges to explain the Raman shift. This is confirmed by the large decrease of the intensity ratio of the \(2D\) mode to the \(G\) mode.
TUE 9
Separation and Optical Properties of (5,4) SWCNTs

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Because Single-wall carbon nanotubes (SWCNTs) are always produced as mixtures of various structures, structure sorting is very important for both fundamental research and applications. We have developed multicolumn gel chromatography method for the precise chirality sorting of semiconducting SWCNTs and have obtained 13 different single-chirality SWCNTs¹.

Very recently, we have improved the multicolumn method and optimized it for the small diameter SWCNTs. In this work, we have separated (5,4) SWCNTs from HiPco SWCNT. In the Raman spectrum of the aqueous solution of (5,4) SWCNT, single radial breathing mode peak at 373 cm⁻¹ and highly softened TO phonon at 1497 cm⁻¹ were observed. Moreover, it shows many bright photoluminescence (PL) peaks in an excitation- emission PL map. These new PL peaks can be assigned to emissions from (5,4) SWCNT oxides² that were produced in a heavy dispersion process before the separation. These unusual optical properties were probably caused by smallness of diameter, namely the curvature effect of (5,4) SWCNT.

References

² Y. Miyauuchi et al., Nat. Photonics 6 (2013) 2013547.

TUE 10
The Effect of annealing on optical and structural properties of Zinc oxide nanocrystals

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The optical and vibrational properties of zinc oxide nanocrystals, grown by vapor transport method, were investigated following thermal annealing treatment in oxygen-, Argon- and vapor Zn-rich conditions as well as at various temperatures. Raman scattering and other characterization techniques were utilized to show the effect of temperature annealing in various environments on optical and structural properties of the nanocrystals. Dramatic changes in the defect-luminescence were observed depending on the different annealing treatments. Combining optical charac-
terization methodes with Scanning electron microscopy and X-ray diffraction reveals the structural changes induced by annealing.

**TUE 11**

**Metallocene-filled single-walled carbon nanotubes: synthesis, inner tube growth properties and electronic structure**

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The applications of single-walled carbon nanotubes (SWCNTs) require the development of methods to control their electronic properties. One of the most promising approaches is the filling of the SWCNT inner channels. Encapsulation of metallocene molecules may significantly modify the SWCNT electronic properties and give the opportunity of the DWCNT synthesis. We have performed the filling of eDIPS SWCNTs of 1.7-nm mean diameter with nickelocene, cobaltocene and ferrocene molecules and their transformation into the DWCNTs via thermal annealing. Using multifrequency Raman spectroscopy we analyze the growth rates and activation energy for the formation of inner tubes with different diameters. From a detailed analysis of the XPS and UPS data, we demonstrate that the doping level of filled SWCNTs can be fine-tuned by annealing and that both n- and p-doping can be achieved. This opens the way to a further development towards the application of such nanohybrids as components of electronic devices.

The work is supported by the FWF grant. M.K. also acknowledges the ÖAW for a DOC-fFORTE fellowship.

**TUE 12**

**The mechanism of low-voltage field emission**

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The mechanism of low-voltage field emission from a carbon nanotube (CNT) was studied at room temperature in electrostatic and electrodynamics modes. It is shown the contact of CNT-emitter with 3D metallic cathode is a Schottky barrier. The potential barriers at both ends of CNT-emitter are the cause of charge carrier localization over nanotube length and have a decisive influence on mechanism of the field emission. Experimental studies of field emission from CNT-emitters show that near the potential barriers arise Friedel oscillations and plasma oscillations of the electron-hole gas which lead to the following effects: (i) the voltage threshold Vth appears on IV curve of field emission; (ii) the resonance peaks of conductivity appear on IV curve at voltage near the Van Hove singularities; (iii) the emission current consists of
DC and AC components; (iii) the field emission is always accompanied by the light emission. Based on experimental data the mechanism of low-voltage field emission from the CNT-emitter may be explained by collective tunneling of electrons through the potential barrier to vacuum.

**TUE 13**

**From isotope labeled CH$_3$CN to N$_2$ inside single-walled carbon nanotubes**

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The observation of one-dimensional N$_2$ inside single-walled carbon nanotubes raises the questions, how are the N$_2$ formed and how do they manage to make their way to this peculiar place? We have used N$^{15}$ and C$^{13}$ isotope labeled acetonitrile during the synthesis of single-walled carbon nanotubes to investigate this process. The isotope shifts of phonons and vibrons are observed by Raman spectroscopy and x-ray absorption. We identify the catalytic decomposition of acetonitrile as the initial step in the reaction pathway to single-walled carbon nanotubes containing encapsulated N$_2$.

**TUE 14**

**Growth of separated individual SWCNTs from metal: matrix templates**

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Metal: matrix templates deposited by physical vapor deposition (PVD) were used to grow separated, individual single-walled carbon nanotubes (SWCNTs). The templates are thin films of 2 nm thickness, where the metal is either segregated as nanoparticles (NPs) or diluted in the matrix. The upper limit of the NP diameter was confined by the film thickness. The function of the matrix is to prevent the metal particle from coalescence during nanotube growth by chemical vapor deposition. SEM, TEM, AFM, and Raman mapping were used for template and carbon nanotube characterization.

SWCNTs with a narrow, monomodal diameter distribution are obtained from templates with NPs of 2 nm diameter. About 50 % of the SWCNTs detected by Raman mapping have a diameter between 1.3 nm and 1.5 nm. Smaller SWCNT diameters
down to 0.8 nm are obtained from templates where the metal is diluted in the matrix. For these templates a bimodal SWCNT diameter distribution was observed. The two maxima of the CNT diameter distribution were found at about 0.8 nm to 1.0 nm and at about 1.2 nm to 1.4 nm, respectively. The CNTs are in their majority separated each from other.

TUE 15
Fabrication of periodically ordered diamond nano-structures by nanosphere lithography

Maria Domonkos\textsuperscript{1,2}, Tibor Izak\textsuperscript{1}, Lucie Stolcova\textsuperscript{2}, Jan Proska\textsuperscript{2}, Alexander Kromka\textsuperscript{1}
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Structured diamond films are required for several uses as photonic crystals, (bio-) sensors, biomedicine, etc. Often, these uses require fabrication of nano-sized features with assistance of EBL or FIB techniques. However, EBL/FIB techniques are expensive and time consuming; especially for processing large areas. Nanosphere lithography offers an economically acceptable alternative. Here we present a technology which allows a fabrication of periodically ordered diamond nano-structures over large areas. The technological process starts with the deposition of polystyrene spheres (PS) monolayer (spheres 250 or 471 nm) on seeded quartz or Si substrates by Langmuir-Blodgett method. The self-assembled PS are employed as a mask for reactive ion etching (RIE) used for reducing a PS diameter to 100 and 200 nm, respectively. The processed substrates are finally used for growing arrays of ordered diamond nano-structures. The geometry of formed arrays is controlled by PS diameter (100-1500 nm) and RIE parameters. The presented technology is simple and cheap, and allows a preparation of periodically ordered diamond hollows. This work was supported by the grants P108/12/G108 and P205/13/20110S.

TUE 16
Pressure-induced insulator-to-metal transition in Rb\textsubscript{4}C\textsubscript{60} investigated by optical spectroscopy

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Alkali-metal fullerides $A_xC_{60}$ are among the most investigated fullerene-based compounds: $A_3C_{60}$ exhibits superconductivity, whereas $A_4C_{60}$ is considered as a Mott-Jahn-Teller insulator, which undergoes an insulator-to-metal transition (IMT) under pressure. For the clarification of the mechanism of the IMT we carried out optical reflectivity and transmission measurements on the alkali fulleride Rb$_4$C$_{60}$ as a function of pressure. The vibrational and electronic spectra were studied and the samples exhibited a bad metal behavior in the measured pressure range (0.8 - 8 GPa). From our data we conclude that the underlying mechanism of the IMT is the pressure-induced
closing of the charge gap, and a nanoscale phase separation which is also discussed in the literature can be excluded.

**TUE 17**

**Anti-Stokes contribution to double resonance Raman processes in graphene**

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The most relevant two-phonon band in the Raman spectrum of graphene is the 2D band. In addition, there are numerous other combination bands - with much smaller intensities - in the observed spectra (e.g. 2D’ or D+D”). Their origin can be understood within the double resonance theory. However, the calculations on single-layer graphene found in the literature took into account only the Stokes processes for both electron-phonon interaction steps. This leads to the creation of two phonons thus gives the positive combination of the phonon frequencies in the Raman shift. We calculated the Raman spectra considering the Stokes - anti-Stokes combinations as well: one phonon is created and another is annihilated. As a consequence features at the differences of the phonon frequencies may show up. Tight binding calculations were carried out including the electron-light and electron-phonon matrix elements explicitly.

**TUE 18**

**Single-walled carbon nanotube functionalization by isotope labelled ferrocene**

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Carbon rich fillers like ferrocene (FeCp2) can be transformed into an inner tube with extremely small diameter if they are filled into HiPco tubes. For FeCp2 in HiPco new non-dispersive Raman bands appear in the D-band region after annealing at 800 C. These bands can be very strong and are resonance enhanced in the red. Originally the bands were ascribed to the D band of the inner tubes but the high intensity and the missing of corresponding overtones made this unlikely. Alternatively the bands were assigned to periodic perturbations of the outer tubes on the inner tubes. To shine more light on the origin of the new Raman lines we functionalized the HiPco tubes with isotope labelled FeCp2. The new lines turned out to be sensitive to H/D substitution in FeCp2 which is a strong indication for their origin from an unusual stable hydrocarbon molecule. Extensive Raman experiments and DFT calculations for various hydrogenated and deuterated molecules in combination with mass-spectrometric investigations are used to obtain information on the nature of
the compound. From such analyses a well defined extended conjugated hydrocarbon system is the most likely structure of the new objects.

**TUE 19**

**Raman Spectra for Characterization of Defective Nanocarbons**

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In this paper we have performed the comparative Raman study of sp\(^2\)-carbon based nanocarbons, namely sp\(^2\)/sp\(^3\) nanodiamond derived composites, onion-like carbon, multiwalled carbon nanotubes (MWNTs) produced by different techniques and MWNTs with laterally deposited graphene flakes. These nanocarbons contain graphene flake fragments of different size which can be considered as building blocks of their structure. The basic attention has been paid to behavior of D (disorder-induced), G (tangential mode) and 2D (two-phonon scattering)-bands in the Raman spectra with the focus directed toward their use for nanocarbon characterization. Raman data consideration is combined with HRTEM characterization of nanocarbons and temperature dependences of the conductivity and magnetoconductivity. A ratio of intensities I\(^2\)D/ID has demonstrated almost a linear dependence on the diameter of MWNTs produced with two different types of catalysts. An existence of a critical size of defective (curved) graphene flakes (which are responsible for the appearance of 2D bands) can be proposed on the base of data obtained.

**TUE 20**

**Resonant Raman scattering of suspended graphene amplified by an Au dimer antenna**

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The localized surface plasmon resonance (LSPR) of metallic nanoparticles is widely used to amplify the Raman signals of analytes in their vicinity. However, there are still open questions concerning the physical nature of the process involved in the huge
Tuesday, March 11th

amplification of the Raman signal. It was reported that the maximum amplification occurs at an excitation wavelength that is higher in energy than the LSPR extinction maximum. This was shown on large areas with many bowtie antennas, averaging the plasmonic response (1). In our study, we deposited single-layer graphene on top of an individual gold dimer antenna. The graphene is suspended by the antenna. We observe a strained signal in the vicinity of the dimer antenna where the EM-field of the plasmon is strongest (2). The plasmonic antenna was characterized using dark field spectroscopy to measure the LSPR. We investigate the Raman scattering intensity of the strained graphene as a function of the excitation wavelength. An amplification of the signal from the strained graphene was observed, but not of the unstrained signal.

(2) Hegg et al., Nanoletters 13(1), 2013

TUE 21
Atomic scale study of self-interstitials in graphene
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Crystallographic defects play a key role in determining the properties of crystalline materials. The new class of two-dimensional materials, foremost graphene, have enabled atomically resolved studies of such defects, concentrating on, e.g., vacancies, grain boundaries, dislocations, and foreign atom substitutions. However, implantation and atomic resolution imaging of self-interstitials has so far not been conducted in any material. Here, we deposit individual carbon atoms into single layer graphene at soft landing energies. We present images of all the interstitial dimer structures predicted earlier, employing low-voltage aberration-corrected high-resolution transmission electron microscopy. We demonstrate accumulation of the interstitials into larger aggregates and dislocation dipoles, which we predict to have strong local curvature, and to be energetically favourable configurations as compared to isolated interstitial dimers. Our results constitute an important contribution to the basic knowledge on crystallographic defects, and lay out a pathway into engineering the properties of graphene by forcing the crystal into a state of metastable supersaturation.

TUE 22
Deposition of Small Diameter Semiconducting Single-Walled Carbon Nanotubes Using Light Induced Dielectrophoresis
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Dielectrophoresis (DEP) has shown to be an efficient technique for single-walled carbon nanotube (SWCNT) device-fabrication [1,2], especially for metallic (m-) SWCNTs and for medium and large diameter semiconducting (s-) SWCNTs. In the process of using DEP for fabricating SWCNT based photodetectors operating below 1000nm wavelength, we encountered difficulties in the depositing small diameter s-SWCNTs. We attribute this behavior to the theoretically predicted small polarizability of s-SWCNTs having a large bandgap (3). To overcome this problem we try to find ways to influence the DEP response of small diameter s-SWCNTs. We will show that light induced DEP can enhance the deposition of small diameter s-SWCNTs, which we attribute to light induced changes in their polarizabilities. The conclusions are based on electrical measurements of the formed s-SWCNT devices and their characterization by scanning electron microscopy. The results are valuable for fabrications of small diameter s-SWCNT devices.

(1) A. Vijayaraghavan et al., Nano Lett. 7, 1556-1560 (2007)
(2) M. Ganzhorn et al., Adv. Mater. 23, 1734-1738 (2011)

TUE 23
Transforming Graphene Nanoribbons into Carbon Nanotubes

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Longitudinal cleavage of the carbon nanotubes (CNTs) leads to the formation of narrow carbon strips of different widths, called graphene nanoribbons (GNRs). While we learn about the different means by which the CNTs can be cut into the flatten sheets, no one has successfully illustrated how these flimsy ribbon structures can be transformed to attain a tubular geometry in laboratory. As an approach to this issue, we have attempted the nano-test tube chemistry where reaction is conducted inside the interior space of the parent CNT templates. GNRs are generated from a perylene derivative. A thermally-induced, self-intertwining of GNRs into CNTs is achieved under vigorous annealing, resulting in CNTs with chiral indices of (7, 2) and (8,
1. Optical measurements performed on the newly grown CNTs indicate a substantial increase in these two chiralities, matching the chiralities predicted for the CNTs formed through the twisting of GNRs with width, N=5. Our finding completes the missing link for the conversion of GNRs into CNTs, offering a promising alternative towards future chirality tuning and contemporary nanomaterials engineering.


**TUE 24**

**High pressure-low temperature Raman scattering in bulk 2H-MoS2**

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A key issue in resonant Raman scattering studies is the role played by intermediate exciton states. The effect of temperature (at ambient pressure) and pressure (at ambient temperature) on tuning the A1 and B1 exciton energies resonance has been previously shown for bulk 2H-MoS2 (1). A measure of the Raman cross section is obtained by "normalizing" the scattering intensity of the resonant A1g optical phonon mode to the intensity of the non-resonant E2g mode.

Here, we explore the first and second order Raman resonant behavior of 2H-MoS2, using the diamond anvil cell with He as pressure transmitting medium in the T-P range of 6 to 300 K and up to 6 GPa. According to calculations that take into account the combined effects of temperature and pressure, the maximum in the resonance, which is found at low temperature at ambient pressure and peaks around 3.8 GPa at room temperature (1), is expected to shift towards lower pressures with decreasing temperature. This trend is indeed observed in the experiments (2).


**TUE 25**

**Atomically Thin Membranes for Strain Studies**

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Single and multilayer graphene, BN and MoS₂ are suspended on 2-10 μm diameter holes. Devices are characterized using Raman, SEM and AFM. Membranes are then incorporated into a pressure cell to controllably strain the membranes. Technical details on membrane preparation, characterization data and deflection measurements for graphene are presented and discussed.
TUE 26
Negative correlation between charge carrier density and mobility fluctuations in graphene

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By carrying out simultaneous longitudinal and Hall measurements in graphene, we find that the 1/f noise for the charge carrier density is negatively correlated to that of mobility, with a governing behavior that differs significantly from the relation between their mean values. The correlation in the noise data can be quantitatively explained by a single parameter theory whose underlying physics is the trapping and de-trapping of the fluctuating charge carriers by the oppositely charged Coulomb scattering centers. This can alter the effective density of long-range scattering centers in a transient manner, with the consequent fluctuating effect on the mobility.

TUE 27
Magnetic field induced interferences in an ultraclean p-n junction

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We have developed a technology that allows suspending graphene and complementing it with bottom and top-gate structures following Ref. (1). Recently we have demonstrated that with this technique a ballistic p-n junction can be formed and intriguing Fabry-Perot oscillations were observed from the electrons localized in the cavities formed by local gates. We will go beyond our recent publication (2) and also show electric transport measurements in magnetic field, where striking features appear. Since these measurements on the p-n junction are in the completely ballistic regime they display different behaviour from the previous results on diffusive junctions (3). We observe a large number of dispersive and non-dispersing resonances in the bipolar regime, which are related to snaking trajectories along the p-n interface. The theoretical calculations clearly reproduce the measured features, and the simulated current density plots give further insight to the nature of the conductance oscillations.
TUE 28
Diameter controlled CVD growth of nitrogen-incorporated single-walled carbon nanotubes

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As we synthesized single-walled carbon nanotubes (SWNTs) using acetonitrile (AcN)-mixed ethanol (EtOH) feedstock, the SWNT mean diameter was dramatically reduced as AcN was added [1, 2]. Surprisingly, the main nitrogen configuration was found to be encapsulated diatomic N2 molecules in the interior of SWNTs with the content of 1 at % (3). As the sequence of feedstock was switched during synthesis, SWNT diameter was changed along the vertically aligned array. We have revealed continuous junctions by high-resolution transmission electron microscopy (4). This diameter modulation was reversible upon the sequence of feedstock introduction. By using 15N isotope of acetonitrile, the catalytic decomposition of acetonitrile in the initial reaction step was studied (5). The initial decomposition process of acetonitrile on metal clusters is directly measured by using FT-ICR (Fourier Transform Ion Cyclotron Resonance) mass spectrometer.

(1) T. Thurakitseree et al., Carbon 50 (2012) 2635.
(2) T. Thurakitseree et al., pssb 249 (2012) 2404.
(3) C. Kramberger et al., Carbon, 55 (2013) 196.
(4) T. Thurakitseree et al., ACS Nano 7 (2013) 2205.

TUE 29
Preliminary toxicity testing of gold nanoparticles functionalized with CA 15-3 for future applications in selective photothermolysis of pancreatic cancer

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In the previous years a new concept based on a combination of NIR active nanoparticles and LASER irradiation called nanophotothermolysis was proposed to prevent
and control the proliferation and lysis of cancer cells. We aimed to develop a novel nanophotothermolysis system for pancreatic cancer based on a new compound containing gold nanoparticles (GNPs) and CA 15-3 peptide. GNPs were synthesized using the reduction method of HAuCl in the presence of sodium citrate. The obtained citrate capped gold nanoparticles were further functionalized with the CA 15-3 peptide. UV-Vis, DLS and AFM techniques were employed in order to characterize the synthesized nanocomposite. Material biocompatibility was assessed using MTT assay as well as annexin V staining for apoptosis detection on PANC-1 cells. The newly synthesized nanomaterial showed severe citotoxicity at 5 μg/mL, neutral at 10 μg/mL, and proliferative effects for 50 μg/mL. Similar results were obtained in the case of annexin V staining, small concentration showing potent pro-apoptotic effects. GNPs-CA 15-3 presents a high potential for selective targeted nanophotothermolysis of pancreatic cancer.

TUE 30
An all-optical blister test on freestanding graphene
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Due to its exceptional mechanical properties, such as its high Young’s modulus and ultrastrong adhesion, graphene is a prominent candidate for electro- and optomechanical devices. Mechanically exfoliated freestanding graphene has the best prerequisites to study the intrinsic properties without influence of the substrate. Here, we study the spatially resolved Raman response of a pressurized freestanding graphene membrane that hermetically seals a 8 μm diameter circular pit etched in a Si/SiO₂ substrate.

Applying an external pressure ranging from 1 atm to vacuum results in bulging of the graphene membrane and subsequent strain. In such a microcavity, the Raman intensity sensitively depends on the distance between the graphene membrane and the Si substrate that acts as a bottom mirror of the cavity. A spatially resolved analysis of the intensity of the G and 2D mode features as a function of pressure provides direct topological information on the blister without external disturbance. At each pressure, an average strain can thus be deduced. This allows a detailed analysis of the frequencies of the G and 2D mode features under known pressure and strain conditions.
**TUE 31**  
Electronic transport properties of covalently functionalized carbon nanotubes

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Carbon nanotubes (CNTs) are an interesting material for spintronic applications. Magnetoresistance (MR) in multiwalled CNTs can be as large as 60% for contacts with high magnetic polarization (1). However, the size of the MR observed depends strongly on the current regime and on the type of CNT device measured. The investigations are often difficult to compare, because the various studies in this field differ in the types of CNTs, as well as in the contact material used and are carried out in different transport regimes.

We present a way to compare the MR of different devices from single-wall and multiwalled CNTs with respect to the current regime. Temperature dependent data confirm tunneling MR as the main effect. We show that the size of the MR effect depends on the strength of the tunnel barrier. MR in organic materials can be mimicked by the tunneling anisotropic magnetoresistance (TAMR), an effect that occurs even without any spin polarized injection (2). The presence of the Hanle effect in our samples rules out TAMR as the dominant process and proves successful spin injection.

(2) M. Grünewald et al., PRB 84, 125208 (2011)

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**TUE 32**  
Thermal Transport in Helically Coiled Carbon Nanotubes

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Theoretical study of the phonon thermal conductivity of helically coiled carbon nanotubes (HCCNTs) is performed. The phonon dispersions for all polarizations are determined and three-phonon Umklapp processes are calculated exactly taking into account all phonon relaxation channels which are allowed by the conservation laws. Grüneisen parameter, as a function of the phonon wave vector and polarization branch, is calculated for each vibrational mode. Boundary scattering rate is taken into account within the relaxation time approximation. Temperature dependent crossover from ballistic to diffusive transport regime, as well as length and helical step dependant phonon transport in HCCNTs are studied. In order to make a comparison, all the calculations are performed also on an ensemble of the straight CNTs: thermal conductivity of HCCNTs is found to be considerably lower due to
the changed morphology manifested in lower phonon group velocities and reduced number of transport channels at temperatures of several Kelvins already.

**TUE 33**

**Resonant tunnelling in graphene - boron nitride - graphene heterostructures**

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Physics of tunnelling between two two-dimensional electron gases (2DEG) was revitalized recently with the advent of new unconventional 2DEG system – graphene and a whole new class of artificial materials – van-der-Waals heterostructures. Most fruitful counterparts in these heterostructures are graphene and hexagonal boron nitride (hBN) owing to their exceptionally high crystal quality and small lattice mismatch. Atomically clean interfaces between 2D crystals form during fabrication, as evidenced by cross-sectional TEM, lead to high quality of heterostructures and bring new physics. In such heterostructures, when two graphene layers are separated by ultra-thin hBN spacer, the electron tunnelling between two graphene layers becomes possible. In previously reported graphene tunnelling field effect transistors (TFET) devices the tunnelling occurs inelastically. We show that in aligned graphene-based TFET the electrons can tunnel with momentum conservation, leading to resonant tunnelling and therefore to negative differential conductance. We discuss physics of resonant tunnelling in this new system and outline viable applications.

**TUE 34**

**Topography mapping of graphene**

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Thermodynamic prerequisites lead to the accepted phenomenon that graphene forms ripples in the third dimension when prepared as freestanding membrane. This theoretical concept has been confirmed experimentally by the work of Meyer et al., who showed changes in the diffraction condition of electrons due to a rippling of the membrane on the nanoscale. Inspired by this work we developed a method to construct 3D maps of freestanding graphene, allowing to quantify the rippling. To achieve this, the membrane’s inclination at each point is derived from evaluation of tilt series in transmission electron microscopy. Combining inclination information in at least two noncolinear directions allows to convert the inclination maps to 3D information. With this elaborated procedure it is possible to reconstruct the topography of the buckled/rippled membranes with spatial resolution in the nanometers
range. Our methodic development has been successfully tested on freestanding few-layer graphene derived from epitaxial graphene on SiC and will be refined with low defective samples of scotch-tape graphene, CVD graphene and GO.

TUE 35
CA 15-3 functionalized multi-walled carbon nanotubes for immunomodulatory anticancer applications.

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In the previous years a new concept called anticancer vaccine was proposed to prevent and control the proliferation and expansion of cancer cells by eliciting an immune boost in biological systems. We aimed to construct a novel carbon nanobiomaterial containing both carbon nanotubes and an immunogenic peptide, two elements with strong immunostimulating and antitumor activity. The nanoconstruct will be used in anticancer vaccine applications.

Methods. Pristine MWCNT and CA 15-3 peptide were purchased. MWCNT-CA 15-3 was obtained through sonication(Virtis 1100 sonicator, 5X30 seconds). Removal of agglomerates of unbound MWCNT was than performed by centrifugation and selective dimension filtering. UV-Vis spectroscopy and atomic force microscopy were used to characterize the novel construct. Material toxicity was assessed using MTT assay and annexin V staining for apoptosis detection on PANC-1 cells.

Results. The synthesized nanomaterial showed little or no citotoxicity for 5 and 10 μg/mL concentrations, respectively. However, for 50 μg/mL the MWCNT-CA 15-3 showed significant toxic, pro-apoptotic effect.

Conclusions. MWCNT-CA 15-3 represent a material of high applicative potential.

TUE 36
Revealing the adsorption mechanisms of nitrooxides on ultra-pure, metallicity-sorted carbon nanotubes

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Carbon nanotubes are a natural choice as gas sensor components given their high surface to volume ratio, electronic properties and capability to mediate chemical re-
actions. However, a realistic assessment of the interaction of the tube wall and the adsorption processes during gas phase reactions has always been elusive. Making use of ultra-clean single-walled carbon nanotubes, we have followed the adsorption kinetics of NO\textsubscript{2} and found a physisorption mechanism. Additionally, the adsorption reaction directly depends on the metallic character of the samples. Franck-Condon satellites, hitherto undetected in nanotube-NO\textsubscript{x} systems, were resolved in the N 1s X-ray absorption signal, revealing a weak chemisorption, which is intrinsically related to NO dimer molecules. This has allowed us to identify that an additional signal observed in the higher binding energy region of the core level C 1s photoemission signal is due to the C=O species of ketene groups formed as reaction by-products. These results pave the way toward the optimization of nanotube-based sensors with tailored sensitivity and selectivity to different species at room temperature.

**TUE 37**

**Spin Lifetime of Strongly Interacting Spin Systems in Chemically Synthesized Graphene Multi-layers**

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A chemically synthesized graphitic material where the structural coherence between the layers is missing approximates very well the assembly of graphene sheets. Our multi-frequency (9.4 GHz to 420 GHz) electron spin resonance (ESR) study clearly identifies itinerant and localized electrons below 50 K. The metallic signal ascribed to the conduction electrons in graphene is characterized by a remarkably long spin lifetime of 65 ns. Above this temperature incoherent in-plane and inter-plane scattering give a motionally narrowed single line at g = 2.0044.

**TUE 38**

**Photosynthetic reaction center/carbon nanotube bundle composites**

László Nagy\textsuperscript{1}, Kata Hajdu\textsuperscript{1}, Szabolcs Torma\textsuperscript{1}, Emil Nyerki\textsuperscript{1}, Dóra Fejes\textsuperscript{2}, Klára Hernádi\textsuperscript{2}, Endre Horváth\textsuperscript{3}, Arnaud Magrez\textsuperscript{3}, László Forró\textsuperscript{3}

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Since their discovery, carbon nanotubes (CNTs) have attracted intense attention to broad range of potential applications. In contrast to the 1D isolated single walled carbon nanotubes (SWCNT), 2D films made of thousands of tubes have been introduced as more advantageous building blocks for new types of applications in mechanically flexible and stretchable, optically transparent electronic systems. In our experiments we combined photosynthetic reaction center proteins (RC, the light energy converter
units in living cells), purified from purple bacteria, with multiwalled carbon nanotube (MWCNT) bundles. The change in the conductivity of the bare MWCNT bundles and the RC/MWCNT composite after light excitation was measured and compared. We found that the electrical conductivity under light excitation depends on the intrinsic conductivity of individual tubes within the bundles and on structural characteristics, like geometry (diameter, length, spatial arrangement, interconnects, etc.) and the electronic coupling with the RCs.

**TUE 39**

Defect-Induced Carrier Localization in Helium Ion Irradiated Graphene

Shu Nakaharai\(^1,2\), Tomohiko Iijima\(^3\), Shinichi Ogawa\(^4\), Songlin Li\(^1\), Kazuhito Tsukagoshi\(^1\), Shintaro Sato\(^2\), Naoki Yokoyama\(^2\)

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We present the effect of charge transport tuning in graphene which is based on carrier localization induced by intentionally-introduced crystalline defects. Atomic size defects are generated by applying an accelerated helium ion beam to a monolayer graphene sheet, and these defects work as scatterers for electrons (1). We found that the current in the defective graphene decreased exponentially as the defect density increased to 1%, and the current also exhibited exponential decay as the sample size increased. Current on/off switching by gate biasing with an on/off ratio of two-orders of magnitude was achieved at room temperature. We discuss that the mechanism of charge carrier transport control can be understood in terms of a transport gap generated by the localization of electrons (2). Transistor operation in our original dual-gated device with a helium ion irradiated graphene channel (3) will also be presented. This research is granted by JSPS through FIRST Program initiated by CSTP.


**TUE 40**

3D Numerical Simulations of New Micro-strip-line Open-Stub Structures with Carbon Nanotube Bumps for Shrinking Distributed Passive Components in MMICs

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Monolithic Microwave Integrated Circuits (MMICs) are playing an important role
in today’s telecommunication developments. In the present MMIC chip design, a large area of the chip is taken up by passive components, such as spiral inductors, even though many efforts have been made to reduce their size. In this paper, we propose a new micro-strip line structure with carbon nanotube (CNT) bumps (1), where the advantages of CNTs: high aspect ratio and high electrical conductivity are successfully used. We investigate the S-parameters of a 1/4 wavelength micro-strip line resonant circuit having an open-stub with CNT bumps by 3D simulations. CNT bumps are assumed to be consisted of vertically aligned MWNTs. The resonant frequency of the circuit can be reduced from 55GHz to 15GHz by adding the bumps under the stub, which suggests that it is possible for the new structure to shrink the stub length about 70% to obtain the same resonant frequency. Moreover, several types of distributed passive circuits, such as filter, power divider, couplers and matching circuits, can be shrunk similarly. This is probably due to the increase of high frequency current path length.

(1) T. Iwai, P-A-2006-229

TUE 41
Self-Assembly of Diamondoid-Derivatives inside Carbon Nanotubes: Toward One-Dimensional Diamond Crystalline Formation

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Diamond nanowires (DNWs) are one-dimensional (1D) nanomaterials composed of sp³ carbons. To date, DNWs with diameters of >50 nm have been synthesized, whereas the synthesis of thin DNWs with sub-nm diameter remains a formidable challenge. We have recently reported the possible formation of ultrathin DNWs inside carbon nanotubes (CNTs) by means of thermal coalescence of diamondoids, which can be regarded as nano-sized diamond fragments (1). However, the current synthetic method provides DNWs in extremely low yield, which makes it difficult to perform detailed studies of their properties and structural features.

In the present work, we study high-yield synthesis of ultrathin DNWs by employing various diamondoid-derivatives as precursors. As suggested by high-resolution TEM observations and optical measurements, some particular diamondoid-derivatives readily form self-assembled arrays inside CNTs. The self-assembly of precursors is crucial for 1D crystalline formation. Possible transformation of these aligned molecules into DNWs is currently in progress. Detailed discussion will be presented in the conference.
TUE 42
Wide Spectral Ellipsometry of Fullerenes and Conjugated Polymers

Jacek Gasiorowski\textsuperscript{1,2}, Kurt Hingerl\textsuperscript{2}, Reghu Menon\textsuperscript{3}, Helmut Neugebauer\textsuperscript{1}, Karin Wiesauer\textsuperscript{4}, Cigdem Yumusak\textsuperscript{1,5}, Niyazi S. Sarici\textsuperscript{1,6}

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The wide spectral characterization of organic semiconductors such as fullerenes and conjugated polymers is important from both fundamental and application points of view. Usually, the determination of optical constants from conventional reflection and/or absorption (R,T) measurements may be hindered by experimental effects like scattering or interference. In contrast, with ellipsometry, the real and imaginary parts of the dielectric function and the refractive index can be determined accurately. By modeling ellipsometry data for thin films with known thickness, the complex dielectric function is obtained directly, which is usually not the case for R,T measurements. The imaginary part of the dielectric function is the characteristic response for allowed absorption processes. In this work we present a study of the optical properties of fullerenes as well as pristine and iodine doped MDMO-PPV by using spectroscopic ellipsometry. The results are compared to conventional R,T measurements. The study was performed for a wide energy range between 0.05 (far-IR) and 6.5 eV (far UV) of undoped and doped organic semiconductors to determine precisely the differences in their optical properties.

TUE 43
Electrically tunable electron-state of MoS\textsubscript{2} thin film: First-principles calculations

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MoS\textsubscript{2} has been attracted a lot of research interest because of its layer structure, intrinsic band-gap, and optical properties \cite{1}. Many recent experiments reported that the conducting properties of MoS\textsubscript{2} are modulated by external electric field under gate bias process \cite{2, 3}. However, electronic structure of MoS\textsubscript{2} film under external electric field is still unclear. In this work, we demonstrate the possibility of controlling the conducting channel in MoS\textsubscript{2} thin film by applying electric field based on the first-principles calculations. Our calculations show that the MoS\textsubscript{2} thin film undergoes...
a semiconductor-metal transition under applied electric field. Furthermore, we find that the unoccupied nearly free states in the MoS$_2$ shifts downward and finally crosses the top valence band of the MoS$_2$ during this process. Because of this shift to lower energy, the nearly free state becomes occupied and acts as the conducting channel of the MoS$_2$, which could lead to the superconducting behavior.


**TUE 44**
**Low temperature plasma assisted synthesis of WS$_2$ thin films**

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We show here for the first time the low temperature plasma assisted synthesis of WS$_2$ thin films by using a H$_2$S plasma to sulfurize WO$_3$ films deposited by magnetron sputtering. The high sulfur reactivity in the H$_2$S plasma allows a direct solid state transformation from WO$_3$ to WS$_2$ at 500°C. This is a step towards semiconductor compatible growth of transition metal dichalcogenide thin films without the need for the highly elevated temperatures deemed necessary for thermal conversion of the materials. By integrating these films into device structures it was found that the electrical conductivity of WS$_2$ films is highly sensitive to NH$_3$ adsorption. A sensitivity of 1.4 ppm at room temperature has been achieved demonstrating the potential of 2D transition metal dichalcogenides for sensing.

**TUE 45**
**Transparent conductive films of filled single-wall carbon nanotubes**

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The electronic structure of single-wall carbon nanotubes (SWNTs) can be changed by introduction into their inner space different molecules - acceptors of electrons. In this case, the Fermi level of host nanotube is shifted into valence band. This should decrease the material electrical resistance. However, usually the electro-physical measurements are hindered in a low quality final material, filled from melt. In this work we have made a gas phase filling of SWNTs with two types of acceptors – iodine and CuCl. In both cases, the structure and optical transparency of SWNT films...
were weakly changed after filling. Nevertheless, the optical absorption bands, corresponding to E11 transition (for iodine)(1) and both E11 and E22 transitions (for CuCl) have been suppressed. HRTEM measurements have revealed the well-ordered one-dimensional crystals inside nanotubes. The electrical resistance of filled SWNT films decreased more than one order of magnitude (down to 70 Ohm/square) after filling. This shows a high potential of such films for optoelectronics. The work is supported by RFBR grants 13-02-01354, 14-02-31818, 14-02-31829.


TUE 46
Boundary value chemical modification of holes in perforated graphite

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Perforated graphite can be synthesized by heating of graphite oxide in high-temperature fluids at a temperature is above 200 °C. The resulting material retain a layered structure and has a defects in the form of etched holes with diameter of 1-2 nm in graphene sheets. Further chemical modification of perforated graphite was carried out by fluorination, chlorination, bromination and iodination. The main motive of the chemical structure of these samples is the bonding of the halogen atoms to carbon atoms from the edges of the holes. Concentration of fluorine atoms is correspond to superstoichiometric CF1,2. In chlorinated samples ratio of C-Cl bonds is more 1%, brominated sample has about 15% of bromine atoms covalently bonded to carbon, and iodide sample has 0.5% of iodine atoms. The presence of chemically modified holes in the graphene layers promotes the penetration of Li+ ions during electrochemical cycling and high specific capacity double-layer supercapacitors.

TUE 47
Shaping of titania nanocrystals with carbon materials for photocatalytic applications

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In the present work differently shaped TiO2 microcrystals were synthesized by hydrothermal method in the presence of multiwalled carbon nanotubes, active carbon, graphite and carbon aerogel, which promoted the crystallization process. The precursor (Ti(OBu)4), was added into HCl followed by the addition of HF and the chosen nanocarbon. The mixture was transferred into an autoclave. The hydrothermal synthesis was conducted for 1 - 24 h and the products were purified. The
morphology and microstructure of the obtained materials were characterized by SEM, TEM, HR-TEM, while the crystal phase identification was examined by XRD and the surface chemistry by XPS. Their photocatalytic activity was investigated by the degradation of phenol in aqueous solution under near UV-irradiation, using Aerioxide P25 as reference.

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TUE 48
Light Emission from optically active Tunnel Junctions

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Optical antennas consisting of plasmonic materials provide extreme light localization and small mode volumes, thereby boosting the sensitivity and signal-to-noise ratio in applications ranging from light generation to photodetection. However, most of the optical antennas studied to date operate on a light-in / light-out basis.

To directly convert low-energy electrons into propagating photons we study (localized) surface plasmon polariton (SPP) mediated two-step momentum downconversion. SPPs are excited by low-energy electron tunneling and are subsequently converted to free-propagating photons. We present our latest experimental results, investigating light emission from inelastic electron tunneling in a scanning tunneling microscope (STM) configuration as well as the integration of two-dimensional materials into the downconversion process.

TUE 49
Infrared nano-imaging of conduction electrons in carbon nanotubes separated by type

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We present a nano-FTIR study on carbon nanotubes separated by type taken by scattering type near-field infrared microscopy using a quantum cascade laser with 10.5 μm central wavelength (tuning range between 955-1030 cm⁻¹) as well as a coherent broadband mid-infrared laser beam (850-1300 cm⁻¹). The carbon nanotube films consist of bundles with about 50 nm average thickness. Besides the usual AFM topography data the interferometric detection of the optical signal reveals local optical information including the absolute scattering efficiency (amplitude) as well as
phase of the scattering. The s-SNOM technique results in both amplitude and phase values of the scattered infrared light. The exciting radiation interacts with the free (Drude) carriers from the metallic nanotubes. The observed optical contrasts are strongly related to the complex dielectric function of the studied material. Both amplitude and phase show a remarkable uniformity, proving the high purity of our samples. Additionally, the scattering amplitude from the metallic samples was found to be consistently higher than that from the semiconducting ones, indicating higher conductivity.

**TUE 50**

**Tip-enhanced Raman scattering: surface light-matter interaction and plasmonic coupling**

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Novel two dimensional materials, single-molecule studies and nanostructures require a characterization tool with surface sensitivity and spatial resolution below the diffraction limit. Here, we demonstrate how tip-enhanced Raman spectroscopy (TERS) can satisfy these requirements. Despite the possibility to obtain information not accessible with standard Raman spectroscopy, few experimental investigations have been made for a better understanding of the near-field light-matter interaction and the conservation of selection rules in a subwavelength regime. The double nature of the tip-enhanced Raman scattering, which involves a strong gradient field coupled to plasmons, is revealed studying Ge and Si doped GaN epilayers. As an example, we show mapping of the free carrier concentration on highly Si doped GaN surfaces, based on the plasmonic tip-sample interaction. Graphene fins deposited on gold are also studied. The evanescent field, confined between the gold substrate and the gold tip, further enhances the Raman signal and allows the local probing of strain and doping on the top of the fins with 25 nm spatial resolution.
**TUE 51**

**Photoluminescence of freestanding single and few-layer MoS$_2$**

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Monolayers of molybdenum disulfide (MoS$_2$), unlike the bulk material, have a direct band gap; therefore their photoluminescence is strongly enhanced compared to the bulk (1). We present a photoluminescence study of freestanding and Si/SiO$_2$-supported single- and few-layer MoS$_2$. The single-layer exciton peak (A) is only observed in freestanding MoS$_2$. The photoluminescence of supported single-layer MoS$_2$ is instead originating from the A$^-$ (trion) peak as the MoS$_2$ is n-type doped from the substrate (2). In bilayer MoS$_2$, the van der Waals interaction with the substrate is decreasing the indirect band gap energy by up to $\approx 80$ meV. Furthermore, the photoluminescence spectra of suspended MoS$_2$ can be influenced by interference effects.


**TUE 52**

**Raman spectroscopy of dichalcogenide misfit layer nanotubes**

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Misfit layer nanotubes represent a family of novel nanomaterials (1). They are built of alternating layers of transition metal dichalcogenides TX$_2$ (T=Sn,Nb,Ta,Ti,V,Cr; X=S,Se) and layers MX (M=Sn,Pb, rare earth metal). In the TX$_2$ layers transition metal atoms are sandwiched between six chalcogenide atoms whereas the MX layer commonly adopts a distorted rock salt structure. The layers are stacked along the $c$-axis and while the layers share a common $b$ axis length, the $a$ axes are incommensurate.

Here, we present TEM and Raman measurements of (PbS)$_{1.14}$NbS$_2$ nanotubes and NbS$_2$ nanotubes intercalated with lead that elucidate the internal structure of the nanotubes as well the stacking induced changes of the vibrational properties. While the Raman spectra generally can be thought of as a superposition of the intralayer Raman modes of the misfit layers, interlayer interaction leads to drastic frequency shifts with respect to the NbS$_2$ parent material. Based on the comparison of the two
investigated compounds models such as the charge transfer mechanism are subjected to a critical discussion.


**TUE 53**
The non-dispersive intermediate frequency Raman modes and their overtones in carbon nanotubes

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We present resonance Raman measurements of single-wall carbon nanotubes in the spectral region of 846 cm⁻¹ and 1692 cm⁻¹. We analysed a HiPCO sample using laser excitation energies between 1.58 eV and 2.73 eV, focussing on the characteristic peak around 846 cm⁻¹ in the intermediate frequency region (IFM) and its overtone around 1692 cm⁻¹. Especially the latter was controversially discussed in the past. Both peaks slightly depend on the excitation laser energy in shape, intensity and peak position. We assign these peaks to oTO (out-of-plane transversal optical) related Γ-point phonons stemming from different carbon nanotubes being in or close to the resonance of the exciting laser. Our findings suggest slightly lower oTO Γ-point frequencies compared to prior calculations. We support our analysis by simulating the sample’s vibrational density of states and the corresponding Raman spectra.

**TUE 54**
Distinguishing individual and ensemble carbon nanotubes by Raman spectroscopy

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Raman spectroscopy on single-walled carbon nanotubes (SWCNTs) is one of the most powerful methods to analyse their structural, mechanical, optical, and electronic properties. Besides the radial breathing modes, analysis of the position and lineshape of D and G modes allows the determination of defect concentration and metallic / semiconducting content. However, it is highly important to differentiate the influence of individualisation on the acquired Raman signal compared to typical ensemble measurements.

Our samples were grown from patterned iron catalyst particles by CVD in a tube furnace system using ethanol as a precursor. Using ST-cut quartz as a substrate, we obtain perfectly aligned, mostly individual tubes, as confirmed by Raman spectroscopy, AFM and SEM imaging.

We present Raman spectra acquired under different excitation wavelengths from individual SWCNTs compared to SWCNTs in areas with higher density. We will discuss
whether the typically acquired Raman spectra from nanotube ensembles can be modelled by a superposition of individual SWCNT spectra. This is important when e.g. using the Raman intensities of $D$ and $G$ modes for sample characterisation.

TUE 55
Conductance measurement through individual organic molecules

Ivan Pentegov$^1$, Verena Schendel$^1$, Bogdana Borca$^1$, Ulrike Kraft$^1$, Hagen Klauk$^1$, Peter Wahl$^{1,2}$, Uta Schlickum$^1$, Klaus Kern$^{1,3}$
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A good understanding of electronic properties at the individual molecular level and possible ways to tune the charge transport through unimolecular junctions are needed for future molecular based electronic devices. Scanning Tunneling Microscopy and Spectroscopy (STM/STS), represent the ideal tool to characterize and manipulate single atoms and molecules. For these purposes we operate a low temperature (6 K) STM in ultra-high vacuum. The organic molecules pentacene and derivates containing a thio-group were thermally evaporated on a clean and crystalline Cu(111) surface. The submolecular resolution of the STM allows contacting selected individual molecules at the desired site and measure the flow of the electrical current through this metal-unimolecular-metal junction. A different conductance is obtained through pentacene and the sulfur containing molecules. If the functionalized side is bonded to a metal atom the conductance is strongly modified. In this way, the conductance is varied by a gating-like mechanism.
08:30 – 09:00  K. Yanagi, Tokyo
Charge Manipulation in Molecules Encapsulated Inside Single-Wall Carbon Nanotubes

09:00 – 09:30  J. Zaumseil, Erlangen
Mapping Charge Transport in Carbon Nanotube Networks by Electroluminescence and Raman Microscopy

09:30 – 10:00  A. Khlobystov, Nottingham
From Nanotubes to Nano-Containers and Nano-Reactors

10:00 – 10:30 coffee break

10:30 – 11:00  N. Grobert, Oxford

11:00 – 11:30  R. Krupke, Karlsruhe
Fabrication of carbon nanotube nanogap electrodes by helium ion sputtering for molecular contacts

11:30 – 12:00  A. Ferrari, Cambridge
Raman Spectroscopy in Graphene and Layered Materials

12:00 – 17:00 mini workshops

17:00 – 18:30 Dinner

18:30 – 19:00  Y. Miyata, Tokyo
Controlled growth of graphene-related materials using carbon nanostructures with well-defined edges

19:00 – 19:30  H. Cheng, Shenyang
Growth and Kinetics of Single-Crystal Graphene Domains by CVD

19:30 – 20:00  J. Robertson, Cambridge
Progress in Chemical Vapour Deposition of High Density Carbon Nanotube forests and Graphene, and their Applications

20:00 – 20:30  Y. Ohno, Nagoya
Flexible devices based on carbon nanotube thin films
08:30
Charge Manipulation in Molecules Encapsulated Inside Single-Wall Carbon Nanotubes
Kazuhiro Yanagi\textsuperscript{1}
\textsuperscript{1}Department of Physics, Tokyo Metropolitan University, Tokyo

According to Gauss’s law of electromagnetism, surface charges on conductive cylindrical tubes cannot induce electric fields inside hollow spaces. In this context, we are interested in determining what happens when the size of the tubes becomes “nano”, such that the diameter of the cylinder is approximately 1 nm. Single-wall carbon nanotubes (SWCNTs) are cylindrical graphitic nanotubes that can encapsulate various types of molecules. The electrochemical doping technique can introduce negative or positive surface charges on the nanotubes through the formation of electric double layers on their surfaces. Several studies have performed electrochemical doping upon SWCNTs encapsulating molecules, however, it is still unclear whether the charges of the encapsulated molecules can be controlled by the formation of the electric double layers on the nanotube surfaces. Here we report clear experimental evidence for the charge manipulation of encapsulated molecules using electrochemical doping techniques. Electron extraction of encapsulated \( \pi \)-conjugated molecules, such as \( \beta \)-carotene, was clearly achieved.

Reference: Yanagi et al., PRL 110, 086801 (2013)
09:00

Mapping Charge Transport in Carbon Nanotube Networks by Electroluminescence and Raman Microscopy

Jana Zaumseil

Materials Science and Engineering, FAU Erlangen-Nürnberg, Erlangen

Field-effect transistors (FETs) based on semiconducting single-walled carbon nanotubes (s-SWNT) are promising building blocks for flexible electronics. Here we introduce two techniques to map current paths and charge carrier density within operating random and aligned s-SWNT network FETs: near-infrared electroluminescence (EL) and in-situ Raman microscopy. We use networks of s-SWNT with certain chiralities, which are extracted by dispersion in conjugated polymer solutions. After removal of the polymer top-gate FETs show high on/off ratios, balanced ambipolar transport and near-infrared electroluminescence with narrow linewidths. Mapping the emission from these networks during a gate voltage sweep allows us to visualize preferential current paths (1). Further, it is possible to map the distribution of charges within electrolyte-gated s-SWNT FETs. The $G'$-peak position of the nanotubes shifts with accumulated charge carrier density. This allows us to visualize the carrier distribution in an operating FET and reveals a strong dependence on SWNT network density and source-drain bias (2).

(1) ACS Nano, 7 (2013) 7428-7435.
09:30
From Nanotubes to Nano-Containers and Nano-Reactors
Andrei N. Khlobystov\textsuperscript{1,2}
\textsuperscript{1}School of Chemistry, University of Nottingham, University Park, Nottingham, U.K.
\textsuperscript{2}Nottingham Nanotechnology and Nanoscience Centre, University of Nottingham, U.K.

High aspect ratio (quasi-1D) nanostructures have potential to revolutionise the way we use, make and study molecules. Our research aims to enable characterisation and manipulation of molecules at a single-molecule level, visualisation of mechanisms of chemical reactions in real space and time, and synthesis of molecules within nanosized containers. Understanding interactions of molecules with nanostructures of different types forms a fundamental core of our work, as the 1D nanomaterials serve as a bridge between the molecular world and the macro world. Our work helps to establish a precise control of geometries and orientations of extended molecular arrays urgently needed for nano-device applications. Exploration of chemical reactivity of molecules confined in nanotubes gives us a new powerful set of tools to control the direction, selectivity and kinetics of chemical reactions. Methodology of molecular confinement at the nanoscale developed in our research offers new opportunities for preparative synthetic chemistry of the XXI century leading to high-value products that cannot be synthesised under traditional conditions, and a new generation of recyclable nano-catalysts.
10:30

Nicole Grobert\textsuperscript{1}
\textsuperscript{1}Department of Materials, University of Oxford, UK
Carbon nanotube nanogap electrodes have been used as electrodes to contact individual large organic molecules. However, the reliable fabrication of a truly nanometer-sized gap remains a challenge with established techniques (1,2).

Recently, successful patterning of graphene with a helium ion beam was demonstrated (3,4). We now report on using helium ion beam lithography to sputter a nanogap of only $2.8 \pm 0.6$ nm into single metallic carbon nanotubes embedded in a device geometry. The high reproducibility of the gap size provides us with a reliable nanogap electrode testbed for contacting small organic molecules. To demonstrate its functionality, we present electrical measurements on an oligo(phenylene ethynylene) molecule, a common type of molecular wire.

(2) Marquardt et al., Nat. Nano. 5 (2010) 863
(3) Bell et al., Nanotechnology 20 (2009) 455301
(4) Lemme et al., ACS Nano 3 (2009) 2674
Raman Spectroscopy in Graphene and Layered Materials
Andrea Carlo Ferrari
Cambridge Graphene Centre, University of Cambridge, Cambridge

Raman spectroscopy is an integral part of graphene research[1-3]. I will review the state of the art, future directions and open questions in Raman spectroscopy of graphene [3-6]. There is an increasing interest in the physics and applications of few layer graphene samples. I will discuss the interlayer shear mode, and show that the corresponding Raman peak, named C, measures the interlayer coupling[7]. A variety of layered materials can also be exfoliated to produce a whole range of two dimensional crystals [8,9]. Similar shear and layer breathing modes are present in all these materials, and their detection provides a direct probe of interlayer interactions [10]

18:30

Controlled growth of graphene-related materials using carbon nanostructures with well-defined edges

Yasumitsu Miyata\textsuperscript{1,2}

\textsuperscript{1}Department of Physics, Tokyo Metropolitan University, Tokyo, Japan
\textsuperscript{2}JST, PRESTO, Kawaguchi, Japan

In this talk, we will present an approach using “carbon nanostructures with well-defined edges” for the controlled growth of graphene nanoribbons, carbon nanotubes, and hexagonal boron nitride (hBN). For the nanoribbon growth, some organic molecules are selected as a building block and polymerized to form graphene nanoribbons in the inner space of nanotubes (1,2). Furthermore, we find that such nanoribbons can be transformed into carbon nanotubes with specific chirality by thermal annealing (2), and these tubes are extracted from the parent tubes by simple sonication process in solution (3). For the hBN growth, we use the zigzag edge of graphene as an epitaxial substrate of hBN (4), and reveal the selective formation of B-C bond at the interface.

Growth and Kinetics of Single-Crystal Graphene Domains by CVD
Teng Ma\textsuperscript{1}, Libo Gao\textsuperscript{1}, Wencai Ren\textsuperscript{1}, Xiuyun Zhang\textsuperscript{2}, Feng Ding\textsuperscript{2}, Hui-Ming Cheng\textsuperscript{1}
\textsuperscript{1}Shenyang National Lab. for Materials Science, Institute of Metal Research, CAS, Shenyang 110016, China
\textsuperscript{2}Institute of Textiles and Clothing, Hong Kong Polytechnic University, Kowloon, Hong Kong, China

The controlled growth of large-area single-crystal graphene is desired for electronics and optoelectronics. The edges of graphene influence the electronic properties and chemical reactivity of graphene, and of course its growth. We synthesized millimeter-size single crystal graphene grains and films on Pt substrates by CVD\textsuperscript{[1]}. The single crystal graphene grains has high crystallinity and high electrical mobility. We further demonstrated the growth of single-crystal graphene domains with controlled edges that range from zigzag to armchair orientations via growth-etching-regrowth in the CVD process\textsuperscript{[2]}. We have observed that both the growth and etching rates of a single-crystal graphene domain increase linearly with the slanted angle of its edges from 0 to \textasciitilde 19 and that the rates for an armchair edge are faster than those for a zigzag edge. Such edge-structure-dependent growth/etching kinetics of graphene can be well explained at the atomic level based on the concentrations of the kinks on various edges, and allow the evolution and control of the edge and morphology in single-crystal graphene following the classical kinetic Wulff construction theory.
The document discusses progress in chemical vapour deposition of high density carbon nanotube forests and graphene, and their applications. The authors present the growth of the highest density carbon nanotube forests yet reported, with mass density over 1.5 gm/cm$^3$, approaching the maximum theoretical packing density for carbon rods. They also grow single and few wall CNTs with very high area density, over $10^{13}$ cm$^{-2}$, as required for interconnect or thermal interface applications, and extend this to growth on conducting substrates. There have been considerable advances in CVD of graphene, based on measuring the state of Cu and Ni substrates during growth. This allowed the reduction of growth temperature by use of different hydrocarbon precursors. The catalytic solid state conversion of a-C into graphene was developed as a uniform process. Finally, they explain how high work function oxide (MoO$_3$) layers give a band alignment conducive to high efficiency graphene electrode OLEDs.
Flexible devices based on carbon nanotube thin films

Yutaka Ohno

1Department of Quantum Engineering, Nagoya University, Nagoya

Flexible and stretchable electronics are attracting much attention because of the variety of possible new applications from flexible e-papers though sensors and medical devices having an affinity with human body. Among various kinds of electronic materials, carbon nanotube thin films have advantages in flexibility, stretchability, performance, and cost because of the excellent electronic and mechanical properties and processability. Their optical transparency also attractive to realize transparent electron devices.

In the presentation, I will talk about recent progresses on flexible electronics based on carbon nanotube thin films, including capacitive touch sensors, [1] high-mobility carbon nanotube thin-film transistors (TFTs) and integrated circuits (ICs), [2] all-carbon ICs demonstrating excellent stretchability and mouldability [3], high-mobility TFTs fabricated with high-speed flexographic printing technique [4].

References
[1] N. Fukaya et al. (submitted)
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Graphene plasmonics, transport, theory
Real-space mapping of graphene plasmons
Rainer Hillenbrand\textsuperscript{1}
\textsuperscript{1}CIC nanoGUNE, San Sebastian

Near-field microscopy studies and real-space imaging of localized and propagating graphene plasmons\cite{1,2} will be presented. We visualize and measure the most fundamental properties such as the polariton wavelength and propagation length, and most intriguingly, how near fields can be electrically controlled by applying a gate voltage. We also apply near-field microscopy to study the reflection of graphene plasmons at grain boundaries in CVD graphene\cite{3,4}, and at the gaps in graphene on SiC, which appear at the steps between SiC terraces\cite{5}.

(2) Z. Fei, et al., Nature 487, 82 (2012)  
(3) Z. Fei, et al., Nature Nanotech. 8, 821 (2013)  
(4) M. Schnell, et al., submitted  
Mid-IR photodetection with graphene plasmonic superstructures
Marcus Freitag

IBM T. J. Watson Research Center, Yorktown Heights

Graphene, patterned into arrays of nanoribbons (GNRs), exhibits standing plasmon resonances that we use for photodetection in the mid-IR. The plasmon energy is tunable by designing the GNR width, and the energy is also in-situ tunable by application of a gate voltage to the GNR detector. Interaction with the underlying polar dielectric leads to hybrid plasmon-phonon modes with altered dispersion (avoided crossings) and longer lifetime (sharper resonances) than the plasmon itself. Finally, since our photodetector works as a bolometric device, it is also sensitive to indirect heating by photons absorbed in the dielectric, which we prove by photocurrent spectroscopy. This work was performed in collaboration with Tony Low, Hugen Yan, Fengnian Xia, Wenjuan Zhu, Luis Martin-Moreno, Francisco Guinea, and Phaedon Avouris.
Optics and opto-electronics of graphene is one of most vibrant, rapidly developing and exciting areas which has already led to some commercial applications. Rather than being just another new photonic material, it combines a wide palette of unique aspects which promise breakthroughs in several outstanding problems of nanophotonics and optoelectronics, including broadband photodetection and sensing, on-chip manipulation of nanoscale optical fields and lasing.

In this talk, the most recent developments of graphene nano-photonics and photoconversion for near-infrared and infrared frequencies are being reviewed. Strong interactions between graphene and nanoscale light-emitters are controlled and detected by tuning graphene from an absorbing to plasmonic material. Additionally, we discuss the role of electron interactions on the photoconversion processes. Using techniques from solid-state cavity quantum electrodynamics (QED) to strongly couple graphene to optical fields, we discuss new avenues in quantum information processing, imaging, and sensing.
Two-dimensional materials such as graphene can achieve spectacular performance but are highly sensitive to disorder from the environment. We have developed techniques to controllably 'stack' graphene on insulating hexagonal boron nitride, which dramatically reduces disorder and increases performance. In addition, these heterostructures can display novel behavior due to the presence of 'superlattice' potentials arising from the graphene-BN stacking. In recent work, we have extended these techniques to create fully encapsulated devices whose performance approaches the ideal behavior of graphene. These techniques can be used to create heterostructures of other 2D materials such as MoS$_2$ and WSe$_2$. I will describe our studies of basic science and applications of these devices.
11:00

**Topology, symmetry and edge transport in a graphene quantum spin Hall state**

Benjamin Hunt

Dept. of Physics, MIT, Cambridge

Low-dimensional electronic systems have traditionally been obtained by electrostatic confinement of electrons, either in heterostructures or in intrinsically nanoscale materials such as nanowires. Recently, a new method has emerged with the recognition that robust, gapless edge and surface states can exist on the boundaries of gapped bulk phases with particular topological properties. These are generically known as “symmetry-protected topological (SPT) phases” because the nature of the charge carriers in SPT edge and surface states is intimately tied to the symmetry of the bulk. In two dimensions, a familiar example is the quantum spin Hall (QSH) state in which the current is carried by a pair of counterpropagating, spin-polarized helical edge states. I will describe our recent experimental realization of such helical states at the edge of a graphene flake subjected to very large magnetic fields. In contrast to the time-reversal-symmetric quantum spin Hall effect in HgTe and InAs/GaSb quantum wells, the variant of the QSH state in graphene is protected by a symmetry of planar spin rotations that emerges as electron spins in a half-filled Landau level are polarized by the applied field. The properties of the resulting helical edge states can be modulated by balancing the applied field against an intrinsic antiferromagnetic instability, which tends to spontaneously break the spin-rotation symmetry. In the resulting canted antiferromagnetic state, we observe transport signatures of gapped edge states, which constitute a new kind of one-dimensional electronic system with a tunable bandgap and spin-momentum locking.
11:30

Transport in Structurally and Chemically Modified Graphene: Emergence of Novel Properties in the Quantum Regimes

Stephan Roche\textsuperscript{1,2}

\textsuperscript{1}Catalan Institute of Nanoscience and Nanotechnology
\textsuperscript{2}ICREA, Institució Catalana de Recerca i Estudis Avancats, Spain

In this talk, I will first present essential transport properties in realistic models of polycrystalline graphene, as well as new features produced by the interaction between graphene and boron-nitride substrate (emergence of secondary Dirac points and Hofstadter butterfly).

I will further report on some unique fingerprints of disordered graphene in the quantum Hall regime such as the formation of novel types of impurity-pinned magnetic states, at the origin of new Hall conductance plateaus, or the stability of a Quantum Spin Hall Effect phase upon increasing spin-orbit coupling through adatoms deposition. Finally, an hitherto unknown spin relaxation mechanism unique to graphene will be unveiled, and exciting horizons for the advent of Graphene Spintronics will be commented.

Technical methods presented in this talk are now fully available at www.introductiontographene.org
Anharmonic effects in superconductors, metallic hydrides, and layered materials

Ion Errea\textsuperscript{1,2}, Matteo Calandra\textsuperscript{1}, Francesco Mauri\textsuperscript{1}
\textsuperscript{1}Universit\’e Pierre et Marie Curie, Paris
\textsuperscript{2}IKERBASQUE, Basque Foundation for Science, Bilbao

Describing vibrations of atoms is of paramount importance in the physical properties of solids. Nowadays, phonon dispersions in the harmonic approximation are routinely calculated from first-principles. Nevertheless, whenever the displacements of the atoms largely exceed the range in which the harmonic potential is valid, the harmonic approximation completely fails.

Here we present a newly developed approach to treat strongly anharmonic systems valid at any temperature. We demonstrate the validity of the method calculating the phonon spectra in agreement with experiments in palladium hydrides. We also show that the large isotope anomaly in superconducting palladium hydrides (the superconducting temperature is higher the heavier the H isotope) is entirely due to the huge anharmonicity of hydrogen rattling modes.

The method is suited to study the behavior of charge density waves (CDW) in layered metallic dichalcogenides like NbSe\textsubscript{2}, which are prototypical examples of 2D materials beyond graphene. We are able to describe theoretically for the first time the temperature-dependent softening of the phonon branches associated to the CDW instability in good agreement with experiments.
19:00
Microscopic view on the ultrafast carrier dynamics in graphene
Ermin Malic¹
¹Theoretical Physics, TU Berlin, Berlin

We review our recent investigations on the coupled carrier and phonon dynamics in optically excited graphene. Combining microscopic time-, momentum-, and angle-resolved calculations with high-resolution experiments, we obtain new insights into distinct ultrafast phenomena in graphene: (i) We show the appearance of a highly anisotropic carrier population and discuss its consequences on polarization-sensitive differential transmission. (ii) We predict significant Auger-induced carrier multiplication in the low excitation regime. Applying strong magnetic fields, we even demonstrate both in theory and experiment the predominant role of Auger scattering in Landau-quantized graphene. (iii) In strong excited graphene, we show the appearance of phonon-induced transient population inversion that has been measured in a recent time-resolved ARPES study. (iv) We demonstrate optical generation of a coherently controllable charge current and discuss its graphene-specific Coulomb-induced decay. (v) Finally, we present fluence-dependent mechanisms responsible for the observed photoluminescence in graphene.
Effect of anisotropic band curvature on carrier multiplication in graphene

Denis Basko

LPMMC, Centre National de la Recherche Scientifique and Université Grenoble 1, Grenoble, France

I will discuss relaxation of an excited electron in the conduction band of intrinsic graphene at zero temperature due to production of interband electron-hole pairs by Coulomb interaction. Generally, it is well known that due to the combined energy and momentum conservation conditions, this process is allowed or forbidden, depending on whether the electronic dispersion is convex or concave. In graphene, the linear Dirac spectrum is exactly on the borderline. This fact gave rise to an intense debate in the literature about the possibility of carrier multiplication in graphene. In fact, at optical energies, the electronic dispersion noticeably deviates from the Dirac one. I will show that the electronic band curvature, being anisotropic because of trigonal warping, suppresses relaxation for a range of directions of the initial electron momentum. For other directions, relaxation is allowed and I will give an explicit expression for its rate.

THU 1
Si-related photoluminescence centers created by merging diamond and amorphous silicon

Štěpán Potocký\textsuperscript{1}, Jakub Holovský\textsuperscript{1}, Zdeněk Remes\textsuperscript{1}, Martin Müller\textsuperscript{1}, Jan Kočka\textsuperscript{1}, Alexander Kromka\textsuperscript{1}

\textsuperscript{1}Institute of Physics AVCR, v.v.i., Prague

Photoluminescence properties of optical centers in diamond are outstanding due to high quantum yields, negligible photobleaching, no blinking and longer lifetimes compared to molecular dyes. Moreover, photoluminescence (PL) properties of such color centers localized near the surface are also sensitive to the surface termination (i.e. surface charges) as their electronic levels are influenced by the Fermi level position. In this contribution, an incorporation of Si atoms into substitutional position in diamond lattice and a reproducible creation of color centers by using hydrogenated amorphous silicon are investigated with view to achieve strong PL at 740 nm. Optical activity and efficiency of Si color centers is correlated with technological parameters (layer thickness, temperature, gas composition) and surface termination of diamond films (hydrogen vs. oxygen). Steady state as well as time resolved photoluminiscence measurements with ns resolution, Raman spectroscopy, AFM, SEM and nuclear analytic techniques are used to characterize the optical centers, film quality, morphology and chemical composition. This work was financially supported by 14-04790S (GACR) and LH12186 (MSMT).

THU 2
Waveguide-integrated light-emitting carbon nanotubes

F. Pyatkov\textsuperscript{1,2,3}, S. Khasminskaya\textsuperscript{1}, B. Flavel\textsuperscript{1}, W. Pernice\textsuperscript{1,2}, R. Krupke\textsuperscript{1,2,3}

\textsuperscript{1}Karlsruhe Institute of Technology
\textsuperscript{2}DFG Center for Functional Nanostructures, Karlsruhe
\textsuperscript{3}Darmstadt University of Technology

Carbon nanotubes can be envisioned as wave-guide integrated light sources for future on-chip data communication due to their unique structural, electrical and optical properties. The challenge thereby is to integrate and electrically contact solution processed nanotubes across CMOS compatible waveguide structures and to enforce efficient coupling of light from the nanotube into the waveguide. We will show how light from an electrically-driven carbon nanotube can be coupled directly into a photonic waveguide (1). We realize wafer scale, broadband sources integrated with nanophotonic circuits allowing for propagation of light over centimeter distances. Moreover, we show that the spectral properties of the emitter can be controlled directly on chip with passive devices using Mach-Zehnder interferometers and grating structures. The direct, near-field coupling of electrically generated light into a waveguide, opposed to far-field fiber coupling of external light sources, opens new avenues for compact optoelectronic systems in a CMOS compatible framework.

(1) S. Khasminskaya et al., arXiv:1306.5632
THU 3
Modulating the growth of Nitrogen Doped Single-Walled Carbon Nanotubes using support free catalytic methods

Carlos Reinoso¹, Lei Shi¹, Antonio Briones-Leon¹, Thomas Pichler¹, Paola Ayala¹
¹Faculty of Physics, University of Vienna. Vienna, Austria

Nitrogen (N)-doped single-walled carbon nanotubes (SWCNTs) are the focus of several studies. Changes in their properties have been predicted following the N bonding configuration on the nanotube’s wall. Therefore, understanding the N bonding environment and doping levels is particularly important to achieve their potential applications. However, compared to their multi-walled counterparts, N-doped SWCNT have often been applied without proper understanding of the state of the dopants. We have used a modified high-vacuum chemical vapor deposition method with proven feasibility to produce substitutionally N-doped SWCNTs. The catalytic methods used so far have always left high amount of contaminants and this has been significantly improved additionally investigating the catalyst role in the N incorporation. We focus on this using multi-frequency resonant Raman spectroscopy, which has allowed understanding the diameter and defect concentration of the tubes. Furthermore, the dispersion of the 2D band upon varying amount of N has been investigated. The N incorporation and doping levels have been explored with XPS.

THU 4
Graphene based hybrid optomechanics

Antoine Reserbat-Plantey¹, Louis Gaudreau¹, Kevin Schädler¹, Ioannis Tsioutsios¹, Johannes Guettinger¹, Andrea Tabani², Christine Muschik¹, Darrick Chang¹, Costanza Toninelli², Andrea Bachtold¹, Frank Koppens¹
¹ICFO, The Institute of Photonic Sciences. Mediterranean Technology Park, 08860 Castelldefels (Barcelona), Spain
²LENS, 50019 Sesto Fiorentino, Italy

The existence of vacuum forces is one of the most striking consequences of quantum mechanics. These vacuum fluctuations can induce strong potentials which we will exploit in a practical scheme for quantum sensing (1). Position measurements at the quantum level are of central importance for many applications but very challenging. Typically, methods based on optical forces are used (3), but these are generally weak and difficult to apply to many materials. An important promising high-quality nanoresonator is graphene, due to its low mass and high quality factor (2-3). Here, we use a single emitter as a transducer for the local near-field electromagnetic fields between emitter and graphene, which enables a position measurement using light fields. This system paves the way for an original type of hybrid optomechanical coupling which does not need optical cavity. We show here the full experimental scheme and preliminary results.
THU 5

Tailoring the photoluminescence of double-walled carbon nanotubes filled with linear carbon chains via density gradient ultracentrifugation.

Philip A. Rohringer\textsuperscript{1}, Lei Shi\textsuperscript{1}, Carlos Reinoso\textsuperscript{1}, Kazuhiro Yanagi\textsuperscript{2}, Thomas Pichler\textsuperscript{1}

\textsuperscript{1}Faculty of Physics, University of Vienna, Austria
\textsuperscript{2}Department of Physics, Tokyo Metropolitan University, Japan

Double-Walled Carbon Nanotubes (DWCNT) came into focus of research due to their capability of acting as growth reactors for linear carbon chains (lcc). By annealing CVD-grown DWCNT at high temperatures after growth we can obtain DWCNT with a very high growth yield of lcc. The lcc alter the optical properties of the DWCNT: Photoluminescence (PL) intensity of filled DWCNT is enhanced, depending on the inner tube diameter similar to the effect of filling SWCNT with ferrocene\textsuperscript{(1)}. Interestingly, applying density gradient ultracentrifugation after different sonication treatments to the filled DWCNT as it has been done recently with unfilled DWCNT, leads to a counterintuitive extraction process: inner tubes of DWCNT are extracted from the DWCNT, but the lcc stay within these extracted tubes as it can be seen in the evolution of the PL enhancement after applying different solubilization techniques. For small tubes, the PL enhancement factor compared to extracted unfilled tubes stays constant although the overall PL quantum yield is enhanced greatly due to the extraction.


THU 6

N-doped graphene with controlled doping degree

Maxim Rybin\textsuperscript{1}, Igor Sokolov\textsuperscript{2}, Tatiana Vasilieva\textsuperscript{3}, Mikhail Vasiliev\textsuperscript{3}, Elena Obraztsova\textsuperscript{1}

\textsuperscript{1}A.M. Prokhorov General Physics Institute, Moscow, Russia
\textsuperscript{2}The Federal State Unitary Enterprise All-Russia Research Institute of Automatics, Moscow, Russia
\textsuperscript{3}The Moscow Institute of Physics and Technology, Moscow, Russia

Graphene is a two dimensional carbon material with unique electrical, optical and mechanical properties. These properties can be enhanced or reduced by graphene doping with different atoms (N, B, S, F). In this work we present a double step process of fabrication of nitrogen doped graphene with a coverage area of 10x10 mm and a doping coefficient controlled. At first graphene films were synthesized by chemical vapor deposition method\textsuperscript{[1, 2]} and then graphene films were doped using electron-beam plasma\textsuperscript{(3)} of mixture of different gases (ammonia, nitrogen, argon, oxygen) with different concentration, temperature and pressure. The idea of experiments was damaging an ideal carbon lattice and embedding the nitrogen atoms instead.
of carbon. The prepared samples were characterized by XPS, Raman and optical absorption spectroscopy. The presence of C-N bondings has been confirmed by appearance of new bands in X-ray photo spectra and by Raman spectra changing. The work was supported by SP-4499.2013.3, RFBR-13-02-12181, 14-02-31639.

(1) Rybin et al., PSS(c) 7 (11-12), 2785 (2010)
(2) Rusakov et al., JNO 8, 78 (2013)

**THU 7**

Fabrication and characterization of carbon-based spintronic devices

J. Samm$^1$, J. Gramich$^1$, A. Baumgartner$^1$, M. Weiss$^1$, C. Schönenberger$^1$

$^1$Department of Physics, University of Basel

The implementation of ferromagnetic (FM) contacts in complex nanoelectronic devices with useful reproducibility and yield is challenging due to the complex nature of nano-scale ferromagnets and interfaces, where oxidation, surface roughness and mesoscopic details can induce uncontrolled magnetic anisotropies and contact characteristics.

We report an improved fabrication scheme for carbon based nanospintronic devices and demonstrate the necessity for a careful data analysis to investigate the fundamental physical mechanisms leading to magnetoresistance (1). The processing with a low-density polymer and an optimized recipe allows us to improve the electrical, magnetic and structural quality of FM Permalloy contacts on lateral carbon nanotube (CNT) quantum dot spin valve devices. We show that spintronic nanostructures require an extended data analysis, since the magnetization can affect all characteristic parameters of a conductance feature, leading to seemingly anomalous spin transport. In addition, we report measurements on CNT quantum dot spin valves that seem not to be compatible with the orthodox theories for spin transport in such structures.

(1) arXiv:1312.0159

**THU 8**

Preparation of environmental cell with graphene sandwich structure for high resolution TEM observation of liquids

Yuki Sasaki$^1$, Ryo Kitaura$^1$, Hisanori Shinohara$^1$

$^1$Chemistry, Nagoya university, Nagoya

High-resolution transmission electron microscopy (HRTEM) provides real-time atomic-level structural information on nanomaterials. If HRTEM is applied to observation of liquids, nanostructures of liquids could directly be observed, which leads to a great impact on physical chemistry of liquids. One of the biggest problems for the realization of HRTEM observations of liquids is that samples have to be placed under a high vacuum condition, where almost all of liquids spontaneously vaporize under vacuum condition.
In this work, we have developed an HRTEM observation method of liquids, which incorporates encapsulation of liquids in graphene-sandwiched type environmental cell. Graphene is single atomic layer hexagonal network of carbon, and thus provides almost transparent in HRTEM observation. Because graphene has high thermal conductivity, heat can quickly dissipates through the entire graphene to avoid electron-beam induced heating of specimens. In addition, graphene can stably support various liquids between their inter-layer spaces because it is chemically inert and mechanically very stable. In this poster, details of sample preparation and results of TEM observations are addressed.

THU 9
Tailoring the Electronic Properties of Metallicity Sorted SWCNT: A Combined Photoemission, Optical and Transport Study
Markus Sauer1, Hidetsugu Shiozawa1, Hiromichi Kataura2, Kazuhiro Yanagi3, Thomas Pichler1
1Faculty of Physics, University of Vienna, Strudlhofgasse 4, 1090 Wien, Austria
2Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, Central 4, Higashi 1-1-1, Tsukuba, Ibaraki 305-8562, Japan
3Department of Physics, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

Tuning the electronic properties of SWCNT has turned out to be a popular topic with respect to the wide range of possible nano-electronic applications that emerge from CNT research. As the influence of SWCNT metallicity has often been neglected, we present a study using purely metallic and semiconducting SWCNTs prepared by state-of-the-art metallicity separation techniques. The SWCNTs’ electronic properties have been tailored by Li intercalation to achieve a wide range of doping states. X-ray, UV photoemission and Raman spectroscopy have been combined with transport measurements to be carried out in-situ in ultra high vacuum. Analysis of the valence band illustrates that metallic SWCNTs exhibit higher n-type doping at similar intercalation doses. However, while metallic SWCNTs show the well-known 1D Tomonaga-Luttinger liquid behaviour over the whole intercalation range, semiconducting SWCNTs undergo a transition to a 3D metal already at low intercalation doses. This behaviour is also reflected in transport measurements.

Our study provides a broader basis for understanding the doping process in metallicity separated SWCNTs.
We acknowledge funding by the FWF (P21333-N20).
THU 10

Functionalization of Graphene via Iodonium salts

Ricarda A. Schaefer¹, Ferdinand Hof¹, Frank Hauke¹, Andreas Hirsch¹
¹University of Erlangen-Nuernberg, Institute of Advanced Materials and Processes, Dr. Mackstr. 81, Fuerth

After the discovery of graphene and its properties in 2004, the functionalization of graphene was explored to better understand the chemistry as well as to generate new materials with exciting properties for itself. Therefore, graphene has been functionalized by different approaches using diazonium salts, aryl halides and alkyl halides for example. All these approaches combine the functionalization of graphene from pristine graphite by an exfoliation and activation step of the graphite starting material. This exfoliation and activation can accomplished by an intercalation of the graphite with alkali metals followed by the dispersion of the intercalate in a suitable solvent. We used this route employing potassium as intercalant for generating exfoliated graphene which was then functionalized in situ by iodonium salts. The functionalized material was investigated by thermogravimetric analysis coupled with a gc-ms system for the first time and a method was developed to qualify and quantify the functional groups attached to the carbon framework.


THU 11

Electronic transport properties of covalently functionalized carbon nanotubes

Michael Schnee¹,³, Marlou Slot¹,³, Robert Frielinghaus¹,³, Claire Besson¹,²,³, Paul Kögerler¹,²,³, Claus M. Schneider¹,³, Carola Meyer¹,³
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Carbon nanotubes (CNTs) constitute an electronic framework, whose properties can be influenced by means of chemical functionalization. Such modifications eventually lead to new applications, as e.g. chemical sensors or detectors. Here we present experiments conducted on CNTs functionalized by magnetic molecular complexes covalently bonded to the CNTs. These complexes consist of a core of four metallic ions, stabilized by organic ligands. Additional acetate ligands allow for a covalent attachment of the complexes to the CNTs by ligand exchange. The complex is very versatile and allows for the replacement of the metal ions, altering its magnetic properties. We compare magneto-transport measurements on networks of CNTs functionalized with different metal complexes. Moreover we have conducted quantum transport measurements on individual functionalized CNTs. First results suggest a quantum dot size comparable to the designed device length. This indicates that the wave function is only weakly disturbed by the covalent bonding of a small number
of molecules per device. Therefore, quantum transport spectroscopy can be used to study the interaction between CNTs and the attached molecules.

**THU 12**  
**Optics of two-dimensional semiconducting films in tunable photonic microcavities**

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Many layered metal-chalcogenides (MC) exhibit new attractive properties when cleaved into quasi-two-dimensional (2D) films. However, photonic applications of thin films may be limited due to weak light absorption and surface effects leading to a reduced light emission yield. Incorporation of 2D films in optical microcavities may allow overcoming these drawbacks. Here we fabricate tunable hybrid photonic structures where thin MC films are deposited on a dielectric mirror and are covered by another similar mirror, whose displacement from the films is adjusted by a piezo-stage. The top Bragg mirror has concave pits with the radii in the range 5-30 \( \mu \)m, enabling controlled formation of a few femtolitre microcavities with the MC films at the maximum of the photonic mode field. We realise such devices for MoS\(_2\) single layers and GaSe films with thicknesses 10-60 nm. The film photoluminescence is emitted into several cavity modes with Q-factors up to 7000 and tunable over 200 nm. Based on the cavity volumes and Q-factors, we estimate Purcell enhancement factors up to 13. This work will pave the way to tunable enhanced-performance light-emitting devices based on novel 2D films.

**THU 13**  
**Enhanced optical response of gold-carbon nanohybrid colloidal systems**

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Recently, we implemented a hybrid nanoplasmonic colloidal system by dispersing single-walled carbon nanotubes in gold nanorods suspensions\(^1\). The hybrid structures exhibit enhanced luminescence, overcoming the low-emission yield of carbon nanotubes. This simple, robust and flexible technique enhances even the luminescence of tubes with chiralities whose enhancement was never reported before. The interaction with the gold nanorods affects differently tubes with different chiralities, yielding to different efficiency of the enhancement process. The experimental evidence suggests that the effects we observe are likely to be ascribed to proximity mechanisms.
THU 14

Sp-hybridized carbon chains inside double-walled carbon nanotubes: a route to carbyne

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Carbyne, an infinite sp¹ hybridized carbon chains, has been assigned as the third carbon allotrope. However, due to its extremely instability and strong chemical activity, no unambiguous evidence for its existence has been reported yet. In order to synthesis of long carbon chains (CCs), different kinds of end-capping groups have been used to stable CCs. So far, the longest CCs synthesized in this way consist of 44 contiguous carbon atoms. Here, we report on the nanochemical reaction inside thin double-walled carbon nanotubes (DWCNTs) with inner diameter of around 0.8 nm, which can serve as nanoreactors and protectors for the formation of long CCs (LCCs). Electron microscopy directly observes a very long CC inside thin DWCNT. Furthermore, a new Raman band including several peaks between 1820 and 1880 cm⁻¹ is even higher than the G-band of the CNTs, indicating an extremely high yield of LCCs. Resonance Raman study of the new band excited by dye lasers shows that different CNTs host different LCCs. This study reveals that synthesis of LCCs inside DWCNTs would be a route to grow carbyne.

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THU 15

Magnetic properties of transition metal clusters encapsulated inside carbon nanotubes

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Encapsulated inside single-wall carbon nanotubes (SWCNTs) organometallic molecules and transition metal nanostructures can be arranged in one dimension. We study their magnetic properties by means of X-ray magnetic circular dichroism (XMCD)
and superconducting quantum interference device (SQUID), as well as their structural properties characterized by X-ray diffraction (XRD) and Raman spectroscopy. XMCD is a powerful technique that can probe the spin and orbital magnetic moments of specified orbitals in compounds. The magnetic moments of transition metal 3d orbital in the 1D structure have been evaluated from XMCD at the metal 2p-3d absorption edge. The 3d magnetism evaluated for metal clusters as function of temperature down to 5 K and external magnetic field up to 6T can be fitted well by the Langevin function with hugely enhanced uncompensated spins. No remanence is observed. The data indicate that unlike their bulk states, the metal clusters in SWCNTs cannot be magnetically ordered at temperatures and magnetic fields investigated, while the induced magnetic moments are hugely enhanced. This work was supported by the Austrian Science Fund (FWF).

THU 16
Role of Graphite Oxide at Electronic Transport in Composites with Carbon Nanotubes

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Polymer composites modified with carbon nanotubes (CNT) became commercially available because the incorporation of CNT into the polymer matrix results in significant improvement of composite properties - mechanical strength, electrical conductivity, fracture toughness, electromagnetic shielding properties. In this paper comparative study of MWNT/PE composites produced by different methods was performed. MWNT/PE composites were prepared via thermal mechanical mixing, coagulation precipitation techniques and in situ ethylene polymerization with Ziegler-Natta catalyst supported on MWNTs. Structure of MWNT/PE composites was characterized with TEM, SEM, DSC and in situ XRD study of polymer melting-crystallization cycles. Electromagnetic (EM) response of composites was investigated in broadband region (26-37 GHz and 100-800 GHz). It was found that the EM response of MWNT/PE composites correlates with their electrophysical properties. The results demonstrate perceptivity for composite MWNT/PE preparation via the catalyst distribution on the surface of MWNTs followed by polymerization of ethylene. MWNT/PE composites with high concentration of homogeneously distributed nanotubes are perspective as masterbatches materials.
THU 17
Role of Graphite Oxide at Electronic Transport in Composites with Carbon Nanotubes

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We show that the presence of electrically insulating GO within a SWCNT network strongly enhances electrical conductivity, whereas reduced rGO, even though electrically conductive, suppresses electrical conductivity of a composite network with SWCNTs. Measurements of Young’s modulus and of Raman spectra clearly support our interpretation of the active role of the oxide groups present in GO through electronic doping of metallic SWCNTs. Charge transfer between GO and metallic tubes leads to an attractive electrostatic interaction resulting in a densely packed GO-SWCNT network. Compared to a pristine SWCNT network, the GO-SWCNT composite shows much higher values of the electrical conductivity and Young's modulus.

THU 18
Probing structural integrity of single-walled (HiPCO) carbon nanotubes by dynamic (shock wave) compression

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Probing the limits of structural integrity of carbon nanotubes (CNTs) is a very challenging experimental task. We report on the first study of single walled (HiPCO) CNTs after application of dynamic (shock wave) compression in a recovery assembly. In the shock wave experiment the pressure was ramped to 19 and 36 GPa with each time a new CNT sample but from the same source batch. The recovered samples were characterized by Raman and high-resolution transmission electron microscopy. Exposure to 19 GPa shock revealed the CNT wall disruption along with ”‘unzipping”’ and ”‘cutting”’/shortening of the tubes. These damages are accompanied with substantial increase of D/G-band intensity ratio. Remarkably, ramping shock pressure to 36 GPa resulted in essential CNT destruction (RBM signal disappearance), an unexpected result given the small diameter of HiPCO nanotubes (the predicted collapse p for 0.7 nm diameter tubes is about 1 Mbar!). Along with the nature of the applied
pressure, we discuss other possible reasons which may have caused such effect and
compare our data with the results obtained earlier on shocked DWCNTs (1).

**THU 19**
*From Graphite to Graphene: How Size Affects the Structure of Extended Defects*

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In graphite, the bulk material most closely related to graphene, dislocations and
stacking faults (SF) have been studied in detail by TEM already more than 50 years
ago. It was found that dislocations appear as partial dislocations connected by a
SF ribbon. The separation of the partial dislocations is determined by a balance
between a repulsive force acting between the dislocations to reduce their total strain
energy and an attractive force aiming to minimize the SF area. Already in these
early days the scientists have discussed, how the situation changes when going from
bulk graphite to a thin lamella, even though they did not explicitly went down to
the level of (few-layer) graphene. In this contribution we put our recent experimen-
tal observations and atomistic simulations of dislocations in bilayer graphene in the
context of classical dislocation theory and compare our findings with the proposals
made in early dislocation research. We show that the buckling of the membrane
at dislocations can be derived in a continuous way from thicker lamellae while the
absence of SF energy in bilayer graphene is a discontinuous size effect that does not
have a counterpart in thicker lamellae.

**THU 20**
*High-pressure optical study on bromine-doped SWCNT films*

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The mechanical stability of single-walled carbon nanotubes (SWCNTs) is affected
by filling with molecules or inner walls. Earlier high-pressure optical spectroscopy
studies demonstrated that filling of SWCNTs with inner tubes, C₆₀ molecules or
iodine stabilizes the nanotube walls (1-3). The stabilization effect by the iodine
filling was attributed to the outward repulsive forces between the iodine chains on
the nanotube walls. This result is in contrast with Raman data showing that the iodine filling leads to a destabilization of the nanotubes (4).

Here, we present the results of a high-pressure optical spectroscopy study on SWCNTs filled with bromine. The mechanical stability of bromine-doped SWCNTs under pressure will be discussed for various filling ratios. The results will be compared to those in Refs. (3,4).

(1) B. Anis et al., Phys. Rev. B 86, 155454 (2012);
(2) B. Anis et al., J. Phys. Chem. C 117, 21995 (2013);
(3) B. Anis, PhD Thesis (2013);

THU 21
Resonance Raman Spectroscopy of carbon nanotubes: Pressure effects on G-mode

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We use 488nm and 568nm laser Raman spectroscopy under high pressure to selectively follow evolution of Raman G-mode signals of single-walled carbon nanotubes (SWCNT) of selected diameters and chiralities ((6, 5) and (6, 4)). The G-mode pressure coefficients of tubes from our previous work are consistent with the thick-wall tube model. Here we report the observation of well-resolved G-minus peaks in the Raman spectrum of SWCNTs in a diamond-anvil cell. The pressure coefficients of these identified tubes in water, however, are unexpected, having the high value of over 9cm\(^{-1}\)GPa\(^{-1}\) for the G-plus and the G-minus, and surprisingly the shift rates of the same tubes in hexane have clearly lower values. We also report an abrupt increase of G-minus peak width at about 4GPa superposed on a continuous peak broadening with pressure.

THU 22
Silicon-carbon bond inversions driven by 60 keV electrons in graphene

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Single-layer graphene is arguably an ideal material for atomic resolution electron microscopy. But even in the so-called ‘gentle’ conditions used for atom-by-atom investigations, beam damage effects cannot be neglected. We observed that 60 keV electrons can cause 3-fold coordinated Si dopants found in the graphene lattice to
jump by one site at a time. However, it is very unlikely for a low-voltage electron beam to perturb dopants heavier than carbon (1). Indeed, our first principles molecular dynamics simulations instead show that a C atom next to the Si can be partially ejected from the lattice, but due to their attractive interaction immediately recaptured. Crucially, relaxation of the Si into the position vacated by the ejected C leads to a silicon-carbon bond inversion. Although the dynamics are too fast to capture, a stochastic analysis of temporally separated events is feasible. Our data from over 30 such jumps yields a threshold that is in good agreement with the calculations. Furthermore, while the conversion of 3-fold sites into 4-fold coordinated ones by the ejection of a carbon atom do occur, they are much less likely.

(1) T. Susi et al. ACS Nano 6 (2012) 8837

THU 23
EPR study of photoactive hydrogenated titania nanowires

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Titanium dioxide (TiO₂) is one of the most thoroughly investigated photoactive semiconductor, as it is a compromise between photocatalytic activity and stability in several chemical environments. However, owing to its large, about 3 eV bandgap, the photocatalytic performance is hindered in the visible spectrum. Significant efforts were devoted to increase the limited absorption of TiO₂ under sunlight via narrowing the bandgap by adding metal or nonmetal impurities. However, the photocatalytic efficiency is also decreased by the dopant atoms, which act as recombination centers. This limitation might be overcome using dopant-free TiO₂.

Here, we report on multi-frequency electron paramagnetic resonance spectroscopy (EPR) of hydrogenated TiO₂ nanowires. Hydrogenation is followed by a color change from white to cyan and in major increase of photocatalytic activity. Using multi-frequency EPR, the presence of Ti³⁺ surface states is confirmed in cyan titania. We argue that these surface point defects are responsible for enhanced visible light absorption and for improved photocatalytic performance.

THU 24
Chirality separation of metallic SWCNTs by gel column chromatography

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As-produced single-wall carbon nanotubes (SWCNTs) always contain various structures (chiralities). Recently we reported single chirality separation of semiconducting (S-) SWCNTs using gel column chromatography ¹. In this separation, metallic (M-) SWCNTs were not adsorb to the gel and not separated from each other. Here we report chirality separation of M-SWCNTs.
Proceeding chirality separation of M-SWCNTs, M/S separation of HiPco-SWCNTs was conducted. The separated M-SWCNTs mixture was concentrated and applied to 60 cm long column packed with Sephacryl S-200 gel equilibrated with 0.3% SDS. After flowing 0.3% SDS, the concentration of elution solution changed to 0.4%, 0.5% SDS and 2% sodium cholate. From the optical adsorption spectra of eluted fractions, clear difference of adsorption peaks was observed, indicating chirality separation of M-SWCNTs. The early and late eluted fractions tended to contain M-SWCNTs with optical absorption peaks of longer and shorter wavelengths, respectively. Detailed analyses containing the result of Raman spectroscopy will be presented.


THU 25

**Nanofabrication of sub-10 nm graphene nanoribbons with crystallographic orientation control by STM Lithography**

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The influence of edge orientation on the electronic properties of graphene nanostructures have been predicted long before graphene has been discovered. However, a systematic experimental verification of this fundamental prediction is still lacking, due to the very limited control over the edge orientation of the investigated graphene structures. We apply a nanofabrication technique based on scanning tunneling microscopy, to pattern graphene nanoribbons with nanometer precision and crystallographic orientation control of the edges. Tunneling spectroscopy investigations of these nanoribbons reveal that a band gap opens in both armchair and narrow zigzag nanoribbons, but the origin of the gap opening mechanisms is fundamentally different for the two cases. While armchair ribbons display a quantum confinement gap, in zigzag ribbons electron-electron interactions give rise to edge magnetism leading to the opening of a band gap.

THU 26

**Atomic monolayer deposition on the surface of carbon nanotube mechanical resonators**

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Atoms adsorbed on graphitic surfaces can form a rich variety of different phases, such as vapor, liquid, supercritical fluids, and solids. The solid phase can be either commensurate or incommensurate with the graphene surface. The commensurate solid phase is robust; the crystal formed by the adsorbed atoms is strongly pinned to the underlying carbon surface. Here, we report the formation of monolayers of Xe, Kr, Ar, and Ne on individual nanotubes upon decreasing temperature while keeping a constant pressure of gas into the chamber. The nanotube was employed both as the substrate for adsorption and as a mechanical resonator for detection. We current-annealed it in order to remove contamination adsorbed on the surface. The monolayer of Xe was found to be the most robust phase. Its coverage remains constant at 1/6 over a large temperature range, suggesting the formation of a commensurate solid. With the help of theoretical calculations, we identify the phases of Ar and Ne monolayers as fluids. Kr is less clear, but more likely monolayers of Kr are solid phases. These results underscore that mechanical resonators made from single nanotubes are excellent probes for surface science.

THU 27
Modeling of the functionalization of CNTs - A systematic tight-binding study of the electronic properties

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Carbon nanotubes are wellknown for their remarkable electronic properties. Since the semi-conducting characteristics are directly affected by the nanotube’s chirality, CNTs show a promising potential for applications in semi-conducting device fabrication. Special interest is given to the use as semi-conducting material in field effective transistors. Because of their high linearity in the current-voltage-characteristic, CNTFETs are good candidates for high frequency analogous transistors applied in mobile technology systems. Covalent as well as non-covalent functionalization of CNTs is of great interest in this research field. It could be used for sorting CNTs by its length and chirality, debundeling of CNTs by directly covalently bonded polymers as spacer molecules or reducing the impact of metallic CNTs. Using a simple tight-binding model we try to systematically study the influence of covalent functionalization on the electronic properties of CNTs. Therefore we combine a statistical percolation theory model with the recursive Green’s function method allowing us to randomly generate large-dimensioned CNT structures and to analyze their electronic and transport properties.
THU 28
Electronic transport through defective carbon nanotubes
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The present work aims to describe the transport properties of defective armchair carbon nanotubes (CNTs). The focus is set on monovacancies and divacancies. The calculations of transmission spectra and conductivities are done by a fast recursive equilibrium Green's function formalism, which scales linearly with the length of the tube, allowing to treat large systems [J. Phys. Cond. Mat. 20, 294214 (2008)]. The electronic structure is described by the density functional based tight binding model.

Single defects, double defects and the behavior of single configurations with many defects are studied. Furthermore, the mean influence of certain defect densities and the diameter of the CNT is investigated within a statistical analysis. It is shown that in the limit of small transmission the system is in the regime of strong localization according to the Anderson model. Within this regime the conductivity scales exponentially with the absolute number of defects. Consequently, a localization length can be extracted, which depends linearly on the inverse of the defect density and linearly on the CNT diameter.

THU 29
Magnetotransport in graphene constrictions
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Graphene nanodevices, such as for example nanoconstrictions are interesting systems for studying mesoscopic phenomena. Recent developments in the fabrication of graphene devices have revealed a significant increase in carrier mobility (e.g. 200,000 cm\textsuperscript{2}/Vs in bulk samples), bringing the mean free path ($l_m \geq 500$ nm) in the order of the device dimensions. This allows to investigate different transport regimes, including quantum interference effects and ballistic transport in nanostructured graphene. Here, we report on the observation of quasi one-dimensional transport in graphene nanoconstrictions with widths ranging from 80 to 500 nm encapsulated in hexagonal boron nitride. We discuss the width-dependency of the overall conductance as function of carrier density at zero magnetic field, as well as the dif-
ferences in electrostatic coupling (up to $\alpha \approx 9.4 \times 10^{10} \text{ cm}^{-2} \text{V}^{-1}$) at high and low magnetic fields.

**THU 30**

**Lithography-free fabrication of graphene devices**

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Graphene device fabrication on large-area graphene typically involves electron-beam or optical lithography, followed by graphene etching and metallization of contacts. However, this method introduces compatibility issues, such as the difficulty of removing a resist from the graphene. Therefore we developed a bottom-up, direct-write, lithography-free fabrication method. The method involves direct patterning of graphene by focused ion beam (FIB), immediately followed by Pt contact seed layer deposition via electron-beam induced deposition (EBID) in the same DualBeam (SEM/FIB) system. An in situ Raman microscope allows for direct observation of the graphene before and after FIB processing, from which it was determined that a low Ga-ion dose of $10 \text{ C/m}^2$ is sufficient for graphene removal. Finally an area-selective atomic layer deposition (ALD) process builds the seed layers into pure Pt contacts. With this combination of FIB, EBID and ALD, graphene transistors were fabricated without the use of conventional lithography. First results demonstrate a mobility approaching $500 \text{ cm}^2/\text{Vs}$ and a contact resistance as low as $(40 \pm 100) \Omega$.

**THU 31**

**CVD Graphene for Electrical Quantum Metrology**

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Graphene, a two dimensional material with sp2 hybridized carbon atoms arranged in honey comb lattice, is known for its unique electronic and mechanical properties (1). Soon after the isolation of 2D graphene crystals Quantum Hall effect (QHE) has been observed in this material at room temperature (2). The Quantum Hall plateaus in graphene have large spacing between the Landau levels in comparison to other 2DEGs, which makes it an ideal material for a quantum resistance standard defined by the electron charge and Planck’s constant (3). We will present results for graphene by Chemical Vapor Deposition (CVD) and transferred to $\text{SiO}_2/\text{Si}$ using different techniques. The transferred graphene films were patterned into millimeter scale Hall bar geometry and characterized using confocal Raman spectroscopy. First electrical transport measurements will be presented (4).
THU 32
New Characterization Methods for Environmental Dependence, Voltage/Current Stress and High Frequency Properties of Organic/Nano-material TFTs
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Organic semiconductors, carbon nanotubes, graphene and other two-dimensional materials have attracted great attention as a channel material for thin film transistors (TFTs) partly due to printability/exibility and partly due to high electron mobility. However, the electrical properties of TFTs are strongly affected by the surface conditions, traps and dislocations. In order to develop technologies for practical use, it is important to measure not only the standard DC characteristics, but also a diagnostic test for environmental dependence, voltage/current stress and frequency dependence of TFT properties. In this paper, we report a newly developed measurement system and method for organic/nano-material TFTs. The system is composed of a vacuum deposition chamber and probe-cards for in-situ measurements, which enable us to measure DC performance, changing environmental atmosphere and voltage/current stress conditions. To reveal the frequency dependency, we propose the I-V hysteresis measurement using sine-wave input signals for high impedance devices. We employed Pentacene and DNTT TFTs. This study was supported by the Joint R/D Project of Int. Standards funded by METI of Japan.

THU 33
Self-ordering of iron oxide nanoparticles covered by graphene
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Growing graphene layer over deposited nanoparticles may represent a way how to modify the electronic properties of graphene. In order to optimize the parameters of the nanoparticle deposition a study of the particle ordering using grazing-incidence small angle x-ray scattering (GISAXS) has been performed. GISAXS is a powerful technique for studying the morphology and ordering of nanoparticles in the range of...
1 nm to several microns (1). We have simulated the GISAXS data assuming ellipsoidal particles that are formed in an array described by a short-range order model and determined the particle sizes and mean inter-particle distances. The obtained results have been compared to the particle characteristics obtained by AFM.


THU 34

Effect of the atomic-scale disorder on the electronic- and transport properties of graphene grain boundaries

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Grain boundaries (GBs) substantially affect the electronic and transport properties of the unperturbed graphene lattice. Scanning tunneling microscopy (STM) measurements (1) on CVD grown graphene samples revealed a rich variety of GB structures, from periodical dislocation cores to disordered geometries with no apparent periodicity.

In this work we have performed a systematic analysis of the electronic- and transport properties of GBs of different atomic configurations (2,3). The electronic structure of the GBs are calculated by using ab-initio and tight-binding methods and the transport properties are investigated by wave packet dynamics. Our results highlight the significance of the atomic-scale disorder inside the GBs, especially the role of the two-fold coordinated C atoms which considerably diminish the electron transmission through the GBs. Revealing the connection between the properties of GBs and the CVD growth process may open new opportunities towards optimizing graphene synthesis for future electronic applications.

(1) P. Nemes-Incze, et al., Carbon 64(2013) 178-186
(2) P. Vancsó, et al., Carbon 64(2013) 101-110
THU 35
sp2-sp3 hybridized carbon composites
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In this contribution, we make a comprehensive experimental investigation - synthesis and characterization - of sp2-sp3 hybridized carbon composites. Main focus will be on carbon nanotubes (CNTs), carbon nano-foam (C-foam), and nano-crystalline diamond (NCD). Transformation as well as pre-deposition of selected carbon forms into/with another one form will be presented. Moreover, effect of various substrate pretreatments (nucleation, plasma treatment) and/or employment of different CVD systems (HFCVD, focused MWCVD and pulsed linear antenna MWCVD) will be discussed too. The relation between the CVD process types and final properties of composite structures will be discussed more in detail. Prepared carbon composites were characterized by the method of contact angle measurements, Raman spectroscopy, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).

This work was supported by the grants P108/12/G108, EC FP7 project Electrograph n°266391 and Slovak Research and Development Agency under the contract No. APVV-0365-12.

THU 36
Enhanced Raman Intensity of Defective Graphene
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Reductive and oxidative functionalization sequences of graphite lead to the exfoliation of defect rich graphene sheets. Typically, such systems can be characterized precisely by Scanning Raman Microscopy (SRM) since defects are detectable in the D-Mode of graphene. Herein, we demonstrate that chemically modified graphene exhibits a strongly enhanced overall Raman intensity compared to defect free graphite crystals (HOPG). We present a detailed study of a HOPG crystal decorated with single layers of graphene oxide (GO) in order to quantify the intensity amplification. Consequently, single sheets of defective graphene are screening graphitic substrate sig-
nals by superimposition of the graphitic Raman signature almost completely. Even in large quantities, functionalized bulk material exhibits a pronounced increase in overall Raman intensity compared to pristine material leading to fundamental consequences on the interpretation even of broad Raman data sets.

**THU 37**

**Pt Atomic Layer Deposition on graphene**

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Graphene is a two-dimensional material which has attracted considerable attention for a various range of applications. Due to its high intrinsic charge carrier motilities it is a promising candidate to be used in next-generation electronic devices. For a successful introduction in future devices the ability to deposit metal contacts and dielectrics on graphene is required. Atomic layer deposition (ALD) is the preferred technique to be used for this purpose due to its excellent conformality and precise control of thickness. However the inert nature of the graphene makes it challenging to initiate ALD growth.

In this work, the initial growth of Pt on graphene by ALD is investigated. It is shown that by increasing the oxygen pressure during ALD and by using Cu as the underlying substrate the nucleation can be enhanced. However, this also makes the deposition more selective towards the wrinkles and defects present in the graphene. The enhanced nucleation is caused by the presence of dangling bonds or stain in the graphene at these sites. The results provide more insight into the nucleation of Pt ALD and ALD on graphene in general.

**THU 38**

**Unifying the low-temperature luminescence spectra of carbon nanotubes**

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Photo-excited electron-hole pairs in carbon nanotubes form strongly bound and localized excitons that can recombine radiatively giving rise to near infrared photoluminescence (PL) signals. The subsequent coupling to acoustic phonons leads to asymmetrical meV-broad phonon sidebands in the PL spectrum. Due to the peculiar one-dimensional geometry, the zero phonon line is completely merged into the wings resulting in an overall broad and asymmetric PL line even at low-temperature (1). This picture was recently puzzled by the observation of ultra narrow PL lines in suspended nanotubes (2,3) questioning the electron-phonon mechanisms. Here, we show that both broad and narrow PL lines, as well as a continuous set of profiles bridging these two cases, can all be observed for regular micelle wrapped nanotubes deposited on a substrate. We interpret and quantitatively fit the full variety of experimental PL
lineshapes in a unified framework in terms of modified low energy acoustic phonon coupling to the exciton (4).

(1) Galland et al. PRL 101, 067402 (2008)
(4) Vialla et al. Submitted

THU 39
Nanostructured boron doped diamond films for detection of transferrine

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Boron-doped diamond (BDD) due to its wide potential window is an excellent material for applications in bio-electrochemistry. Transferrins (TF) are iron-binding blood plasma glycoproteins that control the level of free iron in biological fluids. Detection of TF in urine would predict disease of the patients with type 2 diabetes. In this study, two different techniques for fabrication of nanostructured BDD electrode were used. The first one resulting in fabrication of “nano-pillars” includes overgrowing of RF plasma structured intrinsic nanodiamond film by BDD layer. The second technique resulting in fabrication of “nano-cups” uses a direct mask-less etching of BDD film by DC plasma ion etching in O2 and N2 atmosphere. In the article, the effect of BDD film nanostructuring, electrode fabrication and electrochemical response to TF are discussed. For the first time, the TF concentration was determined at the level of 1mg/dl in aqueous solution using a square-wave stripping voltammetry method. The results show that the “nano-cups” electrodes exhibit a more than ten times higher sensitivity than the “nano-pillars”. This work was financially supported by APVV-0365-12 and P108/12/G108.

THU 40
Composite electrodes for supercapacitor application

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Composite electrodes based on a vertically oriented structure of graphene nanoplatelets
Thursday, March 13th

Poster session

and SWCNTs are presented as a promising material enhancing the performance of electric double-layer supercapacitors. The graphene material was exfoliated from a graphite powder using chemical oxidation followed by thermal reduction. Different routes of oxidations as well as different electrode processing are introduced in order to tune up the final structural and electro-chemical properties of composite electrodes. The SWCNTs serve as spacers, preventing the collapse of porous structure necessary for high ions mobility. In addition SWCNTs enhance the electrical conductivity. The electrodes with area of square centimetres and thickness of around 300 um were used for preparation of the supercapacitor cells. Their electrical performance was tested by cyclic voltammetry and charge-discharge procedure using organic electrolyte 1M TEABF4/AN. The cyclic voltammetry results show a nearly-ideal capacitance performance with no contribution of pseudocapacitance or any kinds of unwanted electro-chemistry. The charge-discharge cycles confirmed the reliable electrical performance of prepared capacitor cells.

THU 41

Determining the Van der Waals Radius of Confined Iodine Atoms with Polarized Raman Spectroscopy

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Atoms are the building blocks of our world. Better understanding the properties of the atoms will benefit our further understanding of the matter around us. The size of the atoms is the fundamental parameter to determine atoms’ physical and chemical properties. Here we present a novel optical method to determine the Van der Waals radius of iodine atoms using Raman spectroscopy. The iodine diatomic molecules are diffused into the nano-scale channels of a zeolite single crystal. We found their polarized Raman spectroscopy, which corresponds to iodine molecule’s vibrational motion along the direction of molecular axis, is significantly modified by the interaction between the iodine molecules and the rigid frame of the crystal’s nano-channels. From the number and the lifetime of excitable vibration quantum states of confined iodine molecules determined from Raman spectra, along with the size of the nano-channels, we can estimate the iodine atomic radius to be 2.10 ± 0.05 Å. It is the first time that atomic sizes, which are far beyond the optical diffraction limit, have be resolved optically using Raman spectroscopy with the help of nano-scale structures.
THU 42
Controlling the Growth of Uniform, High Quality Graphene from Solid Sources using Carbon Diffusion Barriers

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⁴Fritz Haber Institut, Berlin

Graphene growth by the catalytic graphitisation of solid carbon sources is a promising alternative to chemical vapour deposition that is equally versatile yet much simpler, cheaper and less hazardous. However, the uniformity and quality so far achieved is generally inferior and growth control remains rudimentary.

We perform complementary in situ measurements(1,2) during annealing of C/Ni stacks to develop a more fundamental understanding of the growth mechanisms and guide process improvement. We find that carbon is uncontrollably fed into the catalyst film during temperature ramping leading to graphene formation well below the maximum process temperature.

Carbon diffusion barriers are introduced as a general, simple method to prevent premature carbon dissolution and thus attain graphene quality and uniformity comparable to that achieved by CVD.(3) A thin Al₂O₃(2nm) barrier inserted into the C/Ni stack is shown to enable growth of uniform monolayer graphene at 600°C with domain sizes exceeding 50μm, and an average Raman D/G ratio of <0.07.(4)

(1) Nano Lett. 2011, 11, 4154
(2) ChemPhysChem 2012, 13, 2544
(3) ACS Nano 2012, 6, 9996
(4) Nano Lett. 2013, 13, 4624

THU 43
Carrier dynamics in graphene under Landau quantization

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We investigate the ultrafast dynamics of low-energetic Dirac electrons in graphene under Landau quantization (1,2). In a joint experiment-theory study, we provide calculations based on the density matrix formalism (3) as well as measurements of the relaxation dynamics via differential transmission spectroscopy.

As a consequence of the linear dispersion at the Dirac points, graphene exhibits a non-equidistant Landau level spectrum which allows to address specific transitions by optical pumping. Exploiting this to selectively excite the energetically lowest Landau levels, we employ pump-probe spectroscopy to explore the carrier dynamics in
this regime. A surprising sign reversal in differential transmission spectra observed both in experiment and theory provides evidence for strong Auger scattering on a picosecond timescale. Our calculations even predict the occurrence of a substantial carrier multiplication in Landau quantized graphene (4).

(1) F. Wendler et al., accepted for publication in APL.
(2) M. Mittendorff et al., submitted.
(3) E. Malic, A. Knorr, Graphene and Carbon Nanotubes: Ultrafast Optics and Relaxation Dynamics, Wiley-VCH.
(4) F. Wendler et al., submitted.

THU 44
Diffusion of Carbon Atoms at the Carbon-Nickel Interface During Graphitization

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Interface dynamics play a crucial role in the Nickel catalyzed synthesis of carbon nanotubes, carbon nanoribbons and graphene. Interface dynamics are studied by deposition of atomic C on Ni at temperatures of 23 – 550 °C. The obtained films are characterized by transition electron microscopy, Raman-spectroscopy, nuclear reaction analysis and X-ray photoelectron spectroscopy. Bulk diffusion and carbon dissolution are found to be negligible under the chosen experimental conditions leaving surface/interface diffusion as the main graphitization mechanism.

Graphitic ordering starts at ∼250 °C and increases further at temperatures > 500 °C. The initial graphitization occurs parallel to the Ni surface. As the growth continues, additional atomic planes turn perpendicular. First results are shown for the Si-Ag system processed under similar deposition conditions.

THU 45
CVD Graphene as large-scale transparent oxygen diffusion barrier in solids

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In this work we explore the possibility of using CVD-grown graphene as transparent, large-area oxygen diffusion barrier that shall ultimately protect electronic devices like OLEDs from decay. While many studies have been done on micrometre-sized samples of both exfoliated and CVD grown graphene and even more on polymer blends with
exfoliated graphene or graphene oxide, few studies have been presented that deal with CVD graphene on commercially relevant areas approaching several cm². We present the preparation of protective CVD graphene layers, their measurement and the effect on oxygen diffusion through polymers on such a large area.

THU 46
Commensurate-incommensurate transition for graphene on hexagonal boron nitride

Colin Robert Woods¹, L. Britnell², A. Eckmann², G. L. Yu¹, R. V. Gorbachev³, A. V. Kreinin¹, J. Park¹, L. A. Ponomarenko¹, M. I. Katnelson⁵, Yu. N. Gornostyrev⁵, C. Casiraghi², A. K. Geim³, K. S. Novoselov¹

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When a crystal is subjected to a periodic potential, under certain circumstances it might adjust itself to follow the periodicity of the potential, resulting in a, so called, commensurate state. Such commensurate-incommensurate transitions are ubiquitous phenomena in many areas of condensed matter physics: from magnetism and dislocations in crystals, to vortices in superconductors, and atomic layers adsorbed on a crystalline surface. We present such a commensurate-incommensurate transition for graphene on top of hexagonal boron nitride (hBN). Depending on the rotational angle between the two hexagonal lattices, graphene can either stretch to adjust to a slightly different hBN periodicity (the commensurate state found for small rotational angles) or exhibit little adjustment (the incommensurate state). In the commensurate state, areas with matching lattice constants are separated by domain walls that accumulate the resulting strain. Such soliton-like objects present significant fundamental interest, and their presence might explain recent observations when the electronic, optical, Raman and other properties of graphene-hBN heterostructures have been notably altered.

THU 47
Resonant Inelastic Light Scattering and optoelectronic properties of MoS₂

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¹Walter Schottky Institut and Physik Department, Technische Universität München, Garching

Novel tow-dimensional layered materials, e.g. MoS₂ are of increasing interest for fundamental research as well as device applications in the areas of electronics, spintronics, optoelectronics, solar energy conversion and sensing. We investigate MoS₂ on various substrates and environments by inelastic light scattering and photocurrent...
measurements. A clear dependence of the phonon spectra on the exciting photon energy occurs in light scattering experiments. We observe signatures of multistep scattering processes strongly pointing towards contribution from phonon-phonon, electron-phonon as well as electronic excitations under resonant conditions. We further find that the Raman $A_{1g}$ mode is most sensitive to changes in environment and supporting substrate material. In particular, the monolayer mode energy is shifted by up to $\pm 2$ cm$^{-1}$ by changing substrate (e.g., SiO$_2$, Sapphire) or environment (e.g., air, water).

We acknowledge financial support by the DFG excellence cluster Nanosystems Initiative Munich (NIM), the Center for NanoScience (CeNS), the DFG project HO 3324/4-3, and BaCaTec.

**THU 48**
**Strong enhancement of Raman scattering from the inactive out-of-plane mode in two-dimensional molybdenum ditelluride**

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A crucial step toward applications of two-dimensional transition metal dichalcogenides is to understand their physical and chemical properties in the atomically-thin regime. Previously, atomic layers of MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$ have been studied extensively. However, MoTe$_2$ has yet to be investigated, though MoTe$_2$ may have great potential for novel applications. Here we investigate the phonon properties of atomically thin MoTe$_2$ by Raman spectroscopy. The Raman spectra of MoTe$_2$ show prominent peaks of the in-plane $E_{12g}$ mode and the out-of-plane $A_{1g}$ mode. Similar to the other dichalcogenides, the $E_{12g}$ mode upshifts, while the $A_{1g}$ mode downshifts with decreasing thickness. Additionally, we observe a strong peak in atomically thin MoTe$_2$. The peak intensity becomes significant with decreasing thickness, but the peak vanishes in a single-layer crystal. Our density functional theory calculations reveal that the peak can be assigned as a Raman inactive mode of the out-of-plane $B'_{12g}$ mode. We attribute the activation of the $B'_{12g}$ mode in the atomic layers to the translation symmetry breaking along the c-axis.
**THU 49**

*Growth of high density carbon nanotube forests on conductive TiSiN layers*

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High-density carbon nanotube forests are envisaged as interconnects in electronic circuits and as passive heat exchangers (heat sinks) in electronic appliances. A key requirement is to grow forests directly on conductive supports. This, however, is very challenging as the catalyst material tends to strongly interact with metallic supports diffusing away from the surface. Here, we overcome this issue by employing TiSiN as catalyst support. TiSiN is metallic, relatively unreactive and amorphous, so the absence of grain boundaries prevents the catalyst from diffusing away from the surface. Using Fe, Co, or Co/Mo catalysts, TiSiN is found to be stable throughout catalyst preparation/synthesis process, and yields CNT forests with area densities close to \(10^{13}\) tubes cm\(^{-2}\) and mass densities of the order of 0.25 g cm\(^{-3}\). The forests and TiSiN support show ohmic conductivity with the lowest resistance is 0.5 kΩ. The diffusion barrier properties of TiSiN are verified by secondary ion mass spectrometry. Sequential growth reveals the forests grow by the root growth mechanism. These results suggest that TiSiN is the favoured substrate for forest growth on conductors.

**THU 50**

*Large-scale Mesoscopic Transport in Nanostructured Graphene*

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We report the first observation of Anderson localization in 2 dimensions, on nanostructured antidot graphene. Through exponential sample-size scaling of conductance, we demonstrate strong electron localization at the charge neutrality point in three sets of nanostructured antidot graphene samples with localization lengths of 1.1 to 3.4 \(\mu m\). The localization length is observed to increase with applied magnetic field, in accurate agreement with the theoretical prediction. The large-scale mesoscopic transport is manifest as a parallel conduction channel to 2 dimensional variable range hopping, with a Coulomb quasigap around the Fermi level. The opening of the correlation quasigap, observable below 25 K through the temperature dependence of conductance, makes possible the exponential suppression of inelastic scatterings and thereby leads to an observed dephasing length of 10 \(\mu m\). Perhaps more important is the fact that we have discovered a way to enhance the dephasing length of electrons, by at least one order of magnitude, so that the electron phase may now be more easily manipulated.
THU 51
Aberration-corrected TEM study of decoration of single graphene edge with single metal atoms

Xixiang Zhang\textsuperscript{1}, Hongtao Wang\textsuperscript{2}, Kun Li\textsuperscript{2}, Qingxiao Wang\textsuperscript{2}, Yingbang Yao\textsuperscript{2}

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Interaction between single noble metal atoms and graphene edges has been investigated via aberration-corrected and monochromated transmission electron microscopy. A collective motion of the Au atom and the nearby carbon atoms is observed in transition between energy-favorable configurations. Most trapping and detrapping processes are assisted by the dangling carbon atoms, which are more susceptible to knock-on displacements by electron irradiation. Thermal energy is lower than the activation barriers in transition among different energy-favorable configurations, which suggests electron-beam irradiation can be an efficient way of engineering the graphene edge with metal atoms.

THU 52
Unravelling inter-wall interactions on optical transition in double-wall carbon nanotubes

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Double-wall carbon nanotube (DWCNT) is one of the most fundamental systems to examine the effect of inter-wall interactions on the optically-allowed electronic transitions. To study the inter-wall coupling in DWCNTs in detail, we develop a direct preparation method of long and clean suspended individual DWCNTs on an open slit by using alcohol catalytic chemical vapor deposition (ACCVD), which enables us to apply two complementary experimental techniques, Rayleigh scattering spectroscopy and TEM observations, on the same DWCNT for characterizations of electronic transition energies in DWCNTs with defined inner and outer wall structures. We found the optical transition energies were downshifted in all the samples. In addition, the degree of the shifts strongly depend on the type of electronic combinations, that is, the shifts in semiconducting tube in semi@metallic are much larger than those in semi@semi. Inter-wall Coulombic screening effect on intra-wall excitons explains these experimental findings. At presentation, we will discuss the experimental procedures and the inter-wall coupling effects in detail.

THU 53
Atomic scale in-situ studies of catalytic reactions between d-elemental clusters and carbon nanostructures inside SWNT

Thilo Zoberbier¹, Thomas Chamberlain², Johannes Biskupek¹, Andrei Khlobystov², Ute Kaiser¹
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²School of Chemistry, University of Nottingham

Catalysis at the nanoscale plays an essential role in the fabrication, the transformation and the functionalization of carbon nanostructures. The control and efficiency of these processes largely depends on the morphologic properties of the catalyst as well as the metal specific chemical properties. However neither the catalytic mechanisms are understood on an atomic level nor is there a systematic understanding of fundamentals why different metal type deviate in their aptitude.

In our experiments aberration corrected HRTEM is used for atomically resolved in situ imaging of chemical reactions between a large range of d-elemental nanoparticles (≈ 1nm) and carbon inside SWNTs. This enables a detailed and systematic study of the processes characterizing the catalytic properties, aptitude and applications of different metals: formation of ordered carbon network in different morphologies, annealing and reorganization processes, ability to assimilate source material and disintegration of carbon structures. Further these investigations allow a study of the underlying metal-specific properties of Pi- and Sigma- bonding, metal-cohesive forces and solubility of carbon in the metal.

THU 54
Atomic layers of hexagonal gallium chalcogenides

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¹Physics Department, Lancaster University, Lancaster

We report density-functional-theory calculations of the electronic band structures, optical absorption spectra, and phonon dispersions of two-dimensional crystals of hexagonal Ga₂X₂ (X=S, Se, and Te).

Our calculations show that all three two-dimensional materials are dynamically stable; stability of hexagonal Ga₂Te₂ is discussed in particular detail. All three structures are shown to be indirect-band-gap semiconductors with a Mexican-hat dispersion of holes near the top of the valence band. We predict the existence of Lifshitz transitions - changes in the Fermi-surface topology of hole-doped Ga₂X₂ - at hole concentrations $n_S = 7.96 \times 10^{13} \text{ cm}^{-2}$, $n_{Se} = 6.13 \times 10^{13} \text{ cm}^{-2}$, and $n_{Te} = 3.54 \times 10^{13} \text{ cm}^{-2}$. 
Electrical properties of MWCNT/Pt-type nanocomposites in the atmosphere of hydrogen, methane or ammonia

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The work presents the outcomes of a comparative analysis of research into the structure and resistance changes of carbon nanotubes coated with platinum nanoparticles. High quality CNTs obtained in the CVD process, 100 to 200 μm long, 10-20 nm in diameter, were employed in the research. An indirect method of bonding the earlier produced platinum nanoparticles to the surface of functionalised carbon nanotubes was applied to deposit platinum nanoparticles onto the surface of carbon nanotubes. Investigations into the structure and morphology of the materials obtained were carried out with the (S)TEM method, and the XPS technique was used to identify the chemical composition of the fabricated nanocomposites. The investigations of changes in the resistance of nanomaterials were carried out with a constant concentration (1 percentage) of hydrogen, methane or ammonia in the presence of synthetic air. The purpose of the research undertaken was the characterisation of the materials produced and to identify the response of the carbon nanotubes-platinum system to hydrogen, methane or ammonia in the atmosphere of synthetic air.
08:30 – 09:00  G. Burkard, Konstanz
Electronic structure and spin-orbit coupling in monolayer transition metal dichalcogenides

09:00 – 09:30  R. Wiesendanger, Hamburg
Spintronics at the single-molecule level

09:30 – 10:00  O. Gaier, Grenoble
Reading Quantum States of Single Spins

10:00 – 10:30  coffee break

10:30 – 11:00  E. Laird, Oxford
A spin-valley qubit in a carbon nanotube

11:00 – 11:30  H. Weber, Erlangen
Magnetoresistance in large-area monolayer and bilayer graphene: interactions and dislocations

11:30 – 12:00  J. Guettinger, Barcelona
Mechanical resonators made of graphene and carbon nanotubes

12:00 – 17:00  mini workshops

17:00 – 17:30  J. Ye, Groningen
Two-Dimensional Electronics based on Ion-Gated Nanosheets

17:30 – 18:00  C. Backes, Dublin
Using Edge and Confinement Effects for in situ Determination of Size and Thickness of Liquid-Exfoliated Nanosheets

18:00 – 18:30  A. Jorio, Belo Horizonte
IWEPNM 2014 Conference Summary

18:30 – 20:00  break

20:00  Bauernbuffet – Farewell
08:30

Electronic structure and spin-orbit coupling in monolayer transition metal dichalcogenides

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Using k·p theory combined with parameters from density functional theory (DFT), we derive a low-energy effective Hamiltonian for monolayer transition metal dichalcogenides (TMDCs) at the K point of the Brillouin zone. The model captures features such as trigonal warping of the valence and conduction bands, the electron-hole symmetry breaking, and the spin splitting of the conduction band. We also consider other points in the Brillouin zone which might be important for transport properties. Concentrating on n-doped systems, we study the effect of perpendicular electric and magnetic fields in the conduction band. We discuss both the intrinsic and the Bychkov-Rashba spin-orbit coupling (SOC) induced by an external electric field and point out interesting differences in the spin-split conduction band between different TMDC compounds. An important consequence of the strong intrinsic SOC is an effective out-of-plane g-factor for the electrons which differs from $g\approx 2$. We identify a new term in the Hamiltonian of the Bychkov-Rashba SOC which does not exist in III-V semiconductors. Finally, we study quantum dots formed by electrostatic gating of two-dimensional TMDCs.
09:00
Spintronics at the single-molecule level
Roland Wiesendanger1
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Molecular spintronics based on the injection, transport, and detection of spin currents through a single magnetic molecule opens up fascinating perspectives for future ultra-low power storage or logic devices. Progress in this exciting field of research depends on a detailed characterization of the electrode-molecule interface at high spatial resolution. We have applied spin-polarized scanning tunneling microscopy (SP-STM) and spectroscopy (SP-STS) [1] to study the energy- and spin-dependent tunneling through individual phthalocyanine molecules as function of the orientation of the molecules with respect to the substrate lattice and as function of the magnetization states of substrate and SP-STM tip. Interestingly, a strong spin-dependent intramolecular contrast is observed related with a significant difference in spin-dependent current flow through the central metal ion and the surrounding ligands [2]. Our experimental results are in good agreement with first-principles calculations including the van-der-Waals interaction between molecule and substrate [3]. More recently, we have studied the spin-splitting of Kondo resonances observed on individual phthalocyanine molecules in the presence of RKKY-type coupling to an underlying ferromagnetic layer covered by a non-magnetic spacer layer by SP-STS [4]. Kondo coupling between metal centers along individual molecular chains has been revealed in salophene-based systems [5]. Moreover, by applying SP-STS to single molecular magnets, such as TbPc2, adsorbed on ferromagnetic nanostructures, we succeeded in imaging spin-split molecular orbitals with sub-molecular spatial resolution, while the magnitude of the exchange splitting was directly determined by spin-resolved tunneling spectroscopy [6]. Finally, we have demonstrated for the first time SP-STM based spin-current induced local switching [7] of spin states of individual TbPc2 molecules, directly revealed by SP-STM imaging before and after each manipulation process.

References:
09:30
Reading Quantum States of Single Spins
Oksana Gaier
1
1Institut Neel, CNRS, Grenoble

I will first resume the basics of molecular magnets and then address the field called molecular quantum spintronics, which combines the concepts of spintronics, molecular electronics and quantum computing. In this context, I will present different techniques that we developed to read and manipulate the spin state of single magnetic molecules (SMM). The first two of them are based on the coupling of a SMM to a single-wall carbon nanotube constituting together with metallic electrodes the read-out quantum dot. In the spin-valve geometry, the localized magnetic moment of the SMM leads to a magnetic field-dependent modulation of the conductance in the nanotube, which is used to retrieve the information about the magnetic state of the SMM. In the case of suspended nanotubes, one can also make use of a strong spin-phonon coupling that we have recently observed in order to investigate the magnetic state of the SMM. The last technique goes back to the use of molecular spin-transistors with which we have not only succeeded to read-out but, in combination with the hyperfine Stark effect, to perform coherent quantum manipulations on a single nuclear qubit on a time scale below a $\mu$s.
A spin-valley qubit in a carbon nanotube
Edward Laird
Materials Department, Oxford University, UK

Carbon nanotubes are potentially attractive materials for electron spin qubits because they can be made free of hyperfine dephasing and because spin-orbit interaction offers a route to all-electrical spin control. However, the existence of the valley degree of freedom and unscreened Coulomb interaction make the qubit readout complicated. Using a new fabrication technique, we have demonstrated combined valley-spin Pauli blockade in a nanotube double quantum dot by exploiting the bandgap to increase the energy splitting between blocked and unblocked states. This effect provides a readout mechanism for a qubit based on two valley-spin states of an electron. Making use of spin-orbit coupling in a bent nanotube, we drive coherent rotations between the qubit states, and demonstrate universal qubit control. The coherence time is found to be 65 ns, surprisingly short given the low density of nuclear spins.
11:00
Magnetoresistance in large-area monolayer and bilayer graphene: interactions and dislocations
Heiko B. Weber

Chair for Applied Physics, University of Erlangen, Erlangen

I will present low-temperature experiments using high-quality epitaxial graphene on SiC(0001). Due to the large sample size of monolayer samples, the data are free of edge effects and represent the physics of quasi-unrestricted two-dimensional graphene. This includes the accurate description of electron-electron interaction by the analysis of the parabolic magnetoresistance[1]. When additional defects are added, a logarithmic correction shows up, which should not be confused with the Kondo effect[2]. Unexpectedly, when choosing bilayer graphene, a strong linear magnetoresistance shows up. This effect is carefully analysed. We present an interpretation in the light of stacking faults and dislocations which we recently discovered in bilayer graphene[3].

Mechanical resonators made of graphene and carbon nanotubes
Johannes Guettinger\textsuperscript{1}
\textsuperscript{1}ICFO-Institute of Photonic Sciences, Barcelona

Graphene and carbon nanotubes offer unique scientific and technological opportunities for the realization of nanoelectromechanical systems (NEMS). The ultra-low mass density and high mechanical strength allowed the fabrication of mechanical resonators, which can be operated at ultra-high frequencies and are excellent sensors of mass and force. In addition, graphene and nanotubes have exceptional electron transport properties, including ballistic conduction over long distances due to the absence of backscattering. It is thus appealing to readout the motion of the resonator by electron transport.

I will discuss our recent results that we have achieved with graphene and nanotube NEMS in our group. In particular with a nanotube resonator, we are able to resolve the thermal motion at cryogenic temperatures and demonstrate ultrahigh force sensitivity [1]. The achieved force sensitivity might allow for the detection of single nuclear spins.

web site: http://bachtoldgroup.icfo.eu/
17:00

Two-Dimensional Electronics based on Ion-Gated Nanosheets

Jianting Ye$^1$

$^1$Device Physics of Complex Materials, Zernike Institute of Advanced Materials, Groningen

An electric double layer transistor (EDLT), a variation of a conventional field effect transistor (FET), is attracting increasing interests because of its ability to accumulate dense carriers, $10^{14}$ cm$^{-2}$, mediated by the movement of organic ions at the channel surface (see Figure). Integrating EDLT with varieties of inorganic nano-sheets (isolated from different layered materials) forms novel two-dimensional electronic systems at organic/inorganic interfaces hosting many controllable electronic phases. In this talk, I will present an experimental study on the field effect control of quantum phase transitions such as metal-insulator transition, superconductivity, and ferromagnetism using EDLT as an effective tool. By applying to a broader range of materials (for instance, varieties of thin films and single crystals), this organic/inorganic interface is promising to act as a rich playground for novel electronic properties and an emerging source of new device functionalities.
17:30
Using Edge and Confinement Effects for in situ Determination of Size and Thickness of Liquid-Exfoliated Nanosheets
Claudia Backes¹, Ronan J. Smith¹, Niall McEvoy², Nina C. Berner², Nils Scheuschner³, Janina Maultzsch², Georg S. Duesberg², Jonathan N. Coleman³
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³Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin

Over the last few years the study of 2-dimensional nanomaterials has become one of the most important areas of both materials science and nanotechnology. While this work originally focused on graphene, the palette of 2D materials currently under study includes transition metal dichalcogenides such as MoS₂ and WSe₂.

We have performed detailed spectroscopic and microscopic analysis on size-selected dispersions of exfoliated MoS₂ nanosheets. This has led to the development of an in situ technique which allows nanosheet concentration, lateral size and thickness to be obtained simultaneously from an optical absorption spectrum. The lateral size measurement relies on the effect of edges on the electronic and optical properties of the nanosheets while the thickness measurement is based on the effect of confinement on the excitonic positions. The combination of concentration-control, size-selection and measurement facilitates the preparation of dispersions with pre-determined properties. For example, monolayer-enriched dispersions can be produced, allowing the first measurement of direct-gap luminescence in liquid suspensions.

18:00
IWEPNM 2014 Conference Summary
Ado Jorio¹,
¹Departamento de Física, Universidade Federal de Minas Gerais, Brazil
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