

Name

XXVIIth
International Winterschool
on Electronic Properties
of Novel Materials

Molecular Nanostructures

Program



Hotel Sonnalp
Kirchberg/Tirol
Austria

02-09 March, 2013

IWEPNM 2013

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

Verein zur Förderung der Internationalen Winterschulen in Kirchberg Austria

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Dear Friend:

Welcome to the 27th International Winterschool on:

Electronic Properties of Novel Materials: "Molecular nanostructures"

This Winterschool is a sequel of twenty-six 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 | accommodation |
| Nils Scheuschner | accommodation, video transfer/recording |
| Reinhard Meinke | sponsoring |
| Amelie Biermann, Nils Rosenkranz | finances |
| Harald Scheel, Emanuele Poliani | receipts, technical assistance |
| Dirk Heinrich | technical assistance |
| Asmus Vierck, Harald Scheel | website |
| Felix Herziger | abstract booklet, e-payment |
| 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 Siegmars

Chairpersons

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

Program Committee

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Scope

This winterschool will provide a platform for reviewing and discussing new developments in the field of electronic properties of molecular nanostructures and their applications. Subjects included are:

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

INFORMATION FOR PARTICIPANTS

Time and location

The IWEPNM 2013 starts on Saturday, 2 March, evening, at the hotel Sonnalp in Kirchberg/Tirol, Austria and extends to Saturday, 9 March, breakfast. There will be a reception party on 2 March, after dinner, and a farewell party including dinner on Friday, 8 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 2013, Hotel Sonnalp, A-6365 Kirchberg/Tirol, Austria

e-mail: info@hotelsonnalp.info, web: www.hotelsonnalp.info

All questions concerning the IWEPNM 2013 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

email: iwepnm-info@physik.tu-berlin.de, web: www.iwepnm.org

Participation

Participation at the IWEPNM 2013 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 in the Kirchberg/Kitzbühel area, please ask at the hotel reception on Saturday evening.

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

Conference Publication

Invited and contributed presentations from IWEPM 2013 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> → **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).

Submission system: <http://mc.manuscriptcentral.com/pssc>

Previous user IDs persist, please check if you already have one. Lost access data can be retrieved via the "password help" section on the website. Otherwise please register by clicking on the respective link (right side - "New User?"). Note that login information is CASE SENSITIVE. Once you are logged in click on "Author Center" to start the submission.

Please use only Western letters for the file name, and only lower-case letters for the format extension. Please use clear, self-explaining file names, e.g. smith_version2.doc. Note that after submitting a manuscript, you can no longer modify it.

IWEPNM 2013
CHAIRPERSONS FOR THE ORAL SESSIONS

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

| | | |
|-------------------|-----------------------------|------------|
| Sunday, 03.03. | morning | Kuzmany |
| | morning, after coffee break | Kürti |
| | evening | Robertson |
| Monday, 04.03. | morning | Mews |
| | morning, after coffee break | Berciaud |
| | evening | Dinse |
| Tuesday, 05.03. | morning | Bolotin |
| | morning, after coffee break | Stampfer |
| | afternoon: Special workshop | Roth |
| | evening | Skakalova |
| Wednesday, 06.03. | morning | Mauri |
| | morning, after coffee break | Simon |
| | evening | Drndic |
| Thursday, 07.03. | morning | Loiseau |
| | morning, after coffee break | Ayala |
| | evening | Neugebauer |
| Friday, 08.03. | morning | Hirsch |
| | morning, after coffee break | Hertel |
| | evening | Roth |

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

Final program

| Sunday March 3 | | | Monday March 4 | | Tuesday March 5 | | Wednesday March 6 | | Thursday March 7 | | Friday March 8 | |
|----------------|---|---|----------------|--|-----------------|---|-------------------|---|------------------|---|----------------|--|
| Topics | Graphene opt-ics and devices | Non-carbon materials, CNT transport | | Graphene transport | | Topological insulators; CNT/graphene applications | | CNT sorting, optics and applications | | Graphene/CNT chemistry, magnetic properties | | |
| 08:30 | Photophysics of graphene, carbon nanotubes, and topological insulators: Symmetry and many-electron effects LOUIE | Electronic and Optical Properties of MoS ₂ at Monolayer Thickness HEINZ | | TUTORIAL: Graphene Mechanics and BN Heterostructures HONE | | TUTORIAL: Topological Surface States in Topological Insulators, Superconductors and Beyond: Discovery and Recent Results HASAN | | Chirality and Length Sorting of SWCNTs using Gel Column Chromatography KATAURA | | Atomically Precise Synthesis of Graphenes: A Bottom-up Approach FENG | | |
| 09:00 | New nanoscale hybrid structures made of C and BN from first principles: optoelectronic devices RUBIO | Tuning electronic and optical properties of monolayer molybdenum disulfide BOLOTIN | | | | | | Control of Colors of SWCNTs: Purification, Electrochromic Properties, and Peapods in a Single-Chirality State YANAGI | | Single Molecule Junctions from Structure Property Correlations and CNT Electrodes MAYOR | | |
| 09:30 | Changes induced by doping on the Raman features of monolayer and bilayer graphene SAUVAJOL | Properties by Design in Dimensionally Reduced Materials GOLDBERGER | | Nanotubes and Graphene at the Boundaries McEUEEN | | Floquet topological insulators DORA | | Optical Properties of Empty and Filled Carbon Nanotubes CAMBRE | | Magnetic excitations of molecular spins on a superconductor FRANKE | | |
| 10:00 | Coffee break | | | | | | | | | | | |
| 10:30 | Raman scattering of suspended graphene enhanced by plasmonic Au nanostructures HEEG | The dawn of silicene LE LAY | | Changes in Fermi surface topology and Hofstadter quantization in graphene superlattices GORBACHEV | | Transport signatures of Majorana fermions in nanowires WIMMER | | Non-dispersive D band in double-walled carbon nanotubes with ultrasmall diameter KURTI | | Assembly and properties of one-dimensional carbon chains TYKWINSKI | | |
| 11:00 | Electrochemical doping of graphene prepared by CVD KALBAC | GaAs nanowire heterostructures: single photon emission and energy harvesting FONTCUBERTA IMORRAL | | Gate-defined Quantum Confinement in Suspended Bilayer Graphene ALLEN | | Tunable electron interactions and robust non-Abelian quantum Hall states in graphene and other Dirac materials ABANIN | | Atomic configuration and properties of carbon-based heteroatomic nanostructures ARENAL | | Single-wall carbon nanotubes and graphene for lasers: from visible to mid-IR spectral range OBRAZTSOVA | | |
| 11:30 | Nanoelectronic Properties and Applications of Chemically Functionalized Graphene HERSAM | TiO ₂ Nanowires: from Basic Science to Applications FORRO | | Visualizing the influence of an isolated Coulomb impurity on the Landau level spectrum in graphene using STM LUICAN-MAYER | | Graphene for spintronics SENEOR | | Graphene and atomically-thin BN examined by TEM and other probes ZETTL | | Chemical exfoliation: reductive dissolution of graphene, nanotubes and other carbon nanoforms PENICAUD | | |

| 12:00 - 17:00 | Mini workshops | Special workshop Nano and Management | Mini workshops | Mini workshops | Mini workshops | Mini workshops |
|---------------|---|--|---|---|---|---|
| 17:00 - 18:30 | Dinner | | | | | |
| 18:30 | Graphene Device Options for Microelectronics Applications LEMMÉ | Optical and electrical properties of individual CdSe nanowires MEWS | Interaction-induced gapped state in charge neutral bilayer graphene VELASCO | Nanotechnology Convergence KIM | CVD Growth of Self-Organized Micro-Honeycomb Network Structure of SWCNTs for Photovoltaic Devices MARUYAMA | 17:00 Clusterfullerenes: Exciting Nanostructures in Endohedral Electrochemistry and Magnetic States DUNSCH |
| 19:00 | Epitaxial graphene on SiC: gateless patterning, efficient switches and a concept for digital circuits WEBER | Spin and charge detection in carbon nanotube double quantum dots BUITELAAR | Tuning the Bands in Epitaxial Graphene on SiC: Intercalation, Doping and Mini-Dirac Cones STARKE | Flexible and stretchable electron devices based on carbon nanotube thin films OHNO | Application of Graphene-Based Nanostructures in Dye Sensitized Solar Cells KAVAN | 17:30 Infrared magneto-spectroscopy of graphene-based systems ORLITA |
| 19:30 | Self-organizing graphene ribbon formation and electrical properties of graphene irradiated with He ions SATO | Electronic States and Unconventional Kondo Physics in Clean Carbon Nanotubes STRUNK | Magnetotransport in graphene with superlattice KRSTIC | Highly-sensitive nanopores for single-molecule DNA analysis GARAJ | Sense and Non Sense of ITO Replacement with CNT KOLARIC | 18:00 Conference Summary KATAURA |
| 20:00 | Electronic properties of CVD graphene and transition metal dichalcogenides DUESBERG | Poster I Monday | Poster II Tuesday | Nanotubes on my mind! Probing the brain with CNT electrodes RICCI | Poster III Thursday | 18:30 - 20:00 Break |
| 20:30 | | | | | | |
| | Graphene optics and devices | Non-carbon materials, CNT transport | Graphene transport | Topological insulators; CNT/graphene applications | CNT sorting, optics and applications | CNT sorting, optics and applications |
| Topics | Sunday March 3 | Monday March 4 | Tuesday March 5 | Wednesday March 6 | Thursday March 7 | Friday March 8 |

PROGRAM

AND

ABSTRACTS

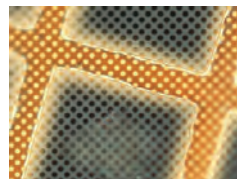


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Graphene has the potential to revolutionise many areas of technology. Graphene's applications are virtually limitless. Sectors to which graphene is particularly suited include electronics, aerospace, automotive, energy, telecommunications and defence.

Contact us to discuss whatever application or research 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.



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2-DTech is a company within The University of Manchester, where graphene was first isolated by Nobel prize winners Professor Sir Andre Geim and Professor Sir Kostya Novoselov.



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- 08:30 – 09:00 **S. G. Louie, Berkeley**
Photophysics of graphene, carbon nanotubes, and topological insulators: Symmetry and many-electron effects
- 09:00 – 09:30 **A. Rubio, San Sebastian**
New nanoscale hybrid structures made of C and BN from first principles: optoelectronic devices
- 09:30 – 10:00 **J.-L. Sauvajol, Montpellier**
Changes induced by doping on the Raman features of mono-layer and bilayer graphene
- 10:00 – 10:30 **Coffee break**
- 10:30 – 11:00 **S. Heeg, Berlin**
Raman scattering of suspended graphene enhanced by plasmonic Au nanostructures
- 11:00 – 11:30 **M. Kalbac, Prague**
Electrochemical doping of graphene prepared by CVD
- 11:30 – 12:00 **M. C. Hersam, Evanston**
Nanoelectronic Properties and Applications of Chemically Functionalized Graphene
- 12:00 – 17:00 **Mini-Workshops**
- 17:00 – 18:30 **Dinner**
- 18:30 – 19:00 **M. C. Lemme, Siegen**
Graphene Device Options for Microelectronics Applications
- 19:00 – 19:30 **H. B. Weber, Erlangen**
Epitaxial graphene on SiC: gateless patterning, efficient switches and a concept for digital circuits
- 19:30 – 20:00 **S. Sato, Tsukuba**
Self-organizing graphene ribbon formation and electrical properties of graphene irradiated with He ions
- 20:00 – 20:30 **G. S. Duesberg, Dublin**
Electronic properties of CVD graphene and transition metal dichalcogenides

Sunday, March 3rd

Graphene optics and devices

08:30**Photophysics of graphene, carbon nanotubes, and topological insulators: Symmetry and many-electron effects**Steven G. Louie¹¹University of California at Berkeley and Lawrence Berkeley National Lab

We discuss the photophysics of graphene, carbon nanotubes (CNTs), and topological insulators. Our ab initio calculations predict prominent exciton features in single- and multi-layer graphene. These features have since been observed experimentally. We show that, for photoemission spectra of doped graphene, previous studies overestimate the quasiparticle-satellite separation and falsely predict a plasmaron excitation. Using an ab initio GW+cumulant approach, we demonstrate that the plasmon satellites may be accurately computed, explaining photoemission measurements without invoking plasmarons. For CNTs, we calculate the optical response of a series of single-walled CNTs of different diameter and chirality. The results explain measured structure-property atlas of SWCNTs and permit derivations of accurate diameter- and chirality-dependent analytical formulas. For topological insulators, we show that the degree of spin polarization of photo-ejected electrons from the surface states is significantly higher than that of the initial states. Moreover, the spin orientation of the photoelectrons can be very different from that of the surface states and is controlled by the incident photon polarization.

09:00**New nanoscale hybrid structures made of C and BN from first principles: optoelectronic devices**Angel Rubio¹¹NanoBio Spectroscopy Group and ETSF Scientific Dev, University of the Basque Country UPV/EHU, Donostia-San Sebastian

There has been much progress in the synthesis and characterization of nanostructures however; there remain immense challenges in understanding their properties and interactions with external probes in order to realize their tremendous potential for applications (molecular electronics, light harvesting and emitting nanostructures). Here we review the recent advances within density-functional based schemes to describe spectroscopic properties of those complex systems. As an application we address the properties of BCN-based nanostructures and address their potential applications. The interpretation of the optical absorption and luminescence, requires a detailed knowledge of the excited state. We will show that BN displays strongly bound excitons whose binding energy increase reducing dimensionality. We show the influence of defects such as vacancies, carbon substitutions as well as graphene/BN nanodomains ("nanoscale patchwork") and address the influence of external E-fields on the excitonic spectra of BN tubes. We summarize the experimental and theoretical studies in those structures and at the end we will make connections with carbon-based materials.

09:30**Changes induced by doping on the Raman features of monolayer and bilayer graphene**Jean-Louis Sauvajol¹¹CNRS-University Montpellier 2, Montpellier

In this communication, we report data recorded by in situ Raman experiments on single-layer (SLG) and bilayer (BLG) graphene during exposure to rubidium vapor. By this way, we have been able to follow continuously the changes of the G and 2D bands features over a broad doping range (up to about 10^{14} electrons/cm²). From the comparison with theoretical predictions, we state that the evolution of the G-mode in SLG is understood as resulting of the competition between adiabatic and non-adiabatic effects in presence of a substrate pinning effect which inhibits the charge-induced lattice expansion of graphene layer [1]. For BLG, the added electrons are shown to be first confined in the top layer before a more symmetric charge repartition at high level doping. The evolution of the 2D band of BLG suggests an unexpected increase of the phonon dispersion upon doping [1].

[1] R. Parret et al. ACS Nano (2012)

10:30**Raman scattering of suspended graphene enhanced by plasmonic Au nano-structures**

Sebastian Heeg¹, Roberto Fernandez-Garcia², Antonios Oikonomou³, Fred Schedin⁴, Rohit Narula¹, Stefan A. Maier², Aravind Vijayaraghavan^{3,4}, Stephanie Reich¹

¹Department of Physics, Freie Universität Berlin, 14195 Berlin, Germany

²Department of Physics, Imperial College London, London SW7 2AZ, UK

³School of Computer Science, The University of Manchester, Manchester M13 9PL, UK

⁴Centre for Mesoscience and Nanotechnology, The University of Manchester, Manchester M13 9PL, UK

Enhanced Raman scattering has become a spectacular application in the field of plasmonics. It combines the generation of highly localized light fields at metal-dielectric interfaces with the variety of properties that can be obtained by Raman spectroscopy. We demonstrate a graphene Raman enhancement up to 10^3 arising from a nanoscale cavity between two closely spaced Au nanodisks. Graphene is suspended between the two disks and partially extends into the cavity [1]. Spatially resolved Raman measurements reveal that the enhancement in the cavity is localized in an area one order of magnitude smaller than the wavelength of the excitation. The enhanced Raman signal exclusively arises from suspended graphene under tensile strain, which is induced by the double structure partially elevating the graphene. This allows us to simultaneously probe strained and unstrained graphene. Raman enhancement in strained graphene can be used to characterise plasmonic enhancement arising from any variety of nano-structure geometries.

[1] Heeg et al., Nanoletters 13(1), 2013

11:00**Electrochemical doping of graphene prepared by CVD**Martin Kalbac^{1,2}, Jing Kong², Ladislav Kavan¹, Mildred S. Dresselhaus^{2,3}¹J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Dolejskova 3, CZ-18223 Prague 8, Czech Republic. Tel: 420 2 6605 3804; Fax: 420 2 8658 2307; E-mail: kalbac@jh-inst.cas.cz²Department of Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts 02139, USA³Department of Physics, MIT, Cambridge, Massachusetts 02139, USA

Recent advances in chemical vapor deposition (CVD) synthesis have now allowed the preparation of large and uniform monolayer graphene flakes. The CVD prepared graphene thus significantly simplifies the materials processing and more detailed studies with such samples can be readily performed. The successful application of graphene requires a detailed understanding of its electronic properties, including both its neutral and doped states. The doping of graphene leads to a shift of the Fermi level and for this reason doping provides a simple way to control the transport and optical properties. In our study the electrochemical charging has been applied to study the influence of a strong doping on the Raman features of chemical vapor deposition -grown single layer graphene. In addition we combined ¹²C and ¹³C graphene to make two layer graphene sheet. Due to a different mass of carbon isotopes the ¹²C and ¹³C graphene layers can be easily distinguished by Raman spectroscopy. Thus the isotopically labeled sample is an ideal system to study effects of the charge on the individual graphene layers in 2-LG.

11:30**Nanoelectronic Properties and Applications of Chemically Functionalized Graphene**Mark C Hersam¹¹Materials Science and Engineering, Northwestern University, Evanston

The outstanding electronic properties of graphene have been established on pristine samples in idealized conditions. However, for nanoelectronics, graphene needs to be interfaced with other materials in a manner that either preserves its intrinsic properties or enhances its functionality. Towards these ends, this talk focuses on chemical functionalization strategies for graphene-based nanoelectronics. For example, well-ordered self-assembled monolayers can be formed on graphene using 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) and 10,12 pentacosadiynoic acid (PCDA). Both PTCDA and PCDA are shown to be an effective seeding layer for high-k dielectrics, enabling wafer-scale fabrication of graphene-based nanoelectronic devices. In addition, atomic oxygen allows for homogeneous functionalization of graphene with epoxide groups in ultra-high vacuum. Importantly, this covalent functionalization method is fully reversible under mild thermal annealing conditions. In addition to chemically doping graphene, epoxidation yields local modification of the graphene bandstructure and provides pathways for further chemical functionalization.

18:30**Graphene Device Options for Microelectronics Applications**Max C. Lemme^{1,2}¹University of Siegen²KTH Royal Institute of Technology

Two different novel graphene devices will be discussed: hot electron transistors (HETs) and pressure sensors. The HET structures consist of a metal collector, a highly doped silicon emitter and a graphene base. High quality thermal SiO₂ and atomic layer deposited Al₂O₃ are used as emitter-base (EBI) and base-collector insulators (BCI), respectively. The collector currents are modulated via the base potential (common emitter configuration) achieving ON-OFF ratios of nearly 10⁵. The sensitivity of pressure sensors benefits from the extraordinary thinness of graphene. The pressure sensor design consists of a monolayer sheet of graphene suspended over a cavity with air at atmospheric pressure trapped beneath the cavity. When the ambient pressure is changed, the air in the cavity presses or pulls the membrane, straining it. Our sensor design shows high sensitivity when compared with conventional silicon based pressure sensors without the need of a strain gauge. The graphene based sensors work due to the piezoresistive effect, which we have demonstrated both theoretically and experimentally.

19:00

Epitaxial graphene on SiC: gateless patterning, efficient switches and a concept for digital circuits

Heiko B. Weber¹

¹Chair for Applied Physics, University of Erlangen, Erlangen

I will present recent progress obtained with the material system epitaxial graphene on SiC (0001). In solid state electronics, functionality is related to material contrast. In that spirit, we introduce a lateral patterning of the charge density in the graphene layer by locally varying intercalation in between the graphene layer and the substrate. Further, we employ the substrate SiC as a semiconductor, which can be used as semiconducting transistor channel. By combining these two material contrasts, we achieve a system which allows the design of switches with high on/off ratio as well as the definition of logical and analog circuits. A variety of functionalities is presented.

19:30**Self-organizing graphene ribbon formation and electrical properties of graphene irradiated with He ions**Shintaro Sato¹, Naoki Yokoyama¹¹Green Nanoelectronics Center (GNC), AIST, Tsukuba

Selective graphene ribbon formation on Cu twin crystals and electrical properties of graphene functionalized by He-ion irradiation are addressed.

We have found that graphene can be preferentially formed on narrow twin crystal regions in Cu film by CVD using methane [1]. The twin crystal region had a (001) or high-index surface, which was sandwiched between Cu crystals having (111) surfaces. The preferential graphene nucleation was probably caused by a difference in surface-dependent adsorption energies of reactants, which were estimated by first principles calculations.

We then address electrical properties of graphene functionalized by He-ion irradiation [2]. Exfoliated graphene was irradiated with He ions with doses of 2.2×10^{15} to 1.3×10^{16} ions/cm², providing graphene with low-density defects. Devices with the functionalized graphene channels demonstrated the modulation of drain current by back gate bias with an on-off ratio of about two orders of magnitude at room temperature.

This work was supported by JSP through the "FIRST Program", initiated by CSTP.

[1] Hayashi, et al. J. Am. Chem. Soc., 134, 12492 (2012)

[2] Nakahare, et al., Proc. IEDM 2012, 72 (2012)

20:00**Electronic properties of CVD graphene and transition metal dichalcogenides**

Georg S Duesberg^{1,2}, Hye-Young Kim¹, Kangho Lee¹, Riley Gentsby^{1,2}, Toby Hallam¹, Niall McEvoy¹, Mustafa Lotya^{1,3}, Jonathan N Coleman^{1,3}, Gyu-Tae Kim⁴

¹Centre for Adaptive Nanostructures and Nanodevices, Dublin

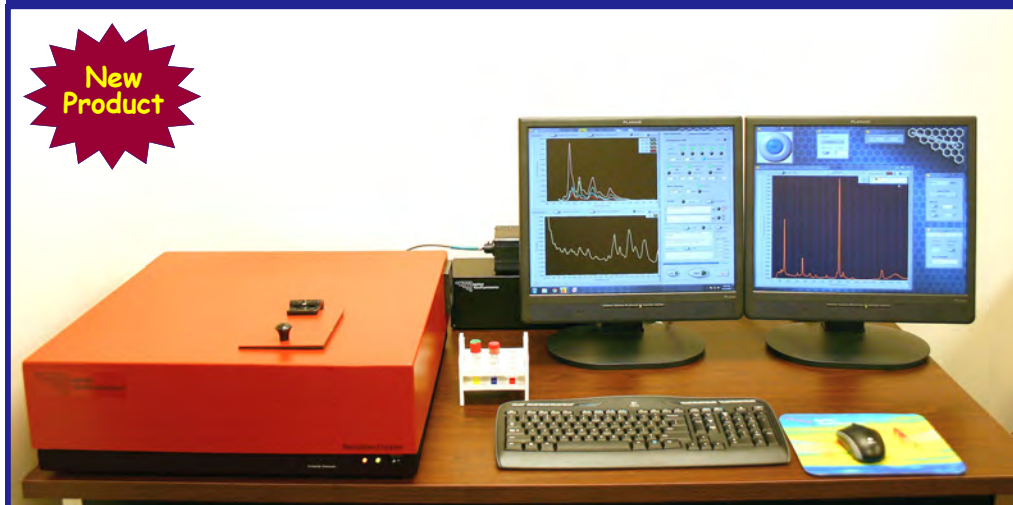
²School of Chemistry, Trinity College Dublin, Dublin

³School of Physics, Trinity College Dublin, Dublin

⁴4 School of Electrical Engineering, Korea University Seoul, 136-713 South Korea

Two dimensional materials have potential applications due to their unique electronic properties. CVD synthesis provides excellent process control and the opportunity to produce large area films which are compatible with existing microprocessing technology. We report on the CVD growth, transfer printing and device integration of graphene. In particular we investigated the electrical properties of chemically doped graphene in diode type configurations. Other 2D layered nano-materials like transition metal dichalcogenides (TMDs) are also expected to have great potential in nano-electronics, sensing and energy harvesting, as they possess a real band gap. We report on the electronic properties of MoS₂ flakes produced through liquid phase exfoliation. Furthermore, preliminary results on the electrical properties of CVD grown TMD films are presented.

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- 08:30 – 09:00 **T. F. Heinz, New York**
Electronic and Optical Properties of MoS₂ at Monolayer Thickness
- 09:00 – 09:30 **K. Bolotin, Nashville**
Tuning electronic and optical properties of monolayer molybdenum disulfide
- 09:30 – 10:00 **J. Goldberger, Columbus**
Properties by Design in Dimensionally Reduced Materials
- 10:00 – 10:30 **Coffee break**
- 10:30 – 11:00 **G. Le Lay, Marseille**
The dawn of silicene
- 11:00 – 11:30 **A. Fontcuberta i Morral, Lausanne**
GaAs nanowire heterostructures: single photon emission and energy harvesting
- 11:30 – 12:00 **L. Forro, Lausanne**
TiO₂ Nanowires: from Basic Science to Applications
- 12:00 – 17:00 **Mini-Workshops**
- 17:00 – 18:30 **Dinner**
- 18:30 – 19:00 **A. Mews, Hamburg**
Optical and electrical properties of individual CdSe nanowires
- 19:00 – 19:30 **M. Buitelaar, London**
Spin and charge detection in carbon nanotube double quantum dots
- 19:30 – 20:00 **C. Strunk, Regensburg**
Electronic States and Unconventional Kondo Physics in Clean Carbon Nanotubes
- 20:00 **Poster I**

Monday, March 4th

Non-carbon materials, CNT transport

08:30**Electronic and Optical Properties of MoS₂ at Monolayer Thickness**Tony F Heinz¹¹Departments of Physics and Electrical Engineering, Columbia University, New York, USA

MoS₂ is a prototype of a family of atomically thin metal dichalcogenides. Although the structure of the monolayer is similar to that of graphene, the A and B sublattice are occupied either by Mo atoms or by a pair of S atoms, rather than by C atoms. This difference in symmetry causes MoS₂ to be a semiconductor with a significant band gap. Through characterization of the optical properties of the material as a function of thickness, we show that quantum confinement effects lead to a crossover in MoS₂ from a bulk indirect gap semiconductor to a direct gap semiconductor at monolayer thickness [1]. As is common for lower-dimensional materials, excitonic effects are also very strong in MoS₂, as we demonstrate through the spectroscopic identification of charged excitons (trions) [2]. Another distinctive feature of this material is the possibility of producing long-lived valley polarization by excitation with circularly polarized light [3], as we show through photoluminescence measurements [3].

[1] K. F. Mak et al., Phys. Rev. Lett. 105, 136805 (2010).

[2] K. F. Mak et al., Nature Mater. (in press)

[3] K. F. Mak et al., Nature Nanotech. 7, 494-498 (2012).

09:00**Tuning electronic and optical properties of monolayer molybdenum disulfide**Kirill Bolotin¹¹Physics, Vanderbilt University, Nashville

Monolayer molybdenum disulfide (MoS₂) is a two-dimensional crystal comprising a single layer of molybdenum atoms sandwiched between two layers of sulfur atoms. Monolayer MoS₂ differs from its celebrated all-carbon cousin, graphene, by the presence of a direct band gap leading to robust light absorption. In this talk, we demonstrate that both electrical and optical properties of MoS₂ can be widely tuned via external influences. First, we investigate carrier scattering mechanisms in MoS₂. We distinguish long-range from short-range scattering by their dependence on the dielectric constant of the material surrounding MoS₂. Second, we discuss the influence of electrical gating on absorption and photoluminescence (PL) of MoS₂ field effect transistors. Concomitant with increasing conductivity, we find a hundredfold decrease of PL intensity with increasing gate voltage. We ascribe our observation to the interactions of excitons in MoS₂ with free carriers. Finally, we study the transition from direct to indirect band gap in MoS₂ under the influence of mechanical strain. The experimental signatures of this transition include strain-induced changes in the PL wavelength and intensity.

09:30**Properties by Design in Dimensionally Reduced Materials**Josh Goldberg¹¹Chemistry, The Ohio State University, Columbus

Similar to how carbon can be sculpted into low-dimensional allotropes such as fullerenes, nanotubes, and graphene, the major premise of our research program is that the framework connectivity of atoms for any crystalline solid can be constrained along specific axes to produce stable, single atom or polyhedron thick (<1 nm) dimensionally-reduced materials with fundamentally different optical and electronic phenomena than the bulk. Here we will describe some of our recent successes in creating different 1D derivatives of the layered transition metal chalcogenide lattice as well as 2D derivatives of the germanium (diamond) lattice. Just as zone-folding methods approximate and correlate how the optoelectronic properties of dimensionally reduced derivatives change, we propose that dimensional reduction can be applied to different lattices to produce a predictable and systematic change in band structure.

10:30

The dawn of silicene

Guy Le Lay¹

¹Aix-Marseille University, CNRS-CINaM, Campus de Luminy, Case 913, F-13288 Marseille-Cedex 09, France

Silicene, graphene's silicon cousin, just born in 2012, is in its infancy. Still, it offers many exciting promises due, typically, to its Dirac fermions, its two-dimensional topological insulator character, the hint for high-temperature superconductivity, and, last but not least, its direct compatibility with current silicon-based electronics. In my talk I will present a state-of the-art review on silicene and draw perspectives for potential applications.

E-mail: guy.lelay@univ-provence.fr

11:00

GaAs nanowire heterostructures: single photon emission and energy harvesting

Anna Fontcuberta i Morral¹

¹EPFL, Lausanne, Switzerland

We present our recent results obtained with high purity GaAs nanowire heterostructures in the areas of quantum photonics and photovoltaics. In particular, we present a new form of quantum dots obtained on the shell of GaAs nanowires. We present the structural and optical characterization, along with the demonstration of single photon emission. Finally we show how GaAs nanowires can be useful for third generation photovoltaics by overcoming the Shockley-Queisser limit.

11:30**TiO₂ Nanowires: from Basic Science to Applications**Laszlo Forro¹¹Laboratory of Physics of Complex Matter, Ecole Polytechnique Fédérale de Lausanne, Switzerland

Titanium dioxide (TiO₂) is one of the most versatile functional materials. From its three polymorphs (anatase, brookite, rutile) the anatase phase is the most popular one. It can be synthesized at different length scales: bulk single crystals, thin films, single crystalline nanotubes/nanowires and nanoparticles. The single crystal studies address the fundamental properties of the material while the lower dimensional forms offer possibilities for various applications such as photovoltaics, spintronics, thermoelectrics, bioengineering etc.

This presentation will start by reporting some key measurements on the bulk material (transport coefficients, ARPES, STM) which are important for understanding the nature of the charge carriers at any length scales. The emphasis will be given to the synthesis and application of single crystalline anatase nanowires. The method of synthesis, beyond the high structural quality, allows the doping and manipulation of nanowires in order to have active nano-sized materials. A broad range of applications, including photovoltaic, fuel cells, sensors and purification membranes will be illustrated.

18:30**Optical and electrical properties of individual CdSe nanowires**Alf Mews¹, Tobias Kipp¹, Sebastian Schäfer¹, Dennis Franz¹, Christian Stelow¹¹Department of Physical Chemistry, University of Hamburg, 20146 Hamburg, Germany

Semiconductor nanowires (NWs) are prepared in solution by using Bismuth particles as a catalyst. In accordance to the VLS-method to grow 1D nanostructure in the gas phase, this approach is called SLS because the Soluble precursors dissolve in the Liquid Bismuth catalyst to form Solid nanowires upon over saturation. Under different reaction conditions, truly quantum wires with diameters of less than 5 nm in diameter are prepared. In this contribution we will focus on the optical and electrical properties of individual CdSe-NWs. By employing single NW PL measurements and also TEM studies on the same individual NWs we establish a detailed structure property relationship. In low-T PL measurements we observe two groups of transitions, which are attributed to the recombination of delocalized and localized charge carriers, respectively. Moreover we combine Electrostatic Force Microscopy (EFM) including tip charging, with simultaneous PL measurements on individual free standing and contacted NWs. Here we study the charge distribution across the NW upon local illumination and show that the PL can be switched off and on upon external charging and recharging, respectively.

19:00

Spin and charge detection in carbon nanotube double quantum dots

Mark Buitelaar¹

¹London Centre for Nanotechnology, University College London, London

In this talk, I will discuss spin and charge readout of carbon nanotube double quantum dots which are of interest for spin-based quantum information processing. During the first part of the talk I will focus on weakly coupled double quantum dots in which certain electron transitions between the dots are forbidden by spin conservation (Pauli blockade). This is important as it allows us to convert the electron spin degree of freedom to a much easier measurable charge state or current. During the second part of the talk I will focus on the technique (radio-frequency reflectometry) that we developed to read out these double dot charge states in a fast and non-invasive way.

19:30**Electronic States and Unconventional Kondo Physics in Clean Carbon Nanotubes**Christoph Strunk¹¹Physics Department, University of Regensburg, Regensburg

Ultraclean carbon nanotubes form quantum dots of well-defined atomic structure at low temperatures. The energy of their electronic states can be revealed by transport spectroscopy. Tracing the energies of ground and excited states as a function of electron numbers in a parallel magnetic field results in detailed information about the band structures, in particular on spin-orbit and KK' -mixing effects. This information is exploited in the analysis of the Kondo effect occurring at larger electron numbers, where the devices become more transmissive. It is shown that the slightly lifted KK' -degeneracy in our device gives rise to satellites of the Kondo peak that are only weakly affected by a magnetic field. The experimental results are compared to state-of-the-art theoretical modeling [1].

[1] S. Smirnov and M. Grifoni, arXiv:1203.4360.

MON 1**Ion irradiation effects on suspended and supported graphene - insights from atomistic simulations**

E. Harriet Ahlgren¹, Jani Kotakoski², Ossi Lehtinen³, Arkady V. Krasheninnikov^{1,4}

¹Physics, University of Helsinki, Finland

²Physics, University of Vienna, Austria

³Physics, University of Ulm, Germany

⁴Applied Physics, Aalto University, Finland

Defects in nanomaterials can have drastic effects on the properties of these materials. This allows, in principle, controlled modification of these materials for example with ion irradiation. While nanomaterials can have a different response to irradiation than their bulk counterparts, existing theories only occasionally apply in their case. Therefore, to answer the question of what are the specific defect production mechanisms in graphene under ion irradiation, we have studied ion irradiation of graphene using molecular dynamics simulations. We show that the defect types in freestanding graphene depend strongly on the energy of the specific ion, defects occurring at distinct energy ranges that differ from one defect to the next. Our results also indicate, that with growing amount of defects, the membrane is stable, even with defect concentrations up to 35% of the atoms missing. Besides freestanding graphene, we have recently extended our studies for graphene on a Pt(111) surface to analyze the effect of the substrate to the defect production mechanisms in graphene under ion irradiation.

MON 2**Photocurrent Spectra of Chirally-Sorted Semiconducting Carbon Nanotube Devices**

Asifur Alam¹, Benjamin S. Flavel¹, Simone Dehm¹, Uli Lemmer², Ralph Krupke^{1,3,4}

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²Light Technology Institute, Karlsruhe Institute of Technology, 76131 Karlsruhe

³DFG Center for Functional Nanostructures (CFN), 76028 Karlsruhe, Germany

⁴Institut für Materialwissenschaft, Technische Universität Darmstadt, 64287 Darmstadt, Germany

We present photocurrent measurements from chirally-sorted (6,5) semiconducting single-walled carbon nanotube devices using scanning photocurrent microscopy (SPCM). A commercially available supercontinuum light source accompanied with an acousto-optic tunable filter illuminates the SPCM setup providing a high intensity laser output at a specified wavelength. Devices are fabricated in arrays on oxidized silicon substrates, making it possible to scan multiple devices at a time. Nanotubes are deposited via dielectrophoresis from monochiral dispersion, characterized by a photoluminescence excitation map and absorption spectrum. Results reveal that

a single scan at 570nm excitation wavelength can produce a photocurrent image with peak values at certain areas. This excitation wavelength coincides with the E_{22} interband-transition wavelength of (6,5) carbon nanotubes provided by the photoluminescence excitation map. Preliminary photocurrent measurements at different wavelengths yield a photocurrent spectrum, which correlates well to the absorption spectrum of the (6,5) dispersion.

MON 3

Mechanical Stability of Peapods Probed by Optical Spectroscopy under Pressure

B. Anis¹, M. Fischer², M. Schreck², K. Haubner³, L. Dunsch³, F. Börrnert³, M. H. Rummeli³, C. A. Kuntscher¹

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Earlier high-pressure Raman work demonstrated that filling of single-walled carbon nanotubes (SWCNTs) with inner tubes or Argon stabilizes the nanotubes walls, whereas iodine or C_{70} filling lead to the destabilization of the nanotubes [1]. The mechanical stability of empty and filled SWCNTs against hydrostatic pressure has been mainly addressed by Raman spectroscopy monitoring the vibrational properties. Pressure experiments on carbon nanotubes using techniques probing the electronic properties, such as optical spectroscopy, are rare. Recently, we demonstrated the stabilization effect of the inner tubes on SWCNTs walls by optical spectroscopy under pressure [2]. Here, we present a high-pressure optical transmission study on the mechanical stability of SWCNTs filled with C_{60} , C_{70} or iodine molecules (so-called peapods). The preparation and characterization of the peapods will be briefly described. Our high-pressure optical measurements demonstrate that different fillers greatly influence the pressure-induced effects in SWCNTs.

[1] A. L. Aguiar et al., J.Phys. Chem. C 115, 5378 (2011)

[2] B. Anis et al., Phys. Rev B 86, 155454 (2012).

MON 4

Alignment of SWCNT in stretched polymer films

Natalia R. Arutyunyan¹, Elena D. Obraztsova¹

¹GPI RAS, Moscow

For the applications in the field of laser technics, it is appropriate to use the elements working in the certain polarization of light. Single-wall carbon nanotubes (SWCNT), due to the unique structure and high aspect ratio, demonstrate the strong anisotropy of the optical properties, and they can successfully play the role of the mode-lockers in the laser resonators. Here, the fabrication of the SWCNT-based polymer films, and the alignment of the dispersed nanotubes via the stretch

of these films is presented. Different types of polymers were used as a matrix: carboxymethylcellulose, polyvinylalcohol and polymethyl methacrylate. After the significant elongation of the films, nanotubes were oriented along the direction of the stretch. The polarized Raman spectra were recorded. The strong anisotropy of the main Raman mode intensities was revealed. The width of the angular orientation of nanotubes was estimated to be 10 degrees.

Acknowledgements. The work was supported by grant RFBR 12-02-31327 mol-a and grant of Russian president MK-5046.2013.2

MON 5

Coulomb staircase behavior at room temperature in macroscale multiwalled carbon nanotube-polybenzimidazole nanofibers

Asaf Avnon¹, Vitality Datsyuk¹ Svetlana Trotsenko¹ Biswajit Mukhopadhyay² Ha-Duong Ngo² Stephanie Reich¹

¹Freie Universität Berlin, Germany

²Technische Universität Berlin, Germany

We prepared polybenzimidazole nanofibers loaded with 6.7% weight of multiwall carbon nanotubes. The nanofibers were made with electrospinning process; they have diameters up to 500 nm and can be several meter long. The electrical conductivity was measured on an individual multiwall-nanotube-polybenzimidazole fiber at room temperature. An electric potential applied to the nanofiber lead to a Coulomb-staircase like dependence of the current. Overall the currents were on the order of 0.01 -0.1 μ A. As the switching occurs in high voltages, this device can be utilized to various high voltages applications. This surprising result suggests that composite nanofibers provide access to 1D measurements in the macroscale already in room temperature.

MON 6

Numerical Simulations of High Heat Dissipation Technology in LSI 3-D packaging using CNT Through Silicon Via (TSV) and Thermal Interface Material (TIM)

Teppei Kawanabe¹, Mizuhisa Nihei², Yuji Awano¹

¹Electronics and Electrical Engineering, Keio University, Yokohama

²Collaborative Research Team Green Nanoelectronics Center (GNC)/National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba

Through silicon via (TSV) technology for 3-D packaging allows stacked silicon chips to interconnect through direct contact to provide high-speed signal processing. One of the biggest challenges in 3-D packaging is thermal management. Conventional TSVs are not suitable for high power heat dissipation. Nano-carbon materials such as Carbon nanotubes (CNTs) and graphene have excellent electrical and thermal conductivities. In this paper, we report numerical simulations of heat dissipation

properties of nano-carbon TSV and TIM towards a high power heat dissipation LSI-3D packaging. By using vertically aligned multi-walled CNTs as both TSV and TIM materials, a boundary temperature just under a heat source decreased about 25K in total, comparing to that without TSVs and with a solder TIM. This result suggests superior heat dissipation properties of nano-carbon 3D packaging.

Acknowledgements: This research is supported by JSPS through its FIRST Program.

MON 7

On the bonding environments of n-type substitutional heteroatoms in SW-CNTs

Georgina Ruiz-Soria¹, Jessica Campos-Delgado², Susi Wintz³, Mauricio Terrones⁴, Hua Jiang⁵, Martin Knupfer³, Thomas Pichler¹, Paola Ayala¹

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²Universite catholique de Louvain, Belgium

³IFW-Dresden, Germany

⁴The Pennsylvania State University, USA

⁵Nanomaterials group, Aalto University, Finland

Tailoring the electronic properties of single-walled carbon nanotubes through the incorporation of heteroatoms represents a key method for their applicability in semiconductor technology. For n-type doping, the synthesis of N and P doped single-walled carbon nanotubes has been reported but up-scalability and controlled production still need to be explored. From the theoretical point of view, the most significant differences between N and P doped SWCNTs arise mainly related to the creation of localized electronic states and the formation of non dispersive bands for the case of P doped tubes. Modification of transport properties due to different scattering centers are also intriguing. Recent studies also suggest that localized magnetic moments must be magnetically coupled through SWCNTs conduction electrons differently in both cases. Conclusive experiments confirming these characteristics can only be given if the materials are produced clean and crystalline. This contribution shows our progress identifying the bonding environments in which P and N substitute C atoms in the SWCNT's wall from combined photoemission and Raman spectroscopy, and analytical imaging.

MON 8

Tailoring morphologies of diamond thin films for neural stem cells culturing

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¹Institute of Physics AS CR, v.v.i., Prague

²Czech Technical University in Prague, Faculty of Nuclear Sciences and Physical Engineering

³Institute of Experimental Medicine, AS CR, v.v.i., Prague

Due to unique properties combination, nano-crystalline diamond (NCD) is promising material for integration with biological systems. In the case of neural cells or neural stem cells (NSC), NCD possess a great potential as biomaterial for central nervous system transplantation and tissue engineering. In this contribution we investigate influence of oxidized NCD surface morphology with: i) flat (as grown), ii) nano-rods and iii) porous structure onto NSCs culturing. Nano-rods (diameter 20-60 nm) were fabricated by etching of flat NCD films, while porous structures (random wires diameter below 20 nm) were directly grown at tailored process conditions. We found that nano-rods were not suitable for NSCs. Nevertheless, on flat NCD and porous structures the 24-48 hours cells seeding resulted to similar number of attached NSCs. After the 6-days seeding, flat NCD were covered by homogeneous NSCs layer, while on samples with porous structure NSCs formed neurospheres, suggesting less preferable conditions for attachment. Further investigations of NSCs to NCD surface adhesion and interaction mechanisms will be discussed. Acknowledgment MSMT for LM2011026 and GACR for P108120910 and P108120996.

MON 9

Sorting and analysis of nanomaterials by band sedimentation centrifugation

Claudia Backes¹, Arlene O'Neill¹, Niall McEvoy², Georg S. Duesberg², Jonathan N. Coleman¹

¹Chemical Physics of Nanostructures, School of Physics, Trinity College Dublin Dublin

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Despite the fact that nanomaterial sources vary (nanotubes, graphene, MoS₂) and different materials have gained center stage in the past, similar challenges have to be faced such as solution phase processing/dispersion and especially the sorting step that has to follow in order to obtain high quality material.

Concerning separation, the potential of density gradient ultracentrifugation has already been very convincingly shown in the case of nanotubes and demonstrated for graphene. However, multiple factors influence the surfactant arrangement and thus the buoyant density and ultimately the sorting efficiency. Furthermore, this methodology is not transferrable to any solvent system and parameter elaboration is tedious. We propose band sedimentation centrifugation (BSC) as versatile and simple alternative not restricted to certain solvents. In BSC, the nanomaterial dispersion is layered on top of a race layer of higher density. The centrifugation is terminated as soon as the material has spread throughout the vial and thus separated according to its sedimentation velocities. We demonstrate different showcases including purification and coarse sorting of graphene dispersions.

MON 10**Fe and Co intercalation of epitaxial graphene on Ir(111)**Maciej Bazarnik¹, Regis Décker¹, Jens Brede¹, Roland Wiesendanger¹¹Interdisciplinary Nanoscience Center Hamburg, University of Hamburg, D-20355 Hamburg, Germany

The catalytic decomposition of hydrocarbons on transition metals is shown to lead to the growth of high quality graphene. The resulting electronic, magnetic, and structural properties of graphene crucially depend on the choice of the metallic substrate. Moreover, the extensively studied graphite intercalation compounds inspired a new route toward tailoring the properties of graphene upon the growth on a chosen substrate by incorporating different intercalants at the graphene-substrate-interface. So far, most efforts in that direction were employed to keep the exotic properties of free-standing graphene intact, open a gap at the Dirac point, or induce superconductivity. Here, we present a growth study of Fe and Co intercalation between graphene and the Ir(111) surface with the goal of preparing a nano-scale hybrid system with exceptional magnetic properties not found in other systems.

MON 11**Intrinsic lineshape of the Raman 2D-mode in freestanding graphene monolayers**Stephane Berciaud¹, Xianglong LI², Louis E. Brus³, Stephen K. Doorn², Tony F. Heinz⁴¹Institut de Physique et Chimie des Matériaux de Strasbourg (UMR 7504), Université de Strasbourg and CNRS, F-67034 Strasbourg, France²Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, New Mexico 87545³Department of Chemistry, Columbia University, New York, NY 10027⁴Departments of Physics and Electrical Engineering, Columbia University, New York, NY 10027

The lineshape of the two-phonon inter-valley (2D) resonant Raman mode is examined in freestanding graphene monolayers. For photon energies in the range 1.53 eV – 2.71 eV, this feature displays significant deviations from the commonly used Lorentzian approximation, and evolves towards a slightly broader, more symmetric peak as the photon energy is decreased. We discuss the possible interpretations for such a peculiar lineshape in terms of broadening induced by the finite lifetime of the photoexcited electrons and holes and broadening caused by trigonal warping of the electron and phonon dispersions. We find that lifetime broadening alone cannot account for our observations and that phonons away from the high symmetry lines contribute to the 2D-mode linewidth. In contrast, supported graphene exhibits a quasi-symmetric and broader 2D-mode feature. The crossover between the freestanding and supported cases is mimicked by electrostatically doping a

freestanding sample at carriers densities above $2 \cdot 10^{11} \text{ cm}^{-2}$. This proves that small amounts of doping smear out the asymmetry of the 2D-mode feature, which can be utilized as a hallmark of a quasi-neutral sample.

MON 12

Study of Substrate-Molecule Interaction in Functionalized Carbon Nanoribbons

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Carbon based hybrid nanostructures are an emerging field of current research. Within a theoretical approach combining density functional and density matrix theory, we found that photo-active molecules, considerably influence the optical properties of carbon nanotubes [1,2]. To obtain further insights on the nature of the molecule-substrate coupling, we extend these studies to functionalized 1-dim graphene nanoribbons and 2-dim graphene. Our theory predicts the splitting of the pristine transitions into multiple resonances exhibiting a considerable spectral shift. Both effects are strongly influenced by the electronic bandstructure of the substrate. This influence is studied for different subbands in the case of nanoribbons reflecting a large variety of bandstructure curvatures (from negative to positive and from linear to parabolic). Furthermore, we discuss the impact of dimensionality on the coupling by investigating ribbons of different widths, which reflect well the behavior towards the 2-dim graphene sheet [3].

[1] E. Malic et al. PRL 106, 097401 (2011)

[2] E. Malic et al. JPCM 24, 394006 (2012)

[3] G. Berghäuser and E. Malic, submitted (2013)

MON 13

The effect of the synthesis method on the morphology of indium-oxide/MWCNT composites

Peter Berki¹, Zoltan Nemeth¹, Balazs Reti¹, Klara Hernadi¹

¹Department of Applied and Environmental Chemistry, University of Szeged, Szeged

Nowadays 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 In₂O₃/MWCNT using an impregnation and a hydrothermal synthesis method. Indium (III) chloride (InCl₃) was used as precursor material to cover the surface of carbon nanotubes, and distilled water and ethanol were used as solvents. In our samples the mass ratio was 4:1 (In₂O₃:MWCNT), and different temperatures were examined during the calcination process: 300°C, 350°C and 400°C, respectively. The produced composite materials were characterized by X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), Raman microscopy, transmission electron microscopy (TEM) and scanning elec-

tron microscopy (SEM) techniques. From these results we could concluded that the composites manufactured with different methods resulted in various morphology. These new multiwalled carbon nanotube based composite materials are very promising candidates for testing as gas sensors or photocatalyst.

MON 14

Bilayer Graphene Grown by Chemical Vapour Deposition (CVD) using Oxidative De-Hydrogenation Chemistry

Laurent Bernard¹, Jacim Jacimovic¹, Massimo Spina¹, Primoz R. Ribic¹, Laszlo Forro¹, Arnaud Magrez¹

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Application of graphene is foreseen in composites, energy production and storage devices, touch screens and electronics. This conviction is the result of theoretical predictions of graphene properties, and relies on the outstanding performances of small sized prototypes fabricated with graphene exfoliated from graphite. Most predictions are yet to be verified experimentally while specifications of large-scale devices remain uncertified. To meet these objectives, extended films of high-quality graphene need to be produced reliably. CVD is the most suitable process yielding graphene from hydrocarbons over transition metal substrates. The most efficient synthesis proceeds from methane at elevated temperature and is not compatible with most applications. The use of oxidative dehydrogenation (ODH) is very promising for graphene growth by CVD as such chemistry has allowed the growth down to 300°C of carbon nanotubes with low defect density. We will report on the optimization of the reaction process shedding light onto graphene growth mechanism by ODH chemistry. The study of transport and optical properties of the resulting graphene will be presented as well.

MON 15

Size dependent electron-phonon coupling in spherical CdSe nanocrystals

Amelie Biermann¹, Sofie Abe², Raquel Gomes², Karel Lambert², Holger Lange^{1,3}, Zeger Hens², Christian Thomsen¹

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Colloidal nanocrystals have attracted a lot of interest because they show fascinating properties such as two-photon absorption, multiple exciton generation and high photoluminescence. The possibility to synthesize defined nanocrystals with a precise control over their size, stoichiometry and crystal structure enables the use in systems like biological sensors, LEDs, lasers and solar cells.

The magnitude of the coupling of excited carriers to phonons within the material contributes to the time scales of different photophysical processes, of high significant

ce for those applications. These processes include for example carrier multiplication rates and relaxation times.

We employ Raman spectroscopy to analyze the coupling strength, finding a defined dependence on the particle size with a minimum coupling at sizes of 5 nm diameter. A comparison between wurtzite and zincblende nanoparticles yields larger Huang-Rhys factors in the wurtzite structure. These results can be used to optimize the synthesis parameters to the specific needs of different optical applications.

MON 16

The Origin of Linear and Nonlinear Damping in Graphene Nanomechanical Resonators

Marc Bockrath¹, Tengfei Miao¹

¹UC Riverside, Riverside

The origin of dissipation in nanoelectromechanical systems (NEMS) remains unresolved. Graphene and carbon nanotubes have emerged as excellent materials to investigate linear and nonlinear damping in NEMS. Here we demonstrate that the quality factor of electrically-driven few-layer graphene drumhead resonators is inversely proportional to temperature in the small amplitude, linear damping regime. At larger drives, the nanomechanical resonance broadens due to nonlinear damping, similar to that found by Eichler et al. (Eichler et al., Nat. Nanotechnol. 2011). The linear and nonlinear damping in graphene resonators can be understood by a model of thermally fluctuating high frequency modes that produce frequency fluctuations in the measured fundamental mode through nonlinear coupling, similar to a tension fluctuation model recently proposed for carbon nanotubes (Barnard et al., PNAS 2012). A model for thin membranes explicitly accounting for the modal nonlinear coupling is given, yielding good agreement with experiment. Our results provide a general framework for understanding the origin of linear and nonlinear damping in nanoscale resonators based on ultrathin membranes.

MON 17

Electronic-Type Separation of SWCNTs via Supramolecular Architectures

Sebastian Bosch^{1,2}, Lukas Zeininger², Frank Hauke^{1,2}, Andreas Hirsch^{1,2}

¹Institute of Advanced Materials and Processes, Fuerth, Germany

²Chair of Organic Chemistry, University Erlangen-Nuremberg, Germany

The implementation of single-walled carbon nanotubes (SWCNTs) into potential applications is still a great challenge due to the polydisperse nature of the pristine material. Among several reviewed separation methods,[1] diazonium chemistry provides simple and fast one-step separations[2] attaching a variety of different functional groups to the sidewalls of predominantly metallic SWCNTs.[3] We demonstrate that the combination of this selective functionalization sequence and host-guest chemistry offers a powerful and direct method for an electronic-type separation

of SWCNTs. The supramolecular architectures of SWCNTs functionalized with a Hamilton receptor and cyanuric acid derivatives are highly soluble in various non-nanotube solvents, depending on the nature of the cyanuric acid guest molecules. In addition to the selectivity and multifunctional dispersibility, these systems are highly appealing as building blocks for self-assembling electronic hybrid materials.

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[2] M. S. P. Shaffer et al., Chem. Soc. Rev., 2012, 41, 4409.

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MON 18

In-situ Raman Spectroelectrochemical Study of Graphene Oxide

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Previously we reported on an effect of a spontaneous electrochemical activation during the electrochemical cycling of a few-layered graphene oxide (FLGO) performing as a conductive additive to a nanocrystalline LiFePO₄ olivine. Based on electrochemical, IR and Raman studies we suggested that a gradual in-situ reduction of FLGO is responsible for this activation. For a better understanding of the changes in the FLGO structure, a thorough in-situ Raman spectroelectrochemistry study combined with ex-situ Raman and X-ray photoelectron spectroscopy of FLGO and graphene nanoplatelets - similar materials but in a different degree of oxidation - were carried out. Raman shifts and evolution of intensities and linewidths of the tangential “graphitic” G mode and the defect-induced D and D’ modes were examined using different fitting models. The derived data show a great complexity of the structural changes occurring during the reduction of FLGO, with a predominant effect of narrowing of the defect distribution and a simultaneous increase of the stacking order. The reversibility of the redox processes was studied as well.

MON 19

Magnetic properties of 1D metal compounds encapsulated in single-walled carbon nanotubes

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We study magnetic properties of 1D metal compounds inside single-walled carbon nanotubes (SWCNT) by using x-ray magnetic circular dichroism (XMCD) and superconducting quantum interference device (SQUID). The iron-nanotube hybrids are initially metallicity-sorted SWCNT encapsulating metallocenes [1,2] or metal acetylacetonates. At elevated temperatures the encapsulated organometallic compounds react with each other to form 1D metal compound clusters. XMCD responses at the metal core-level absorption edges were measured at magnetic fields up to 6 T and temperatures down to 5 K. Using the XMCD sum rules we determine the orbital and spin magnetic moments of the encapsulated metal atoms. It reveals that the magnetic moments of the metal atoms are drastically altered in magnitude as the transformation to the 1D clusters occurs. We discuss on the 1D magnetic properties in relation to the metal, cluster dimension, electronic hybridisation, charge transfer and SWCNT metallicity.

Work supported by the FWF project P621333-N20.

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MON 20

Desorption kinetics of ssDNA from SWNTs

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We have studied the kinetics of desorption of single strand DNA oligomers from colloidal dispersed single-wall carbon nanotubes by fluorescence spectroscopy. We do so by monitoring the rate of desorption from SWNTs after submitting an equilibrated ssDNA-SWNT suspension to a concentration step by which excess ssDNA is removed from the suspension. The concentration of desorbed ssDNA is determined using fluorescence from a marker attached to the ssDNA. Temperature-dependent desorption measurements allow to carry out an Arrhenius analysis. Binding energies obtained from this reveal surprisingly small activation energies of only (70 ± 10) kJ·mol⁻¹ for FAM-(GT)_n oligomers with $n=12,16$. Such small activation energies are typically associated with adsorbate residence times on the order of fraction of a second to seconds at best. The ssDNA-SWNT conjugates studied here however are stable over hours and days even if excess DNA is removed from the suspension. This indicates that the conjugates are not stabilized energetically but kinetically.

MON 21**Influence of CCVD parameters on the chemical state of nitrogen incorporating in carbon nanotubes**

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Here we study an influence of parameters of catalytic chemical vapor deposition (CCVD) process on the concentration and chemical state of nitrogen inserting in carbon nanotubes (CNTs). Arrays of aligned nitrogen-doped CNTs were grown vertically on silicon substrates using an aerosol-assistant CCVD method, where ferrocene, dissolved in a liquid carbon precursor, has been taken as a catalyst source. The temperature of synthesis, catalyst concentration, feedstock composition (trace of carbon dioxide, argon-hydrogen mixture) were varied, and the obtained samples were examined using X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy to determine the chemical forms of nitrogen in the near surface and deep layers of CNTs. We find that temperature has crucial effect on the relative content of pyridinic and graphitic nitrogen in the CNTs. The higher temperature results in the larger amount of graphitic nitrogen. The measurements of field electron emission of arrays of aligned nitrogen-doped CNTs revealed the clear dependence between the electric field threshold and nitrogen concentration.

MON 22**Large area, non-contact graphene conductance mapping by Terahertz Spectroscopy**

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We demonstrate non-contact, centimeter scale quantitative mapping of the sheet conductance of large area chemical vapor deposited graphene films by terahertz time-domain spectroscopy (THz-TDS). Mappings are performed on insulating as well as conducting substrates, allowing fermi level control during conductance mapping through use of a back-gate. THz-TDS has potential as a fast, non-contact metrology method for direct, quantitative mapping of the spatially averaged nanoscopic conductance, carrier mobility, carrier density, and carrier scattering rate on wafer-scale graphene.

Dual configuration micro four point-probe(M4PP) measurements, demonstrated on graphene for the first time, provide comparison to DC conductance, as well as valuable statistical insight into the influence of microscale defects on the conductance. The combination of M4PP and THz-TDS conductance measurements, supported by micro Raman spectroscopy imaging and optical imaging, reveals that investigated films are electrically continuous on the nanoscopic scale with microscopic defects likely originating from the transfer process, dominating the microscale conductance of the investigated graphene film.

MON 23

Structural properties of free-standing graphene membranes derived from epitaxial graphene on 6H-SiC

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Single-crystalline graphene grown on SiC exhibits excellent electronic properties like high charge-carrier mobility and tunability of the local charge-carrier density (doping, gating). By wet-chemical removal of the substrate freestanding bi- and fewlayer membranes are obtained (cf. related presentation), which open new fields for application.

Moreover, such membranes allow for the direct investigation of both the atomic structure and microstructure of the thus derived graphene (e.g., local number of graphene layers, distribution of extended defects) by complementary microscopic techniques like scanning/transmission electron microscopy (SEM, TEM), electron diffraction and Raman microspectroscopy. Hence, additional information about the interaction within the layered system graphene/bufferlayer/SiC substrate as well as the relaxation of strain can be derived to contribute to a more fundamental understanding of the complicated growth system. High-resolution Raman measurements reveal the relaxation of compressive strain within the membranes as the substrate is removed. This relaxation is related to buckling of the membranes (after removal of the SiC) as visualized by AFM and TEM.

MON 24

Polymer/fullerene bulk heterojunction solar cells with embedded $Mo_6S_9-xI_x$ nanowires

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The photovoltaic properties of MoSI-embedded P3HT:PCBM solar cells have been studied and compared to the properties of control P3HT:PCBM cells. Since the MoSI nanowires are electron conductors along the wire axes, in addition to the usual hole conduction via polymer, an electron transport is expected, potentially significantly increasing the cell efficiency. The MoSI-embedded solar cells consisting of 70 nm thick active layer prepared by spin coating and thermal deposition showed significant efficiency increase of 21 % over the control cells and enhanced photon-to-electron conversion efficiency in the red region of the visible spectrum. All MoSI-embedded cells exhibited an open circuit voltage increase of 0.04 V.

MON 25

Charged and strained graphene layers in the Raman response of graphite intercalation compounds

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We present detailed multi frequency resonant Raman measurements of potassium graphite intercalation compounds (GICs) from stage III to VI. GICs consist of graphene layers next to intercalant layers or surrounded by graphene layers in-between. The positions of the G- and 2D-lines as function of staging directly depend on the charge transfer from K to the graphite layers and on the lattice expansion. By ab-initio calculations of the density and the electronic band-structure, we demonstrate that most (but not all) of the transferred charge remains on the graphene sheets adjacent to the intercalant layers. From a detailed line-shape analysis of these G- and 2D-lines, we unambiguously identify the Raman response of charged and uncharged graphene layers, and correlate it to the in-plane lattice constant change due to internal strain of the graphene layers. The outcome of this study demonstrates that Raman spectroscopy is a very powerful tool to identify local internal strain in single and few-layer graphene and their composites, yielding even absolute lattice constants.

Work supported by FWF-I377-N16, and OEAD AMADEUS PROGRAM.

MON 26

Single-walled carbon nanotubes as templates for the controlled formation of sulphur terminated graphitised nanoribbons

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The hollow nature and relative chemical inertness of the concave side of carbon nanotubes (CNTs) makes them ideal candidates for use as both reaction vessels, in which the reactants can be combined, and a 1D template for the controlled formation of products which are unfavoured in the bulk phase.

Encapsulation of the appropriate elemental building blocks, carbon and sulphur, within CNTs results in the formation of sulphur terminated graphene nanoribbons (S-GNRs). Such structures represent a new hybrid form of carbon, with potentially exciting functional properties. Details of the atomic structure of the novel GNR and the effects of the 1D confinement imposed on the S-GNR by the CNT have been probed by AC-HRTEM which reveals unusual dynamic behaviour in which the nanoribbon twists within the CNT. The size, shape and nature of the helical twist can be controlled by using different sized carbon nanotube templates paving the way for the formation of an exciting family of new nanostructures.

1 A. Chuvilin, et al. *Nature Materials* 10, 2011, 687.

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MON 27

Optical study of coronene molecules and graphene nanoribbons encapsulated in single-walled carbon nanotubes

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Single-walled carbon nanotubes (SWCNTs) have been demonstrated to serve not only as containers for polycyclic aromatic molecules (PAHs), but also as nano-reactors for PAHs fusion and polymerization which results in formation of hydrogen terminated graphene nanoribbons. Encapsulation of coronene into SWCNTs and thermally induced reactions inside of nanotube space were studied using photoluminescence, absorption and Raman spectroscopy. Studied nanomaterials showed bright photoluminescence in IR and UV-Vis spectral ranges. Their spectral features exhibited complex resonant structure which is different compared to simple sum of contributions from two initial components: coronene molecules and SWCNTs. Photoluminescence peaks of SWCNTs demonstrated significant red shifts depending on the diameters of nanotubes. Raman spectra recorded from studied samples showed different shifts for positions of radial breathing modes of filled SWCNTs compared to pristine empty SWCNTs. The encapsulation ability is found to correlate strongly with diameter of SWCNTs. Funding by RFBR grants 12-02-31581, 12-02-90805, 11-02-92121 and RAS research projects is acknowledged.

MON 28**Quantum transport in graphene nanoribbons in the presence of a magnetic field.**

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We study electron transport in zigzag graphene nanoribbons (ZGNR) in a perpendicular magnetic field. We consider a ZGNR connected to leads with different doping in the leads and the constriction. Our simulations are based on the modular recursive Green's function method with third-nearest neighbor tight-binding Hamiltonian [1]. These effective single-particle simulations show that the presence of differently doped regions strongly suppresses size quantization signatures even in case when no edge or bulk disorder is present. We also show that size quantization steps in the transmission can reappear at high magnetic fields where plateau regions featuring perfect conduction emerge [2]. The dependence of the measured conductance on the applied back-gate voltage indicates a strong influence of the local doping. When we include the influence of the back-gate voltage on the local doping through voltage dependent on-site energies, improved agreement between experimental data and simulations can be achieved.

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MON 29**Targeted reduction of oxygen groups from graphene oxides via mechanistically proven methods.**

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The efforts to develop graphene as a next-generation material have been dampened by the lack of bulk quantity of graphene materials. To this aim, the chemical oxidation and subsequent reduction towards graphene is one of the most widely accepted methods. Numerous reductants have been introduced for the reduction of graphene oxide to graphene materials. Despite that, it is important to establish mechanistic

cally proven reduction methods to gain precise control and understanding over the modification of graphene oxide. The ability to achieve selective reduction or removal of oxygen groups would consequently allow for the direct tailoring of graphene materials for future applications. As an ongoing effort, our group has investigated on the direct and selective removal of hydroxyl groups on graphene oxide via treatment with ethanethiol-aluminium chloride complexes. Furthermore, a study based on a two-step reaction comprising of a dehydrobromination step showed not only selective removal of hydroxyl groups, but also regeneration of sp² C-C bonds on the graphene materials. The obtained graphene materials also highlighted improved conductivities over prevalent reduced graphene materials.

MON 30

Carbon nanotubes on glass synthesis for organic solar cells semi-transparent contacts

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A Carbon nanotubes chemical vapor deposition process was optimized in order to obtain suitable semi-transparent contacts for bulk heterojunction organic (P3HT/PCBM) solar cells. CNTs were synthesized on bare and FTO glass substrates via "double zone system" CVD, in order to avoid the samples spoiling: through an accurate spatial calibration of the reaction chamber it was possible to reach the required temperature for the CNT synthesis, while maintaining the glass substrate in an appropriate temperature zone, in which the catalyst clustering was feasible without reaching the samples melting point. Synthesis parameters were optimized in terms of deposited film homogeneity, visible spectrum transparency and electrical sheet resistance. First samples of P3HT/PCBM solar cells showed a promising 0,4% in overall energy conversion efficiency.

MON 31

Nanomechanical Mapping of Suspended Graphene

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I present quantitative nanomechanical maps of suspended graphene membranes, both monolayer and multilayer. Peakforce QNM, a new off resonance tapping AFM mode, allows rapid mapping of force response curves at every pixel, two orders of magnitude faster than conventional force volume mapping. A range of nanomechanical properties, including the adhesion, modulus, dissipation and deformation can then be extracted in real time along with the topographic data. Circular holes were created in silicon nitride membranes on silicon supports via a SF₆ etch using a photolithographically defined etch mask. Mechanically exfoliated graphene flakes were then transferred onto the nitride membrane, leaving an array of suspended circular

areas suitable for transmission characterisation methods as TEM as well as AFM. The adhesion of the flakes to the silicon nitride membrane was also investigated, and compared with previously published results on silicon dioxide substrates.

MON 32

Towards Green Chemistry: A new approach to the synthesis of semiconducting SiC nanowires

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Because of enhancing their interesting properties by the radial confinement in 1-D structure, the silicon carbide nanowires (SiCNWs) are promising materials for numerous applications, e.g., as interconnects in integrated circuits, parts of CMOS devices, hydrogen sensors, and composites fillers. Consequently, the synthesis of SiCNWs has been extensively studied and a fast, simple one-step chemical method of branched 1-D SiC nanostructures formation from Si/PTFE mixture via a thermolysis route (SHS) has been proposed. The aim of this study is to further develop the production protocol by decreasing the cost of starting reactants and environmental impact of the synthesis. Thus, the recycled grinded panels of Si-solar panels, as a silicon source, were tested. The parametric optimization of the process was carried out. The possibility of scaling up the production of SiCNWs was confirmed. Products were characterized using XRD, SEM, TEM and Raman spectroscopy and used as fillers in nanocomposites.

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MON 33

Solution-processed Carbon Nanotube Network for High Performance Ambipolar Field-effect Transistors

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The study of carbon nanotube (CNT) thin-film transistors generates significant research interest particularly towards their applications for low-cost, scalable fabrication, large-area and high performance electronic devices. Particular interest is paid towards solution-processed CNT networks since they are much easier to fabricate than single strand CNT transistors, giving more opportunities for applications. However, the true potentials of CNT, i.e. the high carrier mobility, ambipolarity and high on/off ratio are still difficult to achieve in CNT network thin films. We will report ambipolar transistors of aligned CNT networks fabricated from solution. The nanotube solution was obtained using the polymer-wrapping technique, which

shows selective sorting of semiconducting nanotube from the metallic species. The performances of the FET as a function of the coverage of the nanotube film are studied. The best transistors show charge carrier mobility up to $3 \text{ cm}^2/\text{Vs}$ and on/off ratio up to 10^6 in denser films. These results indicate the very high purity of the semiconducting nanotube dispersion.

MON 34

Production of single-wall carbon nanotubes with a very narrow size distribution on chemisorbed nickel catalyst

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The electronic properties of single-wall carbon nanotubes (SWCNTs) depend on their diameter and chirality. However, obtaining SWCNTs of a determined diameter requires complex purification and sorting procedures after their synthesis. A current challenge is to directly produce SWCNTs with a narrow size distribution in CVD processes. Because SWCNTs are usually grown from catalyst nanoparticles that control their diameter, tailoring the diameter distribution requires isolated metal nanoparticles with uniform diameter close to 1 nm, at the CNT growth temperature. This work shows that the use of chemisorbed organometallic compounds as catalyst is an interesting way to approach the diameter control of SWCNTs. Metal acetylacetonate was chemisorbed on silica powders to be used as catalyst for SWCNTs growth at moderate temperature by thermal decomposition of ethylene. Based on HRTEM observations, FTIR and Raman spectroscopies we show that by tuning the amount of chemisorbed Ni acetylacetonate and by adjusting the CVD parameters, the structure of the carbon nanotubes is controlled and clean SWCNTs with a diameter distribution range of 0.8-1.0 nm are produced.

MON 35

Mapping out the band structure of a carbon nanotube in a magnetic field

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gensburg

We present data from electronic transport spectroscopy measurements on an ultra-clean carbon nanotube as a quantum dot at low temperature and finite magnetic field.

The magnetic field with a flux density of up to 17T in combination with a rotatable sample holder allows for angle-resolved B -field analysis of the observed quantum states. Our main focus is on the few-electron spectrum — the sample displays highly regular features down to $N_{el} = 1$ — where sharp Coulomb blockade oscillations enable tracing of multiple excited quantum states. We discuss spin-orbit coupling and KK'-mixing in our sample. The spectroscopic data is compared to state-of-the-art CNT modeling.

MON 36

Free-standing membranes from epitaxial graphene on 6H-SiC

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We present a two-step route to simultaneously prepare arrays of free-standing graphene membranes (few hundred, yield ca. 80 %, size up to $500 \mu^2$) in a robust and chemically inert SiC frame.

The first step includes the well-established growth of single-crystalline graphene on 6H-SiC(0001) by its thermal decomposition at high temperature (i.e. $\sim 1750^\circ\text{C}$) in inert-gas atmosphere. Thus, approximately 1.2 layers of highly crystalline graphene (plus a chemically bond buffer layer) are generated. By intercalation with hydrogen the buffer layer is converted into an additional layer of graphene. Slightly varying the growth conditions offers the possibility to vary the local number of layers. The second step comprises the application of an etching mask and the laser-light assisted electrochemical removal of the 6H-SiC substrate in KOH using a 325 nm UV-laser. The mask allows tailoring shape, size and distribution of the membranes within the final sample. Those membranes are mechanically stable and withstand temperatures exceeding 1000°C (under high-vacuum conditions). Even without any further treatment, the cleanliness of the membranes is sufficient for high-resolution imaging.

MON 37

In Situ Electronic Characterization of Graphene Nanoconstrictions Fabricated in a Transmission Electron Microscope

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We report electronic measurements on graphene nanoconstrictions (GNCs) fabricated in a transmission electron microscope (TEM), and the measurements on GNC conductance with an accurate measurement of constriction width down to 1 nm. To create the GNCs, freely suspended graphene ribbons were fabricated using few-layer and single-layer graphene grown by chemical vapor deposition. The ribbons were loaded into the TEM, and a current-annealing procedure was used to clean the material and improve its electronic characteristics. The TEM beam was then used to sculpt GNCs to a series of desired widths in the range 1–700 nm; after each sculpting step, the sample was imaged by TEM and its electronic properties were measured in situ. GNC conductance was found to be remarkably high, comparable to that of exfoliated graphene samples of similar size. We report the GNC conductance dependence on width and show that the GNCs support large current densities, 2 orders of magnitude higher than that which has been previously reported for graphene nanoribbons and 2000 times higher than that reported for copper.

MON 38

Confocal Raman spectroscopy of graphene on hexagonal boron nitride

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Graphene, a monoatomic carbon membrane with unique electronic properties is a promising candidate for flexible electronics, high frequency applications and spintronics. However, graphene's ultimate surface-to-volume ratio makes the environment, in particular the substrate material, have a pronounced influence onto its intrinsic properties. Here we report a study on the influence of the substrate on the vibrational properties of graphene. In particular, we compare graphene on hexagonal boron nitride (hBN) with graphene on SiO₂ by spatially resolved confocal Raman spectroscopy. By studying the G-line we show that the average doping level and local doping domain fluctuations are significantly suppressed in graphene on hBN with respect to graphene on SiO₂. However, in contrast to the G-line, the 2D-line of graphene on hBN shifts up in frequency compared to the one on SiO₂. We show that this effect is due to a reduction of the Kohn anomaly at K through an

enhanced screening by the dielectric substrate. We prove our theory to be consistent with Raman measurements on graphene surrounded by hBN (stronger screening) and recent findings on suspended graphene (no external screening).

MON 39

Functional surfactant design for nanotube-chromophore energy transfer complexes

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The formation of nanotube-chromophore energy transfer complexes is of great interest for a number of applications, ranging from the collection of solar energy to biomedical sensors. Certain chromophores can π - π stack on the nanotube wall: when they are radiatively excited an exciton is formed, which subsequently passes into the carbon nanotube. The chromophore-nanotube interaction is independent of chirality, resulting in two possible ways of exciting any nanotube: at its individual E_{22} transition energy, and in the chromophore's absorption band. In a previous study (Ernst et al., Adv. Funct. Mat. 2012) we incorporated such a chromophore, perylene, into a surfactant, and showed that the perylene can retain its π -stacking capabilities even as part of a bigger molecule. In this work we explore the different ways such a functional surfactant can be assembled. Different configurations result in varying efficiencies both as a surfactant and in the perylene's ability to form energy transfer complexes with the tubes. We attribute these variations to specific morphological features and thereby arrive at a best practice guide for the design of functional surfactants.

MON 40

Evaluation of bi-metallic catalysts for the growth of carbon nanotube forests

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The catalytic growth of carbon nanotube forests is reported to be enhanced by the use of bi-metallic catalysts. In this work, we systematically study different combinations of Fe, Co, and Ni on alumina support and observe two regimes of catalytic activity enhancement. When the total thickness of catalyst is larger than nominally 1 nm, bi-metallic catalysts outperform the equivalent layers of a single metal, producing taller forests of multi-walled nanotubes. In contrast, for mono-metallic layers thinner than 0.6nm, we observe no significant difference in catalytic activity, provided that the growth conditions are optimized for very thin films. These results indicate that the growth of few- or single-walled nanotubes is, to a large extent, controlled by the activity on the catalyst surface rather than the catalyst composition itself.

MON 41**Growth and characterization of bamboo-like carbon nanotubes on Fe-Co-Cu catalysts prepared by high energy ball milling**Egon Kecenovic¹, Dora Fejes¹, Balazs Reti¹, Klara Hernadi¹¹Department of Applied and Environmental Chemistry, University of Szeged, 6720 Szeged, Rerrich B ter 1, Hungary

Bamboo-shaped CNTs are special nanotubes with unique morphology. The particularly high wall reactivity of N-containing NTs makes them ideal components in fast gas sensors and can be used as matrix fillers in composite materials, where the improved electrical conductivity generated by the N incorporation combined with the mechanical properties of the tubes are the novel factor. Here we present a simple method for the selective growth of bamboo-like CNTs. We employed high energy ball milling method for preparing Fe-Co-Cu (2.5-2.5-1 w%) catalyst on Al₂O₃ support to synthesize bamboo-like CNTs by catalytic chemical vapour deposition (CCVD) from acetylene at 720 °C. N compound was provided during the milling process by ammonia solution. As an important synthesis parameter the effect of milling time on the growth of bamboo-like CNTs was investigated. Morphology and structure of the carbon deposits were characterized by TEM, SEM, Raman and XRD. The results revealed that the diameter distribution was narrower and the yield increased with the milling time. The growth mechanism of the CNTs, and the role of copper contained catalyst were studied.

MON 42**Towards Low Temperature Graphene Growth Using Linear Antennas Microwave Plasma Enhanced CVD System**Frantisek Fendrych¹, Jan Vlcek^{1,2}, Ladislav Peksa¹, Otakar Frank³, Martin Kalbac³, Jana Vejpravova¹¹Department of Magnetic Nanosystems, Institute of Physics AS CR, v.v.i., Prague 8, Czech Republic²Department of Physics and Measurements, Institute of Chemical Technology, Prague 6, Czech Republic³JH Institute of Physical Chemistry of the AS CR, v.v.i., Prague 8, Czech Republic

Graphene (GN) growth for large-area electronic and optical applications has attracted much interest. Recently, it has been suggested that GN can be prepared by low pressure MW systems, such as slit-antenna delivery [1], at temperatures below 450 °C. However, the first results suggested the presence of amorphous carbon in the atomic monolayers. In this work we compare the use of low pressure linear antennas MW plasma delivery system, previously described in [2], working in pulsed and CW mode, respectively, using various ratios of the CH₄ : Ar : H₂ for the growth of GN on Cu foils at 400 - 700 °C. The GN samples were studied by the Raman spectroscopy, AFM, SEM/TEM and transport measurements in order to optimize

the growth conditions such as plasma parameters, gas composition and substrate temperature. In addition, the physical properties were compared to those of the GN monolayers and bilayers prepared by the conventional thermal CVD [3].

[1] Kim J et al, App. Phys. Lett. 98, 091502, 2011.

[2] Fendrych F et al, Journal of Physics D: Applied Physics 43, 374018, 2010.

[3] Kalbac M et al, NanoLetters, 11, 1957, 2011.

MON 43

Electron spin resonance of single-walled carbon nanotubes with aromatic amines

Nuria Ferrer-Anglada¹, Ursula Dettlaff-Weglikowska², Siegmund Roth²

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We analyzed by Electron Spin Resonance (ESR) thin films of single-walled carbon nanotubes (SWCNT) n-doped with aromatic amines, N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD). The samples are networks of carbon nanotubes as thin films. After dipping the pristine films in the amine solution for 24 h we obtained the doped films, SWCNT:TMPD. Adsorption and intercalation of amine molecules may behave like electron donors of carbon nanotubes. In a previous paper it has been shown theoretically that after doping with TMPD, there is an electron transfer that affects the electronic band structure: as a result the band gap decreases significantly, the experimental features from XPS and NEXAFS support these results [1]. In order to obtain an experimental evidence of the electron transfer and their effect on the electronic band structure, we compare and analyze the ESR spectra of the pristine SWCNT and the SWCNT: TMPD doped carbon nanotube films. We observed a clear variation on the ESR spectra, indicating that we could use the ESR to characterize the SWCNT samples.

[1] U. Dettlaff-Weglikowska, G. Kim, L.G. Bulusheva, and S. Roth, Phys. Status Solidi B, 248, 2458 (2011).

MON 44

Ab-initio calculation of thermal conductivity in diamond, graphite and graphene.

Francesco Mauri¹, Giorgia Fugallo¹, Lorenzo Paulatto¹, Michele Lazzeri¹

¹Universite Pierre et Marie Curie / CNRS, Paris

We present a first-principles theoretical approach for evaluating the lattice thermal conductivity based on the exact solution of the Boltzmann transport equation. We use the variational principle and the conjugate gradient scheme, which provide us with an algorithm faster than the one previously used in literature and able to always converge to the exact solution. Three-phonon normal and umklapp collision, isotope scattering and border effects are rigorously treated in the calculation.

The calculations reproduce in detail the exceptional thermal transport properties of diamond, graphite and graphene as a function of temperature and isotope composition. The analysis of the Boltzmann solution allow us to elucidate the mechanisms responsible for the high thermal conductivity of these carbon materials.

MON 45

Raman spectroscopy investigation of graphene grown on copper single crystals

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²Institute of Physics of the AS CR, Prague, Czech Republic

Chemical vapor deposition (CVD) on metals is the most promising way of a large-scale production of continuous graphene layers, yet the exact mechanism of this process is still a matter of discussion. Even though general principles like carbon solubility, role of pressure or temperature are known, detailed understanding of the interplay between the surficial atomic structure of the metal and the resulting graphene is still lacking. In this study we focused on graphene grown on Cu(100), (110) and (111) single crystals by low pressure CVD from methane with either ¹²C or ¹³C isotope. Large-area microRaman mapping together with a thorough statistical evaluation of the data (G and 2D band shifts, linewidths and intensities) are compared against the individual surfaces and their qualities. For example, we might see an extreme and unprecedented narrowing of the 2D mode especially on the flatter parts of the surfaces, predominantly on Cu(100), caused probably by the lack of strain and charge inhomogeneities across the surface on a scale smaller than the laser spot. On the other hand, graphene on Cu(111) shows a higher amount of doping and an overall compression of ca. 0.3%.

MON 46

Environmental Effects on the Low Frequency Raman Active Modes of Carbon Nanotubes

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¹University College Dublin

²Imperial College London

A new method for studying the biophysical solvation of nano-materials is proposed. In this work we present the investigation of the environmental effect on the Raman Spectra of Single Walled Carbon Nanotubes (SWNTs). A specifically tailor-made configuration was developed in order to investigate the low frequency Raman active SWNT modes. Theoretically predicted low frequency Raman active modes, in particular the Radial Breathing Mode (RBM) and modes closer to the laser line, were found to be highly dependent on their environment. The results show that

the frequencies of the modes are not only dependent on the SWNT diameter and the excitation wavelengths, but they are also dependent on environmental factors, including surfactant dissolution. The SWNTs examined were produced using the CoMoCAT method, therefore there is a very narrow size distribution centred around 0.76 nm, and a selection of armchair, chiral and zigzag nanotubes. The Resonance Raman effect was obtained using specific excitations, which enabled chiral selectivity. This investigation, on modes unique to carbon nanotubes, is highly important for the development of a Raman spectroscopy-based probe for Carbon Nanotubes.

MON 47

Covalent functionalization of carbon nanotubes with tetramanganese complexes

Robert Frielinghaus^{1,5}, Claire Besson^{1,2,5}, Anna-Katharina Saelhoff^{1,5}, Asmus Vierck³, Marlou Slot^{1,5}, Lothar Houben^{1,4,5}, Janina Maultzsch³, Paul Kögerler^{1,2,5}, Claus M. Schneider^{1,5}, Carola Meyer^{1,5}

¹Peter Grünberg Institut, Forschungszentrum Jülich, 52425 Jülich, Germany

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³Institut für Festkörperphysik, Technische Universität Berlin, 10623 Berlin, Germany

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⁵JARA – Fundamentals of Future Information Technologies

We present first results on the covalent chemical functionalization of carbon nanotubes (CNTs) with tetramanganese coordination complexes. Raman spectra give indirect evidence of a successful reaction. It can only be achieved for tubes which contain defects with carboxylic groups. Changes in the magnetization behavior of the complexes due to the bonding to the CNTs are analyzed with temperature-dependent SQUID measurements. These results are correlated with bright and dark field high-resolution transmission electron microscopy (HR-TEM) measurements that show the repartition of the complex decoration on the CNTs. The TEM's elemental analysis capabilities, energy-dispersive X-ray and electron energy loss spectroscopy, prove the existence of Mn on the CNTs. We show that a mild oxidation, leaving the nanotubes conductive, is already sufficient for functionalization. This is important for the fabrication of transport devices.

MON 48

High-efficiency flexible organic solar cells using single-wall carbon nanotube thin films as transparent conducting anodes

Shunjiro Fujii^{1,2}, Takeshi Tanaka¹, Hiromichi Kataura^{1,2}

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Organic solar cells (OSCs) have attracted a great attention for their advantages of low-cost and solution-processable fabrications in addition to their compatibility with flexible plastic substrates. Indium tin oxide (ITO) has been mainly used as an anode even for the plastic substrates. However, the poor mechanical stability of ITO sometimes causes device failures when the substrate is bent. In addition, the limited deposits of indium will be a problem for the supply of ITO in future. In this study, we fabricated flexible OSCs using single-wall carbon nanotube (SWCNT) films as transparent conducting anodes. SWCNT film was fabricated by a bar-coating on polyethylene terephthalate (PET) and used as anodes of the OSCs. Transmittance of the film was 80% and sheet resistance was 400 ohms per square. The OSCs were fabricated by spin-coating conjugated polymers and fullerene derivatives as photoactive layer. As a result, replacing ITO with SWCNT film, a power conversion efficiency of the OSC was improved from 1.3% to 1.7% (30% increase). In this presentation, the detailed characteristics and the origin of efficiency enhancement of the OSCs will be discussed.

MON 49

Tuning Single-walled Carbon Nanotube Field-effect Transistors with Self-assembled Monolayers

Florentina Gannott¹, K. Manuel Schweiger¹, Stefan Thiemann¹, Jana Zaumseil¹

¹Nanomaterials for Optoelectronics Group, Institute of Polymer Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg

The electronic and optical properties of single-walled carbon nanotubes (SWNT) are strongly affected by their dielectric environment, e.g. the substrate or dielectric in a field-effect transistor. In particular polar substrates such as SiO₂ are known to quench photoluminescence of SWNTs and cause charge carrier scattering, which reduces mobility. To avoid these effects nanotubes should be separated from the polar substrate surface, for example, by using self-assembled monolayers (SAM) with alkyl chains of different length. In this work we use very long (>100 μm) and aligned SWNT arrays, which were grown by chemical vapour deposition on ST-cut quartz. The pristine SWNTs are subsequently deposited onto various types of densely packed self-assembled monolayers using an optimized polymer transfer process. The transferred SWNT arrays are used to fabricate bottom gate and electrolyte-gated field-effect transistors (FETs). Using these FET structures we study the effect of the transfer process and the end-groups of the SAMs (-CH₃, -CF₃, -CN, -NH₂) on the charge transport, photo- and electroluminescence properties of the SWNT.

MON 50**Characterisation of transition metal dichalcogenide films grown by CVD**

Riley Gatensby^{1,2}, Niall McEvoy¹, Toby Hallam², Georg S. Duesberg^{1,2}

¹School of Chemistry, Trinity College Dublin, Dublin 2, Ireland

²CRANN, Trinity College Dublin, Dublin 2, Ireland

Transition metal dichalcogenide (TMD) thin films have bandgaps that change from indirect to direct with film thickness, with applications in electronics and optoelectronics. Quasi two dimensional molybdenum disulphide and tungsten disulphide films were synthesised by chemical vapour deposition. After sputtering a thin layer (1-10 nm) of the transition metal onto a silicon substrate, adsorption of sulphur vapour at elevated temperatures in a quartz tube furnace was performed. The minimum thickness of metal layers required to produce continuous TMD films was identified.

The resulting materials were characterised by Raman spectroscopy, transmission and scanning electron microscopy as well as Kelvin probe AFM and Photoluminescence spectroscopy. With Raman the well-known A_{1g} and E_{2g}^1 vibrations could be readily identified and resulting film thicknesses could be determined. Further, it was possible to transfer the thin films to arbitrary substrates using PMMA as a support layer. After contacting, electrical measurements are anticipated to relate electrical data with morphological and optical studies.

MON 51**Ultra-High Resolution Transmission Electron Microscopy of Interfaces in CVD Hexagonal Boron Nitride**

Ashley Gibb^{1,2}, Nasim Alem², Jian-Hao Chen², Kris Erickson^{1,2}, Jim Ciston³, Abhay Gautam³, A. Zettl^{2,3,4}

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³National Center for Electron Microscopy, Lawrence Berkeley National Lab

⁴Materials Science Division, Lawrence Berkeley National Lab

Monolayer films of two-dimensional sp^2 materials such as graphene and hexagonal boron nitride (h-BN) have been investigated for use in future devices due to their properties including high mechanical strength, thermal conductivity, stability and interesting electronic properties. Understanding atomic scale defects in these materials is important because they significantly alter the physical properties. Prior Transmission Electron Microscopy (TEM) work has resolved the atomic structure of grain boundaries in CVD graphene [1], but the structure of grain boundaries and many other defects in CVD h-BN have not yet been observed. We have synthesized h-BN using low pressure chemical vapor deposition from borazine. Defects including grain boundaries in monolayer regions of h-BN were imaged using ultra-high resolution aberration corrected transmission electron microscopy. Interestingly,

pentagon and heptagon rings were observed at the interfaces between grains. These defect structures are consistent with recent theoretical predictions of h-BN grain boundaries [2].

1. Kim, K. et al. *ACS Nano* **2011**, 3, 2142–2146.

2. Liu, Y. et al. *ACS Nano* **2012**, 6, 7053.

MON 52

Selective dispersion of wide diameter-range semiconducting carbon nanotubes by polyfluorene derivatives

Widianta Gomulya¹, Guadalupe Diaz Costanzo^{1,2}, Elton J. Figueiredo de Carvalho^{1,3}, Satria Z. Bisri¹, V. J. Derenskyi¹, Martin Fritsch⁴, Nils Fröhlich⁴, Sybille Allard⁴, Pavlo Gordiichuk¹, Andreas Herrmann¹, Siewert J. Marrink¹, M.C. dos Santos³, Ullrich Scherf⁴, Maria A. Loi¹

¹Zernike Institute for Advanced Materials, University of Groningen

²Physics Department, Faculty of Sciences, University of Buenos Aires

³Instituto de Fisica, Universidade de Sao Paulo

⁴Chemistry Department and Institute for Polymer Technology, Wuppertal University

Separation of semiconducting single walled carbon nanotubes (s-SWNTs) using conjugated polymer has extensively been studied in the last 5 years because their non-covalent interaction preserve s-SWNTs original properties. However, current report only show the selectivity toward small diameter s-SWNTs. Separation of big diameter tubes which have more prospects for high performance device applications, remains a big challenge. Here we demonstrated the utilization of polyfluorene-derivatives to select wide diameter s-SWNTs (0.8 to 1.6 nm) with high degree of individualization. Optical spectroscopy including absorption and photoluminescence show the evidence of high quality s-SWNTs dispersion in term of minimal metallic content and low bundling. We perform molecular dynamics simulation to justify the interaction mechanism by calculating the coverage wrapping area and the binding energy between the polymer and the s-SWNTs. The random network FET based on this dispersion showed ambipolar properties with charge mobility higher than $10\text{cm}^2/\text{Vs}$ and on/off ratio more than 10^5 . Our finding may leads to new perspective for big diameter s-SWNTs use for high performance device applications.

MON 53

Mechanical properties of transferred graphene resonators for cavity electro-mechanics experiments

Johannes Guettinger^{1,2}, Peter Weber^{1,2}, Ioannis Tsioutsios^{1,2}, Alex Eichler^{1,2}, Joel Moser^{1,2}, Adrian Bachtold^{1,2}

¹ICFO - Institut de Ciències Fotoniques, Castelldefels (Barcelona), Spain

²ICN - Institut Català de Nanotecnologia, Bellaterra (Barcelona), Spain

Our goal is to couple a graphene mechanical resonator to a superconducting microwave cavity in order to explore quantum motion. In comparison to conventional microfabricated resonators, graphene is ultra-light and therefore shows a larger zero-point motion. Despite the small mass, the two dimensional graphene has a large surface which allows for strong capacitive coupling with the superconducting cavity. In order to couple a superconducting cavity with a graphene resonator on one chip, the graphene device cannot be fabricated using the traditional scotch-tape exfoliation technique on silicon oxide. We therefore use a transfer technique to deposit a single graphene sheet over prefabricated trenches with local gates. First measurements show that the transferred graphene sheets have excellent electronic properties and that the fabricated resonators have a quality factor of 1000 at a temperature of 77 K, which is very promising for future experiments.

MON 54**Inter-layer Raman band in double walled carbon nanotubes and bilayer graphene**

Balint Gyimesi¹, Janos Koltai¹, Adam Rusznyak¹, Viktor Zolyomi², Jenő Kürti¹

¹Department of Biological Physics, Eötvös University, Budapest

²Department of Physics, Lancaster University, Lancaster

Non-dispersive, inter-layer interaction induced Raman band (I band) in the region of the D band has been observed recently for bilayer graphene when the two layers were rotated with respect to each other. Recent experiments show similar observation for double walled carbon nanotubes (DWCNTs) as well. The explanation is based on double resonance theory involving non zone centered phonons. The effect of disorder is replaced by interaction between the two layers. We used two different theoretical methods. 1) Using DFT calculations we determined the perturbation potential due to the interaction between the two layers. Because of the difference in the orientation of the layers this perturbation has a Moire type structure and its Fourier components determine the possible wave vectors in the double resonance process. 2) An allowed wave vector for the I band is the result of two umklapp processes. A possible wave vector can be obtained as the difference of two reciprocal vectors. For DWCNTs two extra constraints exist: k-points are allowed only on the parallel cutting lines according to the given chirality, and the effect of the Van Hove enhancement has to be taken into account.

MON 55**Atomic Resolution Cross Sectional Imaging of Multilayered Graphene/Boron Nitride Electronic Device Structures**

Sarah Haigh¹, Rashid Jalil², Ali Gholinia¹, Simon Romani³, Leonid A. Ponomarenko², Kostya Novoselov², Liam Britnell², Daniel C. Elias², Andre K. Geim², Roman Gorbachev²

¹School of Materials, University of Manchester, Manchester, UK

²Manchester Centre for Mesoscience and Nanotechnology, University of Manchester, Manchester, UK

³Department of Engineering, University of Liverpool, Liverpool, UK

We have studied multilayer graphene/BN heterostructures where single layer and bilayer graphene sheets are individually contacted and encapsulated between insulating spacer layers. We show that a Focused Ion Beam (FIB) Scanning Electron Microscope (SEM) can be used to remove thin cross sections from these multilayered graphene/BN heterostructures with the desired location identified using secondary electron SEM imaging. The extracted cross sections have been imaged using aberration corrected Scanning Transmission Electron Microscopy (STEM) combined with chemical analysis using electron energy loss spectroscopy and energy dispersive x-ray spectroscopy. Our side view observations confirm the location of individual graphene sheets encapsulated between the separate BN layers and also allow precise measurement of interlayer spacings. This novel approach offers the potential for correlation of measured transport properties for individual layers with local structural data and therefore provides a route to better understanding of the unique properties of 2D crystals when integrated into complex devices (Haigh S.J et al Nature Mater. 11, 764-767 (2012)).

MON 56

Carbon nanotubes are quenchers of singlet oxygen generated by photosynthetic reaction centers

Peter Boldog¹, Eva Hideg², Kata Hajdu¹, Melinda Magyar¹, Klara Hernadi³, Endre Horvath⁴, Arnaud Magrez⁴, Laszlo Forro⁴, Laszlo Nagy¹

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⁴Institute of Physics of Complex Matter, Ecole Polytechnique Federale de Lausanne, Switzerland

Photosensitizers may convert light into formation of reactive oxygen species (ROS), which chemicals have extremely high cyto- and potential genotoxicity. Photodynamic ROS reactions are determinative in photodynamic therapy and in damaging the photosynthetic apparatus of plants. The primary events of photosynthesis take place in the reaction center protein (RC), where the energy of light is converted into chemical potential. ROS are formed when RC photochemistry is limited. Reducing the formation of the ROS, thus lessening photooxidative damage and increasing the efficiency of the photochemical energy conversion is of special interest. Carbon nanotubes (CNTs) are also known to react with singlet oxygen. To investigate the possibility of quenching we studied the effect of carbon nanotubes on singlet oxygen

generated by RCs. 1,3-diphenylisobenzofuran (DPBF), a dye responding to singlet oxygen with absorption change, was used to measure singlet oxygen concentrations after excitation of either a photosensitizing dye (methylene blue) or photosynthetic RCs in the presence of carbon nanotubes. Our results indicate that the absorption change of the DPBF decreased in the presence of CNTs.

MON 57**Graphene composite Nanotransfer printing.**

Toby Hallam¹, Daniel Neumaier², Georg S. Duesberg¹

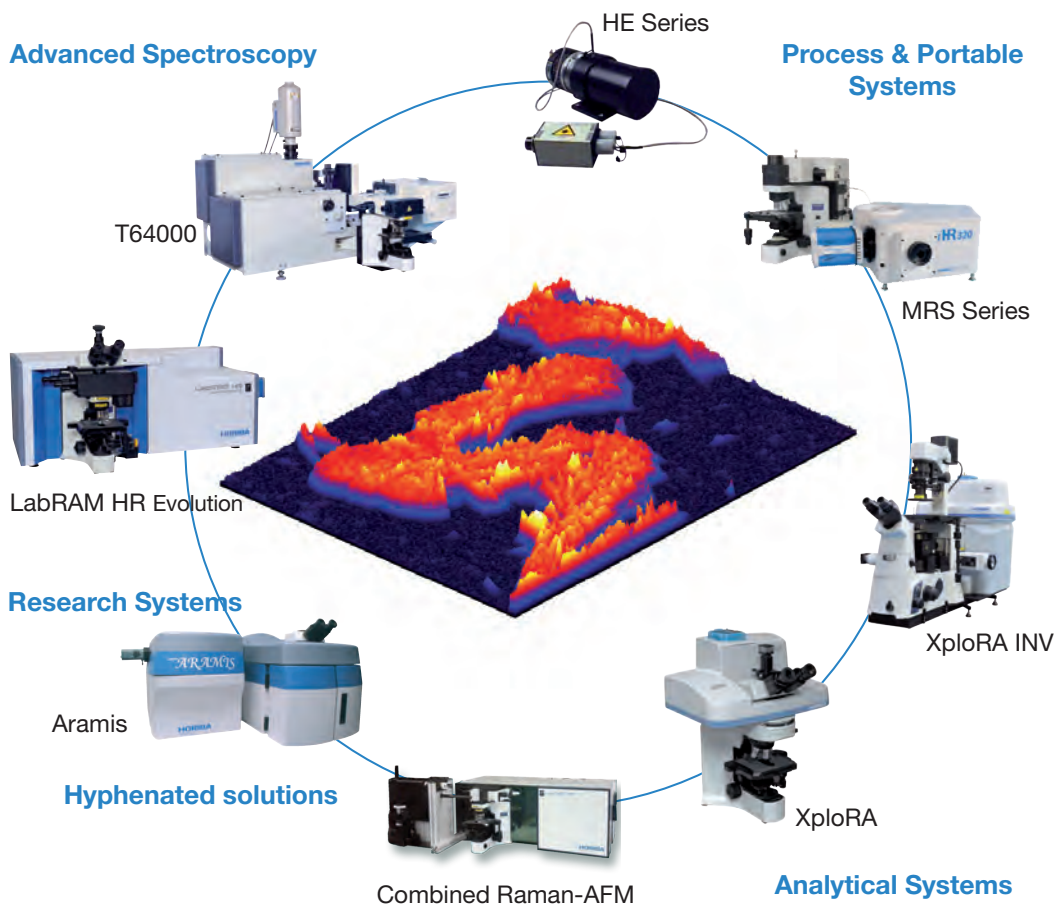
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There are many accepted methods for transferring Chemical Vapour Deposition (CVD) grown graphene from its metal catalyst substrate to a technologically relevant substrate. As roll to roll methods are predicted to be the pathway for the technological exploitation of graphene and scale up, it is appropriate that we investigate transfer printing of graphene.

We will report on transfer printing of graphene as part of a composite film with Aluminium Oxide created by combination of CVD and Atomic Layer Deposition (ALD) techniques. We also discuss the prospect of composite film printing with other CVD-grown 2D materials such as MoS₂.

The Most Complete Line of Solutions from the World Leader in Raman Spectroscopy



- 08:30 – 09:30 **J. Hone, New York**
Tutorial:
Graphene Mechanics and BN Heterostructures
- 09:30 – 10:00 **P. McEuen, Ithaca**
Nanotubes and Graphene at the Boundaries
- 10:00 – 10:30 **Coffee break**
- 10:30 – 11:00 **R. Gorbachev, Manchester**
Changes in Fermi surface topology and Hofstadter quantization in graphene superlattices
- 11:00 – 11:30 **M. Allen, Cambridge**
Gate-defined Quantum Confinement in Suspended Bilayer Graphene
- 11:30 – 12:00 **A. Luican-Mayer, Argonne**
Visualizing the influence of an isolated Coulomb impurity on the Landau level spectrum in graphene using scanning tunneling microscopy
- 12:00 – 17:00 **Mini-Workshops**
- 14:00 – 17:00 **Special Workshop**
Nano and Management
- 17:00 – 18:30 **Dinner**
- 18:30 – 19:00 **J. Velasco Jr, Berkeley**
Interaction-induced gapped state in charge neutral bilayer graphene
- 19:00 – 19:30 **U. Starke, Stuttgart**
Tuning the Bands in Epitaxial Graphene on SiC: Intercalation, Doping and Mini-Dirac Cones
- 19:30 – 20:00 **V. Krstic, Dublin**
Magnetotransport in graphene with potential-superlattice
- 20:00 **Poster II**

Tuesday, March 5th

Graphene transport

08:30

Graphene Mechanics and BN Heterostructures.

James Hone¹

¹Mechanical Engineering, Columbia University, New York

This talk will review: 1. Our recent work in mechanics of graphene, including measurement of high-strength CVD graphene and the effects of defects on strength; 2. Graphene NEMS for RF signal processing, including the world's smallest FM radio transmitter; 3. Ultrahigh performance graphene on BN, and "Hofstadter Butterfly" physics in graphene/BN superlattices.

09:30**Nanotubes and Graphene at the Boundaries**Paul L. McEuen¹¹Kavli Institute at Cornell for Nanoscale Science, Cornell University, Ithaca, NY 14853

Carbon nanotubes and graphene cut across many disciplines with their remarkable structural, thermal, mechanical, optical, and electronic properties. In this talk we will discuss a few fascinating examples at these boundaries where different properties combine to give unique behavior. For example, we will discuss atomic-scale imaging experiments of bilayer graphene that reveal the presence of 1D interlayer strain and shear solitons between the layers. These strain solitons have recently been predicted to give rise to topologically protected 1D electronic edge states. We will also present measurements of the bending stiffness of graphene on micron scales. We find that graphene is thousands of times stiffer than predicted by atomic theories, but in good agreement with calculations that take into account the effects of thermal fluctuations on the bending stiffness. We will also discuss experiments where individual carbon nanotubes are picked up with micron sized tweezers that can strain or buckle the tube. These tweezers double as electrical probes, allowing us to simultaneously study the electronic, optical, and vibrational properties of nanotubes as they are strained/buckled.

10:30**Changes in Fermi surface topology and Hofstadter quantization in graphene superlattices**R. Gorbachev¹, L. A. Ponomarenko¹, D. C. Elias¹, G. L. Yu¹, V. I. Fal'ko², A. K. Geim¹¹School of Physics and Astronomy, University of Manchester, Manchester, UK²Physics Department, Lancaster University, Lancaster , UK

The talk describes our recent progress on graphene / h-BN heterostructures fabricated with control over the angle between crystallographic directions of graphene and h-BN flakes. Moire pattern appearing due to the misalignment and 1.8% difference in lattice size introduces a superlattice potential which leads to a change in Fermi surface's topology. Careful control over the mutual lattice orientation allowed us to adjust the Moire period so that these changes are low enough in energy and can be accessed in transport experiments. Thus, second generation Dirac points are observed at energies $E_S = \hbar v_F / D$ (where D is the moire periodicity) as sharp peaks in resistivity with reversals of the Hall effect sign. In quantizing magnetic fields interplay between the Landau and spatial energy spectra leads to secondary sets of Landau levels, Hofstadter-type cloning of further neutrality points and emerging fractal Quantum Hall States.

11:00**Gate-defined Quantum Confinement in Suspended Bilayer Graphene**Monica Allen¹, Jens Martin², Amir Yacoby¹¹Dept. of Physics, Harvard University, Cambridge, MA²Graphene Centre, National University of Singapore

Devices that confine electrons in graphene have sparked substantial interest due to applications ranging from spin-based quantum computation to sensing. We present a novel approach to quantum confinement utilizing tunnel barriers defined by local electric fields that break sublattice symmetry in suspended bilayer graphene. This technique electrostatically confines charges via band structure control, thereby eliminating the edge and substrate disorder that hinders on-chip etched nanostructures to date. We report clean single electron tunneling through gate-defined quantum dots in two regimes: at zero magnetic field using the energy gap induced by a perpendicular electric field and at finite magnetic fields using Landau level confinement. The observed Coulomb blockade periodicity agrees with electrostatic simulations based on local top-gate geometry, a direct demonstration of local control over the band structure of graphene. This technology integrates quantum confinement with pristine device quality and access to vibrational modes, enabling wide applications from electromechanical sensors to quantum bits.

11:30**Visualizing the influence of an isolated Coulomb impurity on the Landau level spectrum in graphene using scanning tunneling microscopy**Adina Luican-Mayer^{1,2}, Maxim Kharitonov², Guohong Li², CihPin Lu², Ivan Skachko², Alem-Mar Goncalves², Eva Y. Andrei²¹The Center for Nanoscale Materials, Argonne National Laboratory²Department of Physics and Astronomy, Rutgers University

Charged impurities play a crucial role in determining the electronic properties of graphene. We report on experiments that elucidate the effect of an isolated charged impurity on the electronic spectrum of graphene in a magnetic field. Using scanning tunneling microscopy and gated graphene devices, we follow the evolution of quantized Landau levels with carrier density and find that the apparent strength of the impurity is controlled by the partial filling of the Landau levels. At low filling the impurity is cloaked and becomes essentially invisible. The cloaking effect diminishes with filling until, for fully occupied Landau levels, the impurity reaches its maximum strength causing a significant perturbation in the local density of states. In this regime we report the first observation of Landau level splitting due to lifting of the orbital degeneracy.

**Special Workshop
Nano and Management**

Chair: Siegmur Roth

- 14:00 – 14:30 **M. Schmid, Wiesbaden**
Rewards of Scientific Research - A Guide to Patent Protection
- 14:30 – 15:00 **V. Skakalova,**
Experience with a Start-Up in Slovakia
- 15:00 – 15:30 **G. Duisberg,**
Experience in Project Funding: Industry versus University, Ireland versus Germany
- 15:30 – 16:00 **I. Kolaric,**
Project Management: Comparison between Germany and Japan
- 16:00 – 16:30 **D. Carroll,**
Project Management in America: Private and Industry
- 16:30 – 17:00 **S. Roth, Seoul**
General Discussion

Each presenter should allow 10 minutes for discussion within the time-slot. All winterschool participants are welcome to this workshop. Let us hope that the weather will favor this afternoon for a workshop in the lecture hall and the other afternoons for mini workshops at the skiing slopes.

14:00**Rewards of Scientific Research – A Guide to Patent Protection**Michael Schmid¹¹Richardt Patent Attorneys, Wiesbaden

In today's globalized world of free market competition, research and development plays a crucial role in adding value to a company or research institution. This is provided that valuable innovations are safeguarded through professional patent protection. This enables patentees to recoup development costs and gives time to reap the rewards of investment. However, as real-life situation it appears that scientists tend to only concentrate efforts in research and publishing scientific results in reputable journals. This is understandable since research is their major area of expertise and the gap between science and patent protection appears to be too difficult and time intensive to overcome. Since only patents can effectively safeguard innovations against imitators and allows to harvest the fruits of your labors (and thus earn money), we provide you with an overview on patent protection which understandably builds the bridge to your routine research work. We discuss patent protection in a scientifically comprehensible, concrete, tangible and applicable way. The goal is to convey the abstract and rather juristic world of patent protection to the world of everyday scientific research.

15:30

Differences in CNT Research between Japan and Germany

Ivica Kolaric¹

¹Head of Department Functional Materials, Fraunhofer IPA , Stuttgart, Germany

More than 20 Years after its discovery CNT is still due for successful and unique products. Furthermore CNT is getting under pressure from the very recent graphene activities. Today many researchers and industry is shifting their focus from CNT to graphene. Even though that the full potential of CNT is not fully deployed, yet. This change of interest caused by substitution technologies leads in connection with the faster product cycles to an innovation slow down-and by the end to abundance to state of the art materials. The commitments to set the right research questions as well as patience are vital points to transfer the material opportunities of nano carbons into real innovations.

18:30**Interaction-induced gapped state in charge neutral bilayer graphene**Jairo Velasco Jr.¹¹Physics, University of California, Berkeley, Berkeley

Bilayer graphene (BLG) at the charge neutrality point (CNP) possess instability to electronic interactions, and is expected to host a ground state with spontaneously broken symmetries. Within this regime, I will discuss our transport spectroscopy measurements using high quality suspended BLG samples. We observe an insulating state at CNP with a gap of 2 meV, which can be closed by finite doping or a perpendicular electric field of either polarity. For magnetic field B greater than 1T, the gap increases linearly with B . Our work contributes towards understanding the rich interaction-driven physics in BLG. Finally, latest progress on transport spectroscopy measurements of Landau level gaps in these high quality samples will also be discussed.

19:00**Tuning the Bands in Epitaxial Graphene on SiC: Intercalation, Doping and Mini-Dirac Cones**Ulrich Starke¹¹Max-Planck-Institut für Festkörperforschung, Stuttgart

Large area epitaxial graphene is grown on SiC(0001) mediated by an electronically inactive first carbon interface layer. The graphene layers can be decoupled from the SiC substrate by hydrogen intercalation under the interface layer so that the underlying SiC layer is passivated. The interface layer alone transforms into a quasi-free standing monolayer while monolayers and bilayers turn into decoupled bilayers and trilayers. As a result, charge neutral quasi-free standing graphene layers can be obtained. By intercalation of Germanium graphene layers of p- and n-doping - also decoupled - are produced, depending on the amount of Ge material intercalated. Both phases can be prepared in coexistence so that lateral p-n junctions are obtained on a mesoscopic scale. Intercalation of Cu induces a coincidence superstructure on top of the SiC surface, which originates from periodic regions of different bond configuration for the carbon atoms in the graphene layer. As a result, a long range periodic potential is imposed onto the graphene layer, which leads to the development of mini-Dirac cones in the π -band spectrum and a surprisingly strong doping.

19:30**Magnetotransport in graphene with potential-superlattice**Vojislav Krstic¹¹School of Physics, Trinity College Dublin, Dublin

The transport properties of graphene are altered by a wide range of environmental interactions and can originate from molecular and atomic species adsorbed from the atmosphere on the graphene or from the presence of a specific substrate surface. Such interactions can lead to an unintentional doping but most importantly introduce a variety of charge-carrier scattering centres. These scattering centres, being e.g. charged impurities, lattice-strain or resonant scatterers, are randomly distributed all over the graphene and therefore represent a disordered, non-coherent scatterer field within which the charge-carriers are moving. The introduction of a specific symmetry to a scatterer field, as achieved by an imposed potential-superlattice, generates a qualitative change in the (overall) charge-carrier scattering, specifically in the presence of a magnetic field. In the present work the impact of an external magnetic field on the charge-transport in a graphene layer with imposed potential-superlattice is discussed with corresponding magnetotransport measurements in graphene-devices.

TUE 1**Fermi Energy Shift in Substrate-Deposited Metallic Nanotubes: A Raman Scattering Study**

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We report on Fermi energy shifts in metallic single-walled carbon nanotubes occurring when the tubes are deposited from a solution onto a silicon substrate. The Fermi energy shifts are monitored experimentally in the high-energy mode Raman lineshape. The metallic LO mode is affected by a Kohn anomaly and related broadening and asymmetry mechanisms, all of which are in effect at intrinsic Fermi energies and are lifted when the Fermi energy is shifted. We do not observe any changes in the high-energy mode Raman lineshape of semiconducting tubes, in agreement with the absence of the linear electronic bands leading to the Kohn anomaly and the broadening and asymmetry. Our conclusions are verified by combined electrochemical and Raman measurements, which allow us to reproduce the lineshape in solution and on silicon by deliberately shifting the Fermi energy and to quantify the corresponding Fermi energy shifts. These findings affect the commonly used method of discerning metallic from semiconducting nanotubes by their high-energy mode Raman lineshape.

TUE 2**Comparative study of tungsten-trioxide/MWCNT composite materials fabricated by various methods**

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Due to growing demand for special materials this work aimed at preparing nanocomposites and mechanical mixtures with combination of multiwalled carbon nanotubes (MWCNTs) and tungsten-trioxide (WO₃). For this purpose different methods were used: impregnation and hydrothermal synthesis for preparing composite materials, and furthermore milling and ultrasonication for preparing mechanical mixtures. In these synthesis processes different precursors were used: WO₃ and WCl₆. Functionalized and not functionalized MWCNTs were equally used in the procedures. The applied mass ratios of MWCNTs to WO₃ were 1:15 and 1:25, respectively. The produced materials were characterized with X-ray diffraction (XRD), Raman microscopy, transmission- (TEM) and scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy techniques. The multiwalled carbon nanotube based composite materials are promising candidates for testing as gas sensors or

catalysts, and in addition, the mechanical mixtures are also promising candidates for testing as photocatalysts.

TUE 3

Triplet Exciton Dynamics in Single-Wall Carbon Nanotubes

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Triplet excitons in SWNTs may contribute significantly to the dynamics of energy transport, redistribution and charge separation in SWNT based photonic devices. Here we report on femtosecond time-resolved pump-probe spectroscopy, picosecond time-resolved photoluminescence spectroscopy and spin sensitive photoluminescence investigations of triplet excitons in semiconducting SWNTs. We focus on monodisperse (6,5)-SWNTs with a first subband exciton transition at 982 nm. Triplet exciton dynamics are studied using triplet-triplet annihilation and delayed fluorescence (DF) as a probe. Spin sensitive optically detected magnetic resonance (ODMR) provides clear support for the role of triplet excitons for DF. Ground state recovery is found to follow a $t^{-1/2}$ power law characteristic of diffusion limited annihilation reactions in 1D systems. This allows to estimate the triplet exciton diffusion coefficient to be on the order of $10 \text{ cm}^2\text{s}^{-1}$. The power dependence of ODMR data on the other hand suggests that triplet lifetimes are $60 \pm 30 \text{ }\mu\text{s}$.

TUE 4

Probing the layer number and stacking order in few-layer graphene by out-of-plane phonons

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Since the electronic properties of graphene strongly differ with the number of layers and their stacking order, the knowledge about both properties is of crucial importance for the fabrication of microelectronic devices. We present a double-resonant Raman mode in few-layer graphene, which is able to probe the number of graphene layers [1]. This so-called N mode on the low-frequency side of the G mode results from a double-resonant Stokes/anti-Stokes process combining a longitudinal optical (LO) and an out-of-plane (ZO') phonon. Simulations of the double-resonant Raman spectra in bilayer graphene show very good agreement with the experiments. We

also investigated the stacking-order dependence of this mode in ABA and ABC tri-layer graphene and found very good agreement between experiments and theoretical calculations.

[1] F. Herzig, P. May, and J. Maultzsch, Phys. Rev. B 85, 235447 (2012)

TUE 5

The Phase of Iron Catalyst Nanoparticles during Carbon Nanotube Growth

Stephan Hofmann¹, B.C. Bayer¹, C. T. Wirth¹, A. D. Gamalski¹, S. Esconjauregui¹, R. S. Weatherup¹, C. Ducati¹, C. Baetz², J. Robertson¹

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We study the Fe-catalyzed CVD of carbon nanotubes by complementary in-situ grazing-incidence XRD, in-situ X-ray reflectivity and environmental transmission electron microscopy. We find that typical oxide supported Fe catalyst films form widely varying mixtures of bcc and fcc phased Fe nanoparticles upon reduction, which we ascribe to variations in minor commonly present carbon contamination levels. Depending on the as-formed phase composition, different growth modes occur upon hydrocarbon exposure: For γ -rich Fe nanoparticle distributions, metallic Fe is the active catalyst phase, implying that carbide formation is not a prerequisite for nanotube growth. For α -rich catalyst mixtures, Fe₃C formation more readily occurs and constitutes part of the nanotube growth process. We propose that this behavior can be rationalized in terms of kinetically accessible pathways, which we discuss in the context of the bulk iron-carbon phase diagram with the inclusion of phase equilibrium lines for metastable Fe₃C. Our results indicate that kinetic effects dominate the complex catalyst phase evolution during realistic CNT growth recipes.

[1] Wirth et al, Chem. Mat. 24, 4633 (2012)

TUE 6

Transport in graphene with magnetic superlattices

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Graphene's unique band structure is responsible for its remarkable transport properties such as the anomalous Hall effects, the strong suppression of weak localization, or the existence of a minimum conductivity. An important parameter that defines the range of electronic phenomena experimentally accessible in graphene devices is its charge-carrier mobility which is limited by charged impurities, random strain, and resonant (strong) scatterers. By introducing magnetic islands deposited on the graphene the strength of the impurity scattering can be principally controlled by both an external gate and magnetic field. Moreover, these impurities can be arranged on graphene in a periodic pattern, that is, forming a superlattice which

is anticipated to enhance charge-carrier spin-polarization and the overall magnetoresistance. In our study ferromagnetic dot-patterns are grown on graphene and transport measurements under external magnetic field are undertaken.

TUE 7

Modifying the Morphological and Electronic Structure of 2D-Nanomaterials by Ion Irradiation

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We demonstrate that ion irradiation of two-dimensional nanomaterials can be used to induce defects, changes of the morphology and electronic properties if either swift heavy ions (SHI) or slow highly charged ions (HCI) are used as projectiles. For SHI irradiation under glancing incidence angle ($<5^\circ$) we show, using atomic force microscopy (AFM), that graphene and MoS₂ can be folded in an origami like manner. In the case of MoS₂ an additional nanoscaled modification can be observed in the form of long rifts with a width below 10 nm. Graphene on the other hand can be doped by SHI irradiation. Experiments with HCI irradiation perpendicular to the graphene surface have been performed to study whether nanodefects (possibly holes) can be produced. Raman spectroscopy and AFM measurements suggest that this is indeed possible. The size of these nanodefects is on the order of a few nanometers and is thus definitely more than a point size defect.

TUE 8

Dye metachromasy on titanate nanowires: sensing humidity with reversible molecular dimerization

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We report on the reversible dimerization of methylene blue (MB) on titanate nanowires. The self-organizational properties of MB on the surface of this nanostructured material studied by spectroscopic means revealed that the light absorption properties of the MB molecules are humidity dependent. Based on the observed humidity dependent metachromasy, we fabricated a humidity sensor using optical fiber technology which is adapted for medical, industrial or environmental applications. The sensor operates with excellent linearity over the relative humidity (RH) levels ranging from 8 to 98%. The response and recovery time can be reduced to 0.5 s while the device exhibits excellent reproducibility with low hysteresis. These performances led to the implementation of the sensor in a breathing monitoring system. Furthermore, the metachromasy was observed for other dyes. This calls

for a detailed study of molecular configuration on functional surfaces since it can substantially modify the sensitization efficacy of dyes, e.g. in light conversion.

TUE 9

Fast combustion synthesis and characterization of YAG:Ce⁺³ garnet nanopowders

Andrzej Huczko¹, Magdalena Kurcz¹, Piotr Baranowski¹, Slawomir Dyjak², Rita Bhatta³, Balram Pokhrel³, Bhim Prasad Kafle³, Volodymyr Savchyn⁴, Anatoli Popov⁵

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Cerium-doped yttrium aluminum garnet can be used in white light emitting diodes. The YAG powder is formed traditionally by the solid state method, but the product particles are large, irregular and non-homogeneous, which is detrimental for its luminescence properties. Here we present a simple and fast method for synthesizing YAG:Ce⁺³ nanopowder based on solution combustion synthesis from metal nitrate (Ce content between 0,15-10 wt per cent) and fuel (urea, starch or glucose) water mixtures. The calcination of the raw product at 900°C for 2 h yielded crystalline garnet nanopowder with grain size well below 100 nm. The properties of the final product were characterized by TG/DTA, FTIR, XRD, SEM, Raman and cathodoluminescence spectroscopy. This synthesis route provides a potentially new approach to the formation of doped YAG nanopowders.

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

TUE 10

Is it possible to observe light scattering from single-particle excitations in metallic carbon nanotubes? Raman measurements on sparse CNT networks

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We present results of Raman scattering experiments on sparse networks of carbon nanotubes. They were grown by CVD on Si/SiO₂ substrates from Fe/Ni catalyst particles. The samples were not doped but an intentional doping from the environment cannot be excluded. In addition to characteristic phonon lines an increase of the spectral density was observed at the low energy part of the spectrum up to $\approx 800\text{ cm}^{-1}$. This feature is related exclusively to metallic nanotubes and has been detected neither for semiconducting nanotubes nor for reference samples of the un-

processed substrates. The observed increase of the spectral density at low Raman shifts resembles light scattering from single-particle electronic excitations observed in doped semiconductors. We followed this line of explanation and calculated the cross-section for Raman scattering from single-particle excitations in metallic carbon nanotubes. We took the quasilinear dispersion of the electronic energy and included the curvature induced energy gap in calculation. Calculated Raman cross-section is in a good agreement with the observed one for reasonable values of the temperature and the energy gap.

TUE 11

The Implementation of CVD Grown Graphene Devices Using Ag-Nanoparticle Inkjet Printing

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Graphene has become of great interest these past years and many novel and exciting routes to its synthesis have been realized. However, to actualize its potential it is crucial to fabricate devices; and not only to produce them but to develop a commercially relevant production route. Inkjet printing of conductive nanoparticle inks proves to be a promising, clean and easy way to do so. The big advantages of printed feature production are the simplicity, flexibility, economy and high throughput of the process.

We report on the use of a piezoelectric drop-on-demand inkjet printing tool to print conductive patterns of silver nanoparticles onto CVD grown graphene to produce technologically relevant devices such as GFETs, schottky diodes and chemical sensors. The structures are characterised with optical and electron microscopy, Raman spectroscopy and by transport studies. We will discuss the results in the context of scale-up and roll-to-roll processing.

TUE 12

Carbon nanotube nano-electromechanical resonators - driving, damping, detection

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Recent research has shown that the mechanical quality factor of a carbon nanotube nano-electromechanical resonator can rise above 10^5 at cryogenic temperatures. At

these high values, mechanical motion is excited by minute driving forces. At the same time, the electronically nonlinear behaviour of the quantum dot forming inside the carbon nanotube enables detection of the mechanical motion.

With this, we present a rich system where single-electron tunneling directly couples to and influences mechanical motion. A dc current alone is sufficient to excite vibration via feedback effects. In turn, the mechanical vibrations can be suppressed with a magnetic field by means of eddy current dissipation. The quantum dot provides a clean quantum-mechanical few-carrier system, and mechanical effects can be used to perform time-averaged charge measurements. As a perspective, future experiments may show a carbon nanotube as a system coherent in both electronic and mechanical aspects.

TUE 13

Vertical and Longitudinal Multi-layer Graphene Growth Using a New Heat-Beam assisted CVD

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A vertical and longitudinal multi-layer graphene sheet has been grown on the substrate by a catalytic CVD. For the CVD, we employed a new annealing method called "Heat Beam (HB)", in which high temperature inert gas was blown directly to the chip surface in an inert gas-flow chamber, and a safe and chemically stable gas, Diethylacetylene, was used as a hydrocarbon gas source. Although the possible reason/mechanism for the formation of such an interesting graphene structure has not yet been made clear, their electrical, thermal and mechanical properties are very interesting from the point of view of applications. The advantages of HB-CVD include not only a steep temperature-depth profile, but also better scalability for mass production such as in roll-to-roll production system. We investigate the crystalline quality and structure by Raman spectroscopy and TEM. In this work, a 30-nm thick Co thin film was used as a catalytic metal. A nitrogen gas was used as an inert gas. Growth temperature and pressure were about 780°C and ambient pressure, respectively.

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TUE 14

CMOS inverters fabricated from semiconducting SWCNTs encapsulating n- and p-type dopant molecules

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A thin film transistor (TFT) using semiconducting single-wall carbon nanotube (s-SWCNTs) is promising for low-cost and high-performance printed electronics applications. For the practical use of s-SWCNT to logic circuits, however, complementary metal-oxide semiconductor (CMOS) type operation is essential. It is known that a chemical doping can fabricate p- and n-type SWCNT-TFTs, but the external doping requires additional patterning process that is not suitable to the printed electronics. In this work, we tried carrier control of TFT channel by an internal chemical doping using an encapsulation of molecules into s-SWCNTs. High-purity s-SWCNTs were prepared by a gel column chromatography method. N- and p-type s-SWCNT inks were prepared by inserting cobaltocene and F₄TCNQ molecules into the s-SWCNTs, respectively. Then n- and p-type TFTs were successfully prepared on SiO₂/Si substrates and CMOS inverter operation was confirmed. Typical voltage gain was 10. To our knowledge, this result is the world-first demonstration of CMOS inverter operation fabricated simply using molecular encapsulating s-SWCNTs.

TUE 15

Enhanced spontaneous nucleation of diamond nuclei in hot and cold microwave plasma system

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Study of spontaneous nucleation offers a fundamental insight into a better understanding of diamond nucleation, and hence growth process. Moreover, it indicates promising ways to define the balance between diamond growth and renucleation regime and thus, methods for controlling grain size or multilayered growth. In this work two different deposition systems are compared: pulsed-linear antenna (PLAMWP) and focused microwave plasma (FMWP). The effect of pressure, CH₄/H₂ ratio and CO₂ addition was studied. The nucleation density (N_d) typical for non-treated substrates (10^5 cm^{-2}) was improved by four orders to 10^9 cm^{-2} in PLAMWP by increasing of CH₄ and CO₂. The highest N_d in FMWP was one order lower than in PLAMWP. It is due to different plasma character, temperature conditions and surface chemistry. Moreover, in PLAMWP system a bimodal size distribution function of diamond clusters was observed (beside larger clusters also smaller appeared). A possible origin of the bimodal distribution of clusters is discussed, including heterogeneous/homogenous nucleation and growth kinetics. This work was supported by the grants P108/12/0891 and P108/12/G108.

TUE 16**Spin-dependent Tunneling Probed by Superconducting STM Tips at milli-Kelvin Temperatures**

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Probing magnetism on the atomic scale is becoming an essential requirement for the ongoing miniaturization process of logic and data storage devices. Scanning tunneling microscopy (STM) is a powerful technique allowing for spin-dependent tunneling experiments at sub-nanometer spatial resolution. We use a superconducting Vanadium tip with a spin polarization of almost $P = 100\%$ to probe absolute values of the sample's spin polarization at milli-Kelvin temperatures. The spin polarization in the superconducting tip relies on the Zeemann splitting of the quasi-particle density of states in high magnetic fields. We will present first experimental results and analyze them in the framework of Maki's theory on the superconducting quasi-particle density of states. We further discuss the simultaneous existence of both superconductivity and high magnetic fields in the confined geometry of an STM tip.

TUE 17**Thermoelectric and Related Properties of Carbon-Based Materials**

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We analyze the thermoelectric and conduction properties of carbon nanotube networks and composites to identify the mechanisms occurring in different types of material, and how improved properties might be attained for flexible thermoelectric fabrics [1,2] or thin, transparent conducting films [3]. We will also compare the observed electron transport properties with those of graphitic and graphene materials of different types and investigate the role of disorder.

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TUE 18**In-plane force fields and elastic properties of graphene**G. Kalosakas^{1,2}, N.N. Lathiotakis³, C. Galiotis^{1,2}, K. Papagelis^{1,2}¹Materials Science, University of Patras, Patras GR-26504, Greece²ICE-HT/FORTH, PO Box 1414, GR-26504 Rio, Greece³Theoretical and Physical Chemistry Institute, NHRF, Vass. Constantinou 48, Athens GR-11635, Greece

Bond stretching and angle bending force fields, appropriate to describe in-plane motion of graphene sheets, are derived using first principles' methods. The obtained force fields are fitted by analytical anharmonic potential energy functions, providing efficient means of calculations in molecular mechanics simulations. Numerical results regarding the mechanical behavior of graphene monolayers under various loads, like uniaxial tension, hydrostatic tension, and shear stress, are presented, using both molecular dynamics simulations and first principles' methods. Stress-strain curves and elastic constants, such as, Young modulus, Poisson's ratio, bulk modulus, and shear modulus, are calculated. Our results are compared with available experimental estimates, as well as, with corresponding theoretical calculations. Finally, the effect of the anharmonicity of the extracted bond stretching and angle bending potentials on the mechanical properties of graphene are discussed.

TUE 19**Investigation of electromagnetic properties of CNT consisted anisotropic composite materials**Mikhail Kanygin¹, D. S. Bychanok², V. V. Kubarev^{2,3}, S. A. Maksimenko³, P. P. Kuzhir², O. V. Sedelnikova¹, L. G. Bulusheva¹, A. V. Okotrub¹¹Nikolaev Institute of Inorganic Chemistry, SB RAS, Novosibirsk, Russia²Research Institute for Nuclear Problems, Belarusian State University, Minsk, Belarus³Budker Institute of Nuclear Physics, SB RAS, Novosibirsk, Russia

Efficiency of interaction of electromagnetic (EM) radiation with carbon nanotubes (CNT) is determined by CNT conductivity and their orientation relatively to the EM field. In addition in CNT consisting materials resonance effects appear in condition than the length of CNT is comparable with the wavelength of excitation radiation. Anisotropic composite materials were prepared by multiple forge-rolling method. The anisotropic response from obtained composite was measured in the THz, GHz, IR and low-frequency regions. It was found that reflective signal of THz radiation with the orientation of polarization parallel to the CNT is two times higher than in orthogonal orientation. In the GHz region there are 5 times increase of scattering efficiency in the parallel orientation of polarization and CNT. In the IR region changing the intensity of transmitted radiation on 10 percents with changing polarization was found due to the CNT orientation. Investigation of composite films

prepared with different number of forge-rolling cycles in the low-frequency region shows decrease of anisotropic properties of composite with increase of the number of cycles.

TUE 20

Synthesis and transformation of SWCNT nanohybrids filled with different transition metal metallocenes

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It is of great importance to control the properties of single-walled carbon nanotubes (SWCNTs). One of the approaches is given by filling of the tubular channels with appropriate substances such as metallocenes [1]. It further allows encapsulated organic compounds to react within the tubes to form DWCNTs. This makes it possible to get the carbon nanohybrids with well-defined structure and properties. Here we study eDIPS SWCNTs of 1.7 nm mean diameter [2] encapsulating different metallocenes and investigate DWCNT formation processes at elevated temperatures. Raman studies show the filling and the formation of DWCNTs in high yield. We identify the inner-tube formation temperatures for different tube chiralities and metals. Such information is fundamental to possibly exercise control of chirality on the growth of SWCNTs on the bulk scale.

M.S., H.S., T.P and M.K. thank the FWF for support. M.K. also acknowledges the ÖAW for a DOC-ffORTE fellowship.

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TUE 21

Field electron emission from CVD graphene

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Single layer graphene films were obtained by CVD on a copper foil and transferred onto glass or SiO₂/Si substrates. The structural characteristics of the graphene were evaluated with Raman and SEM techniques. Field emission (FE) measurements were performed in diode configuration with flat luminescent screen anodes and with tip shaped anode scanning over the sample surface. Intensive emission with the currents up to 10 μ A was measured for a single emission site located on graphene edges. This intensity of FE is close to the maximal value which may be

observed from a single carbon nanotube. The current-voltage characteristics of FE from graphene demonstrate deviations from the classical Fowler-Nordheim law. The possible mechanisms of observed FE from graphene are discussed.

TUE 22

Synthesis of Functional Nanocrystals and Nanohybrids via Seeded Emulsion Polymerization

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Ultrasmall polymer-coated nanocrystals with sizes between 15 and 110 nm could be prepared by seeded emulsion polymerization in which nanocrystals are used as seeds. The process avoids any treatment with high shear forces or ultrasonication. The number of nanocrystals per seed, the size of the seeds, and the polymer shell thickness can be independently adjusted. Seeded emulsion polymerization allows the introduction of functional groups on the composite surface or inside the bulk polymer by use of functional surfactants, functional polymerizable linkers, or functional monomers. The introduced groups were used e.g. for charge control or coupling reactions. We were also able to fabricate advanced hybrid structures that are fluorescent and plasmonic, magneto-plasmonic or magneto-fluorescent using seeded emulsion polymerization. Iron oxide, gold and cadmium selenide nanocrystals are here coencapsulated with different spatial configuration depending on the desired interaction between the different nanocrystals.

TUE 23

Raman spectroscopy strongly doped of the CVD-graphene

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Raman spectroscopy and in-situ Raman spectroelectrochemistry have been applied to study chemical vapor-deposition-grown graphene coated layers with polyelectrolytes. The doping of graphene leads to a shift of the Fermi level, which is reflected in a change of Raman spectra. In our study we focused on analyzing the change of the Raman intensity of the G and G' bands as a function of the electrode potential. Due to polyelectrolyte coating a strong doping level could be achieved. The intensity of the G' band decreases with increasing magnitude of the electrode potential, but the G band exhibits a more complex behavior. An anomalous increase in the intensity of the G band at both high positive and negative potentials has been observed.

TUE 24**Realistic atomic-scale model for polycrystalline graphene and the related mechanical and electronic properties**J. Kotakoski¹, J. C. Meyer¹, Dinh van Tuan², T. Louvet², F. Ortman², S. Roche^{2,3}¹Universität Wien, Wien²CIN2 (ICN-CSIC) and Universitat Autònoma de Barcelona, Spain³ICREA, Barcelona, Spain

Although experimental studies have recently brought light onto the atomic structure of grain boundaries in graphene, as well as their effect on the magnitude of changes in properties due to their influence, detailed atomic-scale understanding of the origin of the different properties has remained unknown. For this reason, we have established a method to create realistic atomistic models of polycrystalline graphene structures which have random misorientation angles between the different grains and exhibit serpent-like meandering GB structures similar to the experimental images. Using this model, we have shown that — unlike has often been expected — mechanical failure upon stretching a graphene sheet does not start from within individual GBs but rather at points where several GBs meet. From there, the cracks then propagate through the grains (not along the GBs), again similar to recent experimental findings. Our atomistic models have further allowed us to study the charge transport characteristics in realistic polycrystalline graphene samples. Our calculations revealed a remarkably simple scaling law which relates several of the transport properties to the average grain sizes.

TUE 25**Size-dependent Photoluminescence Properties of Graphene Oxides**Daichi Kozawa¹, Yuhei Miyauchi^{1,2}, Shinichiro Mouri¹, Kazunari Matsuda¹¹Institute of Advanced Energy, Kyoto University²JST-PRESTO

Graphene has attracted much attention because of its unique physical properties and numerous applications. One of the methods for modifying the band structure of graphene is chemical treatments and functionalization, and one such functionalized product is graphene oxide (GO). A broad Photoluminescence (PL) is observed in GO.

We studied the size-dependent photoluminescence properties of GO using continuous-wave PL and time-resolved PL spectroscopy. The broad PL spectrum was observed around 1.7 eV in the pristine GO sample. The PL spectra exhibit blue shift and PL lifetime increases significantly using centrifugation treatment of GO sample. Moreover, the PL efficiency increases tenfold by the centrifugation. The atomic force microscopy (AFM) reveals that the size of GO is reduced by the centrifugation. We will discuss the detail of PL properties in GO and the size effect of GO fla-

ke based on the results from pH-dependent PL, PL excitation, time-resolved PL spectroscopy and AFM.

TUE 26

One-dimensional N₂ gas inside single-walled carbon nanotubes

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The unexpected presence of a linear arrangement of co-axially oriented N₂ molecules inside aligned single-walled carbon nanotubes is revealed by high resolution near-edge x-ray absorption spectroscopy. The encapsulated N₂ molecules exhibit free stretching vibrations with a long electronic lifetime of the x-ray-excited anti-bonding π^* states. Molecular dynamics simulations confirm that narrow-diameter nanotubes ($d < 1$ nm) are crucial for stabilizing the linear arrangement of aligned N₂ molecules.

Beamtime at SPRING-8 was granted for proposal 2012A1092. Part of this work was financially supported by Grants-in-Aid for Scientific Research (19054003, 22226006, and 23760180), and the JSPS Core-to-Core Global COE Program "Global Center for Excellence for Mechanical Systems Innovation". C.K. acknowledges the Austrian Academy of Sciences for the APART fellowship 11456. T.T. acknowledges support from the Higher Educational Strategic Scholarships for Frontier Research Network (CHE-PhD-SFR) granted by the Office of Higher Education Commission, Thailand.

TUE 27

Study of the lateral growth of carbon deposits on MWNTs via ethylene decomposition.

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Catalytic CVD carbon nanotube properties significantly depend on the presence of surface impurities and defects. Amorphous carbon, polyaromatic compounds and graphene flakes are the most optional impurities of MWNT surfaces. In this paper we have investigated the kinetics of carbon species deposition on MNWT surface during ethylene decomposition. HR TEM, XRD, temperature dependence conductivity and surface area measurements were used to characterize the structure of carbon deposits forming at variable temperatures, ethylene pressure and

exposure time. The prolonged exposure of MWNTs in CVD conditions may cause the significant imperfection of nanotube structure via the lateral growth of carbon layers. These data are important for the optimization of operation parameters of catalytic reactors for the production high quality MWNT (especially in fluidized bed reactors).

TUE 28

SWCNT growth from C:Ni nanocomposite templates

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Single walled carbon nanotubes (SWCNT) grown from C:Ni nanocomposite thin film templates are studied by Raman mapping, scanning, and transmission electron microscopy. The templates consist of few nm thick films of Ni nanoparticles embedded in a protective matrix of amorphous carbon. They are prepared by ion beam sputtering, which allows a precise control of the particle size, shape, and arrangement in a sub nanometer length scale. SWCNT growth is performed by low pressure chemical vapour deposition in C₂H₂/H₂ at temperatures of about 735°C. The electron micrographs show that a large part of the nanoparticles preserves its initial geometry. The effect of the different particle morphologies on the mean SWCNT diameter and diameter distribution is demonstrated and discussed in the framework of current growth models.

TUE 29

H-terminated diamond as optically transparent impedance sensor for real time monitoring of cell growth

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Cell-based impedance spectroscopy is promising method for cell-based assays and drug discovery applications. It allows continuous and real-time monitoring of cell cultivation. Here we introduce diamond-based impedance sensor as an innovative solution for a wide range of applications in biosensorics and biomedicine. In this study we used intrinsic nanocrystalline diamond (NCD) film to realize fully optically transparent in-plane impedance sensor where the electrodes are realized by p-type

surface conductive channel induced by hydrogen termination of diamond. Cultivation of human osteoblast-like MG 63 cells was monitored by different diamond-based sensors in wide frequency range (100 kHz - 10 Hz) for several days and compared to commercially available reference sensor. The growth of cells were analysed by fluorescence microscopy. The measured impedance curves correspond well to the cell life cycle (adhesion, growth and detachment from the growth substrate). The equivalent electrical circuit of the sensor system was evaluated from the Nyquist plots and discussed in article. This work was supported by the grant P108/12/G108 and it was carried out in frame of the LNSM infrastructure.

TUE 30

Role of the Pressure Transmitting Medium on the Pressure Effects in DWCNTs

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Recently, we carried out a high-pressure optical spectroscopy study on the mechanical stability of double-walled carbon nanotubes (DWCNTs) [1]. In comparison to SWCNTs the pressure-induced shifts of the optical transitions in the outer tubes of DWCNTs are significantly smaller below 10 GPa, showing the stabilization of the outer tubes by the inner tubes. Additionally, the two anomalies at the critical pressures $P_{c1} \sim 3$ GPa and $P_{c2} \sim 7$ GPa in SWCNTs are suppressed due to the stabilization effect and only one anomaly at ~ 12 GPa appears.

It has been demonstrated that the pressure transmitting medium plays an important role for the pressure-induced effects in carbon nanotubes [2]. Here, we present the results of a high-pressure optical spectroscopy study on DWCNTs using alcohol-mixture, argon or nitrogen as pressure transmitting medium. Our results show that a pressure gradient due to the solidification of the pressure medium greatly influences the pressure effects on the optical transitions, i.e., shifts and anomalies.

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TUE 31

The influence of adsorption of volatile organic compounds on the conductivity of multi-walled carbon nanotube aerogels

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Contacts between MWNTs and their interaction with polymer matrix are important

for the tailoring conductivity of polymer-MWNT composites (percolation threshold, the density of localized states at the Fermi level). Recently we have observed the influence of adsorption of different gaseous media on conductivity of multi-walled carbon nanotubes. At the same time the nature of polymer matrix influences on the conductivity of different polymer-MWNT composites. In this paper we have studied the influence of volatile organic compound adsorption on the conductivity of MWNT aerogels consisting of tangled nanotubes. The usage of MWNT aerogels in combination with a controllable filling aerogel matrix with dielectric organic molecules allows us to separate the influence of the disjoining pressure of organic molecule adsorbing between contacting tubes and the influence of the interaction organic molecules with nanotube surfaces influencing on the mobility of charge carriers. Strong dependence of MWNT aerogel conductivity on the wetting ability of organic molecules was observed.

TUE 32

Absolute Raman Cross Section of Rhodamine 6G Confined by Graphene

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Raman enhancement by graphene, the acting mechanism and the magnitude, are still intensely discussed in literature. Recently it was argued that graphene may even decrease the Raman cross section of adsorbed molecules (1). Here we present Raman measurements of rhodamine 6G (R6G) confined between mica and graphene (2). By comparing the R6G Raman cross section to two independent reference cross sections we show that the R6G Raman cross section is enhanced through graphene by one order of magnitude. Possible enhancement mechanisms are discussed.

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TUE 33

Geometry of Nanostructures and Eigenvectors of Matrices

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Very often the basic information about a nanostructure is a topological one. Based on this topological information we have to determine the Descartes coordinates of the atoms. For fullerenes, nanotubes and nanotori the topological coordinate method supplies the necessary information. This method applies the so called bi-lobal eigenvectors of the adjacency matrix for constructing Descartes coordinates for fullerenes. The three bi-lobal eigenvectors are the discrete version of the continuous p_x , p_y and p_z orbitals. A very similar method was found by mathematicians for embedding graphs in Euclidean spaces. It was found however, that the construction of nanotori needs four bi-lobal eigenvectors of the adjacency matrix. This method

was successfully applied to propose a procedure, yielding a single configurational descriptor for any chiral fullerene and its corresponding Schlegel diagram as well. It fails, however, for nanotube junctions, nano coils and other nanostructures. We have found recently a matrix W which can generate the Descartes coordinates for fullerenes, nanotubes, nanotori but, also for nanotube junctions and helical nanocoils as well. Here we present our new method.

TUE 34

Diameter dependence of the defect-induced Raman modes in functionalized carbon nanotubes

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Functionalization of single-walled carbon nanotubes (SWCNTs) typically leads to an increase in intensity of the defect-induced Raman mode (D mode). A large intensity ratio of the D and G modes (D/G ratio) is therefore often used as evidence for successful functionalization.

Here we discuss the effect of the D -mode resonance on the D/G ratio and compare pristine and functionalized SWCNTs. By resonance Raman spectroscopy we study the evolution of the line shape of the $(2)D$ mode of samples enriched with semi-conducting and metallic SWCNTs for excitation energies in the range of 1.51 to 2.71 eV in comparison with the radial breathing mode. In functionalized samples we find that the contribution of small SWCNTs in the $(2)D$ mode disappears. This can change the D/G ratio and has to be taken into account when analyzing the degree of functionalization.

TUE 35

Near-band edge optical properties of exfoliated h-BN layers

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Luminescence properties of h-BN are governed, in the energy range 5.5 - 6 eV, by strong Frenkel-type excitonic effects, highly sensitive to structural defects [1-3]. Nowadays, BN meets a growing interest for graphene engineering. It is therefore

highly desirable to better know optical and electronic properties of thin layers, in correlation with their structural properties. We carry out optical and structural characterizations of this material by combining CL at 4K in the UV range and TEM. Thin layers are obtained by mechanically exfoliating powders and single crystals and reported on SiO₂ substrates for AFM thickness measurements, and then on TEM grids. As for the reference bulk, excitonic emission consists of two series of lines called S and D. Thanks to the CL and TEM imaging capabilities, emission related to D lines, is found to be localized on defects, identified as grain boundaries. Their energies are found to be upshifted as the number of layers decreases, indicating a perturbation in the exciton localization, which will be discussed.

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TUE 36

Nanocomposites consisting of carbon nanotubes coated with platinum nanoparticles

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In presented paper the results of synthesis of carbon nanotubes decorated with platinum nanoparticles by organic colloidal process have been reported. The main purpose of the research was the miscellaneous characterisation of the obtained materials. Nanocomposites consisting of carbon nanotubes coated with platinum nanoparticles may be a valuable material because of combination of unique physical and chemical properties of its components. Both components are characterised by large specific surface area and high value of electric conductivity. High-quality carbon nanotubes were used in the research. Raw nanotubes did not contain metallic impurities or amorphous carbon deposits. Carbon nanotubes - platinum nanoparticles system was fabricated by direct deposition of platinum nanoparticles, produced earlier, onto the surface of carbon nanotubes. Transmission (TEM) and scanning electron microscopy (SEM) were used for characterization of the morphology of nanocomposite as well as the distribution of platinum nanoparticles on the carbon nanotubes surface. High efficiency of used method was confirmed as well as small tendency of platinum nanoparticles to agglomerate.

TUE 37

Field Effect in Graphene Antidot Lattice.

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Single-layer graphene produced via the exfoliation method was patterned (using electron-beam lithography and reactive ion etching) into multiple contact Hall bars,

equipped with several antidot lattices. Each Hall-bar contained four sections: a pristine section as well as three patterned sections with either: one row of holes, five rows of holes or an array (48 rows) of holes. This device enabled the simultaneous comparison of pristine graphene to graphene with a well-defined array of holes.

The devices were created on highly-doped silicon with a 300nm silicon dioxide layer which allowed back-gated measurements to be carried out. The field-effect carrier mobilities as well as the gate bias required to observe a charge-neutrality point (CNP) were determined as a function of temperature (-150C to 100C). While in these measurements, a bandgap could not be observed, the prediction that a few rows of antidot leads to a minimal reduction of carrier mobility was confirmed. The interplay between nanopatterning, gate hysteresis and charge neutrality point offset was also studied.

TUE 38

From Nanotubes to Bulk Single Crystals: Transport and Magnetic Properties of Transition Metal Doped TiO₂

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Titanium dioxide, TiO₂, a wide band gap semiconductor, has a broad range of applications. Few among the others are photo-catalysis, diluted magnetic semiconductors and thermoelectric devices. In all these applications doping the host material is a central issue. In photo-catalysis the goal is to reduce the band-gap and profit more of the visible solar spectrum. In the case of the thermoelectric devices the optimization of the material's properties for a high figure of merit goes via doping studies. Additionally, it has been recently suggested that Co and Mn doped TiO₂ could exhibit ferromagnetic characteristics, which places this compound into the family of diluted magnetic semiconductors (DMS), a potential candidate in spintronics applications.

Here we will report on the synthesis of Mn and Co doped TiO₂ in the form of nanotubes and bulk single crystals. A detailed study of the composition and structure will be shown. The temperature dependence of the resistivity and thermo-electric power will be presented as well as the magnetic properties probed by ESR and SQUID measurements.

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TUE 39**Sensing hydrogen peroxide by carbon nanotube/horse radish peroxidase bio-nanocomposite**

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H₂O₂ is a product of reactions catalysed by several oxidase enzymes and it is essential in environmental and pharmaceutical analyses. The most commonly used enzyme in understanding the biological behaviour of catalysed oxidation of H₂O₂ is horseradish peroxidase (HRP). In our experiments HRP was bound to carboxyl-functionalized multiwalled carbon nanotubes (MWNT-COOH) by N-Hydroxysuccinimide (NHS) and 1-[3-dimethylaminopropyl]-3-ethyl-carbodiimide (EDC) crosslinkers and the efficiency of the binding was optimized at different conditions. The activity of this bio-nanocomposite and the limit of detection (LOD) for H₂O₂ was determined by measuring the fluorescence of tetraguaiacol (which chemical is the product of guaiacol oxidation after addition of H₂O₂) as a function of time. The hydrogen peroxide biosensor we developed exhibited a detection limit of 4 μ M H₂O₂/sec which resolution was better than the one measured in solution by about a factor of two (it was 10 μ M H₂O₂/sec in solution). An attempt has been made to measure the concentration of H₂O₂ in an electrochemical cell with HRP immobilized on electrode of ITO (indium tin oxide, a transparent conductive oxide) and MWNT.

TUE 40**Graphene by liquid phase exfoliation with novel rylene-bisimide-based dyes**

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Graphene, the 2D allotrope of carbon, is one of the most investigated materials in the world. Firstly detected in 2004, it occupied immediately a fundamental role in modern organic chemistry. Due to its outstanding electronic and mechanical properties, it finds application in many fields and constitutes the basis for future technologies, e.g. an alternative to silicon. The growing request is momentarily hindered by the difficulty of producing graphene on an industrial scale. Among the most used synthesis techniques, the liquid-phase exfoliation of graphite stands as an advantageous method. Perylene and high-order rylene bisimide-based surfactant dyes stand among the most promising molecules able to perform the exfoliation

and stabilization of graphite in organic solvents and water. The latter solvent offers also the possibility of a green chemistry scale-up of the whole process. Preliminary results showed that the ultimate thickness of graphene can be reached and its flakes can easily be dispersed in solution. Therefore, the non-covalent functionalization of graphene in solution appears as a tempting approach towards the exfoliation of graphite and an easy access to future 2D materials.

TUE 41

Electronic and vibrational properties of sulfurized diamondoids

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Diamondoids are molecules with diamond-like cage structures of sp^3 -hybridized carbon atoms with hydrogen terminated surfaces. They typically have HOMO-LUMO gaps around 6 eV.

A strong down shift of the HOMO-LUMO gap is predicted for sulfurized diamondoids compared to pure diamondoids. We present Raman spectra of sulfurized diamondoids computed by DFT using the M06-2X functional and the double zeta basis set cc-pVDZ in the program Gaussian 09. In our previous work we showed that the C=C double bond stretch vibration at around 1700 cm^{-1} in several diamondoid compounds is selectively enhanced in resonance Raman spectra. The selective enhancement of this C=C stretch vibration is associated with an elongation of the C=C double bond for the excited state. Because in sulfurized diamondoids the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO) are localized at the C=S bonds, we expect a similar resonance enhancement of the C=S stretch vibration around 1200 cm^{-1} as well.

TUE 42

Permeability studies of quantum dot surrounding diblock copolymer membranes with fluorescent quenching experiments

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The permeability diblock copolymer membranes around core/shell/shell-quantumdot (QD) can be tuned by polymer length, cross-linkage or additional seeded emulsion polymerization in the hydrophobic part of the diblock copolymer. Thus the quantum dots can be shielded totally from the surrounding environment and get protected against ions and small molecules by the hydrophobic polymer shell. This avoids cation exchange reactions over months even at high quencher concentrations giving the possibility of copper based click chemistry of polymer capped QD. Dynamic fluorescence quenching with copper, which was not reported in literature

until now, show a totally passivated QD surface and difference between fluorescence quenching of free and diblock copolymer capped QD. The distance between QD and quenching ion results in a higher tunneling distance and thus in a lower quenching efficiency. These results can be seen in assemble measurements and on single particle level. This allows to study the ion dynamics in ultra-thin polymer membranes by fluorescence spectroscopy using QD as sensor.

TUE 43

Carbon nanowalls growth on three-dimensional structures for energy storage applications

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Graphene related nanostructures have large potential in energy storage applications because of their unique physical and chemical properties. For optimal performance of energy storage device such supercapacitor it is essential to achieve large surface area at lowest equivalent series resistance. Carbon nanowalls (CNWs) are practical realization of graphene containing nanostructures. CNWs are two-dimensional carbon structures that consist of stacked graphene sheets standing vertically on substrates. In this study we synthesize CNWs directly on Ni foam to obtain three-dimensional supercapacitor electrode. CNWs were grown by atmospheric PECVD method. Study of plasma interaction with three-dimensional object will be performed in order to optimize growth conditions. Electrical energy storage performance of CNWs and graphene grown on Ni foam will be compared too.

TUE 44

Structural model of semi-metallic carbon nanotubes

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Depending on the structure, which is directly related to the chiral indices (n_1, n_2) , single-walled carbon nanotubes (SWCNTs) are metals, quasi-metals or direct gap semi-conductors (SC). Unlike SWCNTs, certain types of helically coiled carbon nanotubes (HCCNTs) are foreseen to show semi-metallic properties having high electronic density of states at Fermi level. In a pioneering work of Akagi et al. it is also shown that HCCNTs can be categorized as: narrow gap SC, direct and indirect gap SC and semi-metals.

Our calculations are in support of this result although we adopt a bit different structural model. Within the proposed model, construction of a particular HCCNT is in one-to-one correspondence with the triple connected graph of pentagons, hexagons and heptagons, conventionally defined by a set of numbers $(n_6, n_7, n_5, (b_1, b_2))$, where (b_1, b_2) are the super-cell vectors, while the tiling pattern is given by the

first four parameters. Here, we present technique of construction of semi-metallic HCCNTs introducing particular types of graphs, showing that semi-metallic characteristics are governed by specific distribution of pentagons.

TUE 45

Vertical field-effect transistors based on graphene heterostructures

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Briefly, we prototyped the field effect tunnelling transistors (FETT) based on the graphene vertical heterostructures. In these transistors an atomically thin layer of insulating/semiconducting material serves as a tunnelling barrier between two layers of graphene. FETT operation relies on the tunability of the effective height of the tunnelling barrier via shift of the Fermi level in graphene. FETTs show an unprecedented performance: with the on/off ratio exceeding several millions and device thickness of just several nanometers our devices present an excellent successor of silicon in the post-CMOS era. Mass production via CVD growth techniques combined with the unhampered performance on flexible and transparent substrates also foster their attractiveness.

TUE 46

Magnetoresistance in carbon nanotubes with CoPd contacts

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The injection of spin-polarized electrons from ferromagnetic contacts into nonmagnetic materials is a current challenge in the field of spintronics. Carbon nanotubes (CNTs) have excellent properties to study spin transport, as they exhibit ballistic transport, and are expected to have only small spin-orbit coupling and hyperfine interaction, resulting in long spin dephasing lengths. Much research is currently being done to find a contact material with high spin polarization that forms a stable electronic contact to CNTs. Recently, permalloy and ferromagnet-Pd alloys have shown promising results. We focus our research on CoPd, which is expected to have a high magnetic moment, first characterizing the magnetic behavior via magnetic force microscopy and SQUID. We show that contact geometry has a strong influence on the MR signal. For CoPd contacts with only a single magnetic domain, 2-terminal MR measurements on CNTs show reliable switching. Results for CoPd-contacted CNTs give a relatively large TMR, which is strongly affected

by temperature and applied voltage. This indicates that CoPd-contacted CNTs are an effective and reliable system for studying spin-dependent transport.

TUE 47

Non-covalent Functionalization of Carbon Nanotubes: Novel Tactics for well established Methods

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Single walled carbon nanotubes (SWNTs) are a material with extraordinary physical, chemical and electronic properties and a variety of possible and already implemented applications. The biggest hurdles one has to address concerning their processability, are their poor solubility and the polydispersity of the pristine material.

Commercially available detergents as well as specially designed surfactants have been extensively examined as means to disperse and even separate different types of SWNTs. However, usually no attention is paid to the effect of the temperature on the resulting dispersions. We demonstrate that the different behavior of detergents above and below their Krafft point is reflected in their selectivity and the dispersion efficiency. In addition to multi-phase systems, solvents can also be used to disperse SWNTs in the absence of further stabilizers. While these solvents are a promising route to highly stable nanotube dispersions, they often lack a driving force that provides individualized SWNTs. The addition of an antisolvent like water forces a precipitation of larger species at lower antisolvent quantities, leaving mostly individualized SWNTs in the supernatant.

TUE 48

Spin relaxation in CVD graphene

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We report on spin lifetime measurements on CVD grown PTE supported graphene. Temperature dependence of the thermoelectric power and resistivity reveals that the sample is metallic above 50 K. The chemical potential is shifted by $\epsilon_F = 0.2$ eV relative to the charge neutrality point due to the substrate. At low temperatures below 50 K, however, a metal insulator transition occurs. We attribute the low tempe-

rature charge localization to spatial inhomogeneities. By means of multi-frequency Electron Spin Resonance spectroscopy at room temperature we determined that spin relaxation time, T_1 , is shorter than 11 ns. We interpret the behavior by considering intrinsic and extrinsic effects.

TUE 49

Probing the LO phonons of graphene under tension via the $2D'$ Raman mode

Rohit Narula¹, Stephanie Reich¹

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We use *ab-initio* simulations and perturbation theory to study the $2D'$ Raman mode of graphene subject to biaxial and uniaxial strains up to 2%. We demonstrate that $2D'$ Raman measurements, as a function of polarization and laser energy E_L , can probe the LO phonons of graphene with arbitrary radial and angular extent around Γ . The $2D'$ profile is highly sensitive to uniaxial strain and depends both on polarization and strain orientation. The Grüneisen parameter $\gamma_{2D'} \approx 1.71$ has a mild dependency on the laser energy E_L , and is found to be in good agreement with experiments and comparable in value to γ_G . The shear deformation potential $\beta_{2D'}$ depends strongly on the polarization and strain orientation, becoming negative when the polarizer and analyzer are perpendicular to each other. Finally, we describe a novel and robust method to determine the uniaxial strain by relying solely on polarized measurements of the $2D'$ mode.

TUE 50

Investigating disorder at the grain boundaries of graphene grown by chemical vapor deposition

P. Nemes-Incze^{1,2}, P. Vancso^{1,2}, Z. Osvath^{1,3}, G. I. Mark^{1,2}, X. Jin^{2,4}, Y. S. Kim^{2,4}, C. Hwang^{2,4}, Ph. Lambin⁵, C. Chapelier³, L. P. Biro^{1,2}

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Perturbations of the two dimensional carbon lattice of graphene, such as grain boundaries (GB), have significant influence on the charge transport and mechanical properties of this material. Revealing the structure of GBs can go a long way to

better understand the properties and behavior of graphene grown by chemical vapor deposition (CVD) and enable the tailoring of GB properties. We have studied the atomic and electronic structure of GBs in graphene prepared by CVD, comparing scanning tunneling microscopy (STM) topography and spectroscopy data with ab-initio density functional (VASP) calculations. Our STM measurements show that localized states near the Dirac point, dominate the local density of states (LDOS) of the GBs. Such low energy states are not reproduced by theoretical models which treat the GBs as periodic dislocation cores composed of non hexagonal units. We have extended this model to include disorder in the form of two-coordinated carbon atoms and were able to reproduce the LDOS features measured by STM.

TUE 51

Reinforcement of polymers with SiO₂/MgO coated MWCNTs

Krisztian Nemeth¹, Levente Kovacs¹, Balazs Reti¹, Zoltan Nemeth¹, Mark Posa², Karoly Belina², Klara Hernadi¹

¹Department of Applied and Environmental Chemistry, University of Szeged, Szeged

²Department of Materials Engineering, Kecskemet College, Kecskemet

Because of their high aspect-ratio and strength MWCNTs are expected to be perfect polymer reinforcement materials. Proper inorganic coverage on their surface might help to reduce the aggregation of CNTs and also to overcome consequent dispersability problem. In this work MWCNTs were coated with talc-like oxides to facilitate their incorporation into the polymer matrix. Silica-magnesia mixed oxides were synthesized from different silica precursors and magnesia salts by three different methods. As-prepared materials were characterized by TEM, SEM, Raman spectroscopy and XRD. In order to investigate the change of the polymer's properties samples were also impregnated into the matrix. Three different types of polymers; polyethylene, polypropylene and polyamide were subjected to investigation. Mechanical and thermal (melting and crystallization) properties of the composites were measured by dynamic mechanical analysis (DMA). Results showed that using Mg(NO₃)₂ salt and sol-gel technique with PE polymer produced the best results.

TUE 52

Negligible surface reactivity of 2D topological insulators towards oxygen and water

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⁶ Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

The long-term stability of functional properties of topological insulator materials is crucial for the operation of future topological insulator based devices. Water and oxygen have been reported to be the main sources of surface deterioration by chemical reactions. In the present work we investigate the behavior of the topological surface states on 2D materials bismuth telluride and selenide by ARPES and core level photoemission in a wide range of water and oxygen pressures both in situ (up to 0.1 mbar) and ex situ (at 1 bar). We find that no chemical reactions occur in pure oxygen and in pure water. Water itself does not chemically react with both bismuth telluride and selenide surfaces and only leads to slight p-doping. In dry air, the oxidation of the bismuth telluride surface occurs on the time scale of months, in the case of bismuth selenide not even on the time scale of years. The presence of water, however, promotes the oxidation in air, and we suggest the underlying reactions supported by density functional calculations. All in all, the surface reactivity is found to be negligible.

TUE 53

Ultra-thin flexible organic solar cells based on conjugated polymer/fullerene bulk heterojunctions

Martin Kaltenbrunner^{1,2,3}, Matthew S. White⁴, Eric D. Glowacki⁴, Kateryna Gutnichenko⁴, Tsuyoshi Sekitani^{2,3}, Takao Someya^{2,3}, Helmut Neugebauer⁴, Niyazi Serdar Sariciftci⁴, Siegfried Bauer¹

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Photovoltaic devices for applications like electronic textiles, synthetic skin and robotics require high flexibility and low-weight. Organic photovoltaic solar cells are highly promising in this sector. In this contribution we demonstrate photovoltaic devices on plastic foil substrates less than 2 μm thick, based on conjugated polymer/fullerene bulk heterojunctions, with equal power conversion efficiency to their glass-based counterparts. The devices are constructed on 1.4- μm -thick PET substrates, with poly(3-hexylthiophene) (P3HT) as donor, and (6,6)-phenyl-C61-

butyric acid methyl ester (PCBM) as acceptor components, which form a bulk heterojunction network. Solar cells with 4.2% power conversion efficiency, a specific weight value of 10 W per g, high flexibility and reversible strains of more than 300% are achieved. These ultra-thin organic solar cells are thinner, lighter and more flexible than any other solar cells based on other technologies to date.

TUE 54

Role of localized surface plasmon coupling in tip-enhanced Raman imaging

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Tip-enhanced Raman spectroscopy (TERS) is a comprehensive and non-destructive tool for nanoscale characterization of novel materials. Among them, InGaN/GaN core-shell nanorods aligned in an ordered array are considered for next generation high-efficiency LED for solid state lighting applications. From a TERS measurement of the top part of a single nanorod with 35 nm spatial resolution we obtained several three dimensional images which merge the local mapping of morphology, variation in chemical composition, strain and charge distribution. The analysis of these data reveals a region of Indium clustering constituted by two different polymorphs inside the quantum well layer. In addition, experimental data show an unexpected charge density sensitivity of the method due to coupling between the gold-tip localized surface plasmons (LSPs) and free charge oscillations inside the material. The instant dimer-like nanoantenna created by the tip-sample local interaction strongly increases the efficiency of the Raman scattering. Investigations about this coupling and its geometry are also presented on other systems like graphene and InAs/GaAs quantum dots with the aim of a better understanding of the underlying physics of tip-enhanced Raman scattering.

TUE 55

Estimating the number of injected charge carriers at graphene edges by micro-Raman spectroscopy

Nils Scheuschner¹, Bernat Terres², Felix Kampmann¹, Christoph Stampfer², Janina Maultzsch¹

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²JARA-FIT, Peter Grünberg Institute (PGI-9), Forschungszentrum Jülich and II. Institute of Physics B, RWTH Aachen, Germany

We present micro-Raman measurements from exfoliated as well as lithographically defined graphene edges. We found for both types of graphene edges an upshift of

the G mode and the $2D$ mode. We discuss these upshifts within the scenario of a change of charge carrier concentration due to functionalization at the graphene edges. To estimate a quantitative value for the injected charge carriers at the edge, we present numerical simulations of the Raman measuring process. For these calculations we suggest three empirical models how the charges injected at the edges may be distributed into the edge region of graphene. From the best approximation of the resulting shift of the Raman modes at the edges, we found for the exfoliated edge approximately 5×10^7 charge carriers per cm injected at the edge. This value corresponds to a nearly complete functionalization of the edge. For the lithographically defined edge we found an approximately two to four times higher value, indicating that the effective length of the edge is increased due to roughness at least by the same factor.

TUE 56

Raman spectroscopy of misfit-layer nanotubes

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²Weizmann Institute of Science, Rehovot, Israel

Recently, there were first reports on the synthesis and characterization of nanotubes consisting of alternating layers of SnS and SnS₂ rolled up so as to reduce the lattice mismatch between the two materials [1]. These nanotubes belong to the family of misfit-layer compounds composed of transition metal dichalcogenides TX₂ (T=Sn,Nb,Ti,V,Cr; X=S,Se) and MX layers (M=Sn,Pb,Bi, rare earth metals). In the TX₂ 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 intralayer bonding is much stronger than the van der Waals interlayer interaction.

Here, we present TEM and Raman measurements of SnS/SnS₂ and PbS/NbS₂ nanotubes that elucidate the inner structure of the nanotubes as well as 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, frequency shifts with respect to their bulk counterparts are discussed in terms of charge transfer from the MX to the TX₂ layer.

[1] G. Radovsky et al., Ang. Chem. Int. Ed., 50, 12316 (2011)

TUE 57

Raman spectroscopy on CdSe-nanotube composites

Asmus Vierck¹, Cristina Palencia², Michaela Meyns², Mirjam Volkmann², Christiana Klinke², Beatriz Hernandez Juarez³, Janina Maultzsch¹

¹Institut für Festkörperphysik, Technische Universität Berlin, Germany

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³IMDEA Nanociencia, Madrid - Spain

Hybrid nanomaterials made from semiconductor nanocrystals (NCs) and nanotubes (NTs) have gained high interest in the last years due to their potential use in optoelectronic and photovoltaic devices.

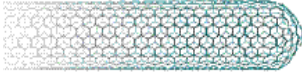
CdSe-nanotube composites were prepared using one-pot synthesis by the hot injection method [1], which allows controlling the CdSe-NC size and shape [2]. As opposed to the common method of creating artificial defects in CNTs to aid sidewall functionalization, our samples do not require such treatment as the NCs attach directly to the CNT sidewalls during growth. In this way we can make sure that the phononic and electronic properties of the composite are influenced only by the components and not by linker molecules or randomly distributed defects.

The influence of attaching CdSe to both CNTs and BN-NTs will be discussed using Raman spectroscopy with regard to the origin of shifting and broadening of present phonon modes.

[1] Juarez, B. H. et al. Carbon Supported CdSe Nanocrystals. *J Am Chem Soc* 130, 15282–15284 (2008).

[2] Juarez, B. H., Klinke, C., Kornowski, A. and Weller, H. Quantum dot attachment and morphology control by carbon nanotubes. *Nano Letters* 7, 3564–3568 (2007).

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- 08:30 – 09:30 **M. Z. Hasan, Princeton**
Tutorial:
Topological Surface States in Topological Insulators, Superconductors and Beyond: Discovery and Recent Results
- 09:30 – 10:00 **B. Dora, Budapest**
Floquet topological insulators
- 10:00 – 10:30 **Coffee break**
- 10:30 – 11:00 **M. Wimmer, Leiden**
Transport signatures of Majorana fermions in nanowires
- 11:00 – 11:30 **D. Abanin, Waterloo**
Tunable electron interactions and robust non-Abelian quantum Hall states in graphene and other Dirac materials
- 11:30 – 12:00 **P. Seneor, Palaiseau-Cedex**
Graphene for spintronics
- 12:00 – 17:00 **Mini-Workshops**
- 17:00 – 18:30 **Dinner**
- 18:30 – 19:00 **J. M. Kim, Oxford**
Nanotechnology Convergence
- 19:00 – 19:30 **Y. Ohno, Nagoya**
Flexible and stretchable electron devices based on carbon nanotube thin films
- 19:30 – 20:00 **S. Garaj, Singapore**
Highly-sensitive graphene nanopores for single-molecule DNA analysis
- 20:00 – 20:30 **D. Ricci, Genova**
Nanotubes on my mind! Probing the brain with CNT electrodes

Wednesday, March 6th

Topological insulators; CNT/graphene applications

08:30**Topological Surface States in Topological Insulators, Superconductors and Beyond: Discovery and Recent Results**M. Zahid Hasan¹¹Princeton University, Department of Physics, Princeton, USA

Topological Insulators are a new phase of electronic matter which realizes a non-quantum-Hall-like topological state in the bulk matter and unlike the quantum Hall liquids can be turned into superconductors at the bulk and/or at the interface. In this talk, I will first review the basic theory of topological matter and experimental probes that reveal topological order. I will discuss experimental results that demonstrate the fundamental properties of topological insulators such as spin-momentum locking, non-trivial Berry's phases, mirror Chern number, absence of backscattering or no U-turn rule, protection by time-reversal symmetry and the existence of room temperature topological order (at the level [1]). I will then discuss the possible exotic roles of broken symmetry phases such as superconductivity and magnetism in doped topological insulators and hetero interfaces and their potential applications in connection to our recent results [2] as well as outline the emerging research frontiers of the field of topological insulators as a whole [1-2].

[1] M.Z. Hasan and C.L. Kane, Rev. of Mod. Phys., 82, 3045 (2010)

[2] S.-Y. Xu, Y. Xia et.al., Science 332, 560 (2011)

09:30**Floquet topological insulators**Balazs Dora¹, Jerome Cayssol², Ferenc Simon¹, Roderich Moessner²¹Budapest University of Technology and Economics, Budapest, Hungary²Max Planck Institute for the Physics of Complex Systems, Dresden, Germany

Time-periodic perturbations can be used to engineer topological properties of matter by altering the Floquet band structure. This is demonstrated for the helical edge state of a spin Hall insulator in the presence of monochromatic circularly polarized light. The inherent spin structure of the edge state is influenced by the Zeeman coupling and not by the orbital effect. Dynamical gaps open in the spectrum due to photons, altering the density of states. The photocurrent (and the magnetization along the edge) develops a finite, helicity dependent expectation value and turns from dissipationless to dissipative with increasing radiation frequency, signalling a change in the topological properties. The connection with Thouless' charge pumping is discussed, together with possible experiments.

10:30**Transport signatures of Majorana fermions in nanowires**Michael Wimmer¹¹Instituut Lorentz, Universiteit Leiden, Leiden

Majorana fermions are particles that are their own antiparticles. To our current knowledge, they do not exist as elementary particles, but can arise as emergent quasi-particles in condensed matter systems. Candidate systems are the $\nu = 5/2$ fractional quantum Hall state, as well as unconventional, topological superconductors.

In the past two years it had been realized that Majorana fermions may arise in hybrid nanostructures involving conventional superconductors and semiconductors that effectively behave like a topological superconductor. Since last year, there are now several experiments that have implemented this theoretical proposals, and have seen first experimental evidence of Majorana fermions.

In my talk, I will review some basic properties of Majorana fermions, and then discuss the experimentally observed signatures and compare them to theoretical predictions.

11:00**Tunable electron interactions and robust non-Abelian quantum Hall states in graphene and other Dirac materials**Dmitry Abanin¹¹Perimeter Institute for Theoretical Physics, Waterloo

Discovery of the fractional quantum Hall effect inspired a concept of quasiparticles with non-Abelian exchange statistics. However, a major limitation for experimental studies of non-Abelian quasiparticles in traditional GaAs-based 2d systems is their lack of tunability: the effective electron interactions in such systems are fixed at values which make non-Abelian states either absent or very fragile. Therefore it is desirable to find alternative, tunable 2d systems that host robust non-Abelian quantum Hall states. Here I will discuss the phase diagram of fractional QH states in recently discovered 2d Dirac materials (graphene, its bilayer, topological insulators). I will show that the effective interactions in these materials can be naturally tuned in a broad range, in contrast to GaAs. The tunability of interactions in Dirac materials allows one to stabilize non-Abelian states, as well as to drive phase transitions between various many-body phases (quantum Hall states, Fermi-liquid-like states, and states with broken translational symmetry) in a controlled manner. This study provides a realistic route to engineering robust fractional and non-Abelian states in Dirac materials.

11:30**Graphene for spintronics**

Pierre Seneor¹, B. Dlubak¹, M.-B. Martin¹, A. Anane¹, C. Deranlot¹, R. Mattana¹, H. Jaffres¹, F. Petroff¹, A. Fert¹, B. Servet¹, S. Xavier¹, M. Sprinkle⁴, C. Berger^{3,4}, W. de Heer⁴

¹Unite Mixte de Physique CNRS/Thales, Palaiseau, France

²Université de Paris-Sud, Orsay, France

³Institut Néel, Grenoble, France

⁴Georgiatech, Atlanta, USA

Spintronics is a paradigm focusing on spin as the information vector and ranging from quantum information to zero-power non-volatile magnetism. Several spintronics devices (logic gates, spin FET, etc) are based on spin transport in a lateral channel between spin polarized contacts. However while spin is acclaimed for information storage, a paradox is that efficient spin transport as remained elusive.

We will present magneto-transport experiments on epitaxial graphene multilayers on SiC showing very large spin signals and spin diffusion length in graphene in the 100 μm range (as high as 285 μm). In the best case, the spin transport efficiency of epitaxial graphene is found to be of 75% of the ideal channel.

Graphene, could turn out as a material of choice for large scale logic circuits and the transport/processing of spin information. Understanding the mechanism of the spin relaxation, improving the spin diffusion length and also testing various concepts of spin gates are the next challenges.

Dlubak et al. Nature Phys 8 557 (2012)

Seneor et al. MRS Bulletin 37 1245 (2012)

18:30**Nanotechnology Convergence**Jung Inn Sohn¹, SeungNam Cha¹, Jong Min Kim¹¹Department of Engineering Science, University of Oxford, Oxford, UK

We present the current and future nanotechnology, especially focusing on the convergence of nano with electronics, and photonics. Nano-electronics will cover the graphene and carbon nanotubes, and their applications in flexible and transparent electrodes, and transistors. Nano-photonics will include quantum-dot displays and other applications.

In this talk, first, we discuss the recent trends in nano-electronics. This will address the nano carbon and its applications with graphene and carbon nanotubes (CNT), covering CNT displays, and lightings. Also, for the applications for the printable electronics, we discuss flexible and transparent electrodes with CNTs and graphene, printable and flexible transistors with organic TFT and CNTs, printable and flexible lighting element with nano carbons. Nano-photonics includes quantum-dot for the displays/lightings and GaN light emitting diode on the glass and the flexible substrates are shown with their images.

19:00**Flexible and stretchable electron devices based on carbon nanotube thin films**Yutaka Ohno^{1,2}¹Department of Quantum Engineering, Nagoya University, Nagoya²Multidisciplinary Institute of Digitalisation and Energy, Aalto University, Finland

Flexible/stretchable electronics has been attracting much attention because of the variety of possible new applications from flexible e-papers to sensing devices having an affinity with human body. Among various kinds of semiconductor materials, carbon nanotube thin films have advantages in flexibility, performance and cost because of the excellent electronic and mechanical properties and processability. Our recent results on carbon nanotube-based flexible and stretchable electronics will be presented, including high-performance carbon nanotube TFTs and ICs realized on a transparent plastic film, all-carbon TFTs demonstrating excellent stretchability, and high-mobility printed TFTs.

19:30**Highly-sensitive graphene nanopores for single-molecule DNA analysis**Slaven Garaj^{1,2,3}¹Graphene Research Centre, National University of Singapore, Singapore²Department of Physics, National University of Singapore, Singapore³Department of Bioengineering, National University of Singapore, Singapore

In a quest to non-destructively analyse individual biomolecules with sub-nm resolution - the paramount challenge in the field of physical DNA and protein sequencing - we developed and investigated the graphene nanopore devices. In a nanopore device, individual DNA molecule in ionic solution is threaded through a nm-scaled pore in a linear fashion, allowing for sequential parts of the molecule to be localised and interrogated within the pore. The properties of the localised part of the molecule can be deduced by measuring ionic current modulation through the obstructed nanopore, or by monitoring current in a nanopore-integrated electrical sensor. We show that nanopore in single-layer graphene membrane has excellent predisposition to achieve single-nucleotide resolution along the length of a DNA molecules. Furthermore, we demonstrate that graphene nanopores have ultrahigh sensitivity on small diameter variations of the threading molecule, as a direct consequence of graphene's monoatomic thickness. Finally, we discuss the physical properties of graphene nanopores, their interaction with the DNA molecules, and implications of our results on the prospects for next-gen DNA sequencing.

20:00**Nanotubes on my mind!****Probing the brain with CNT electrodes**

Davide Ricci¹, Elisa Castagnola¹, Alberto Ansaldo¹, Emma Maggiolini¹, Luciano Fadiga¹

¹RBCS, Istituto Italiano di Tecnologia, Genova

The ability to detect signals among nerve cells using electrodes is one of the founding stones of neuroscience. A variety of different technologies and shapes were employed in the past decades for both recording and stimulation, allowing breakthroughs in our understanding of the physiology of the nervous system and opening the door for the functional restoration of neural paths.

High Surface Area coatings (HSAc) allow to reduce electrode impedance while increasing their signal to noise ratio and charge injection capability.

The talk will report our results obtained using different HSAc and electrodes, showing how carbon nanotubes based ones have distinct advantages, especially when their pristine surface is allowed to act as electrical interface. A discussion about the less than straightforward relationship between modified electrode impedance, signal power spectrum and information on neural signalling will be given, based on *ad hoc* designed *in vivo* experiments.

An outlook of the potentialities that are made available through the use of these tools in clinical practice will be presented, based on a series of preliminary experiments performed during brain surgery.



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- 08:30 – 09:00 **H. Kataura, Tsukuba**
Chirality and Length Sorting of SWCNTs using Gel Column Chromatography
- 09:00 – 09:30 **K. Yanagi, Tokyo**
Control of Colors of Single-Wall Carbon Nanotubes: Purification, Electrochromic Properties, and Peapods in a Single-Chirality State
- 09:30 – 10:00 **S. Cambre, Antwerp**
Optical Properties of Empty and Filled Carbon Nanotubes
- 10:00 – 10:30 **Coffee break**
- 10:30 – 11:00 **J. Kürti, Budapest**
Non-dispersive D band in double-walled carbon nanotubes with ultrasmall diameter
- 11:00 – 11:30 **R. Arenal, Zaragoza**
Atomic configuration and properties of carbon-based heteroatomic nanostructures
- 11:30 – 12:00 **A. Zettl, Berkeley**
Graphene and atomically-thin BN examined by TEM and other probes
- 12:00 – 17:00 **Mini-Workshops**
- 17:00 – 18:30 **Dinner**
- 18:30 – 19:00 **S. Maruyama, Tokyo**
CVD Growth of Self-Organized Micro-Honeycomb Network Structure of Single-Walled Carbon Nanotubes for Photovoltaic Devices
- 19:00 – 19:30 **L. Kavan, Prague**
Application of Graphene-Based Nanostructures in Dye Sensitized Solar Cells
- 19:30 – 20:00 **I. Kolaric, Esslingen**
Sense and Non Sense of ITO Replacement with CNT
- 20:00 **Poster III**

Thursday, March 7th

CNT sorting, optics, and applications

08:30**Chirality and Length Sorting of SWCNTs using Gel Column Chromatography**Hiromichi Kataura^{1,2}, Huaping Liu^{1,2}, Maki Shimizu^{1,2}, Yasuhiro Ito^{1,2}, Shunjiro Fujii^{1,2}, Astushi Hirano^{1,2}, Takeshi Tanaka¹¹Nanosystem Res. Inst., Nat. Inst. of AIST, Tsukuba²CREST, JST, Kawaguchi, Japan

Because single-wall carbon nanotube (SWCNT) is always produced as a mixture of variety of structures, such as diameter, chirality, and length, structure sorting is one of the most important issues in the basic research field and applications. To solve this problem, we have developed multicolumn gel chromatography method for the precise chirality sorting of semiconducting SWCNTs. However, this two-step separation method is not enough for the large scale separation. For a further improvement, we analyzed separation mechanism and found that the interaction between the gel and SWCNTs is highly depending on the the system temperature. Finally, we have realized one-step chirality sorting using temperature controlled gel column chromatography. The remaining structure parameter is the length. The precise length sorting is already possible using size exclusion column, but the sorting range was limited to be shorter than 5 micron. Recently, we found a specific interaction between DNA and silica gel and succeeded to select SWCNTs longer than 10 micron using a silica gel column and DNA as a dispersant. Now all the structural parameters of SWCNTs can be sorted out by the gel column.

09:00**Control of Colors of Single-Wall Carbon Nanotubes: Purification, Electrochromic Properties, and Peapods in a Single-Chirality State**Kazuhiro Yanagi¹¹Department of Physics, Tokyo Metropolitan University, Hachioji

Recent progress of purification techniques on single-wall carbon nanotubes (SWCNTs) enables us to obtain various colored SWCNTs. For example, we can prepare cyan, magenta, and yellow colored SWCNTs using metallic SWCNTs with different diameters. In addition, such colors can be electrically manipulated using electrochemical doping techniques upon thin films of the colored SWCNTs, showing electrochromic properties in visible-light region. Moreover, recently, we achieved single-chirality purification upon SWCNTs with diameter around 1.4 nm, which was sufficiently large for molecular encapsulation, after a two-step purification method using metal/semiconductor sorting and CsCl sorting. As a result, single-chirality C60 peapods were also prepared. Single-chirality purification upon SWCNTs with such large diameter will contribute to the clarification of detailed physical/chemical properties of molecules inside nano-spaces and will also serve an essential role in applications of electronic devices using peapods.

References:

Yanagi et al., Adv. Mater. 23, 2811 (2011)

Kawai, Yanagi et al., J. Am. Chem. Soc. 134, 9545 (2012)

09:30**Optical Properties of Empty and Filled Carbon Nanotubes**Sofie Cambre¹, Christof Christina Verlackt¹, Jochen Campo¹, Charlie Beirnaert¹, Wim Wenseleers¹¹Physics department, University of Antwerp, Belgium

Solubilization of carbon nanotubes (NTs) with bile salt surfactants[1] has enabled major advances in their processing, purification, and spectroscopic study. The regular, unperturbing coating yields much narrower spectral linewidths than other surfactants, allowing e.g. to resolve the spectroscopic features of empty (pristine) and water-filled (opened) NTs, even for the very thinnest tubes, where only a single file of water molecules fits inside the nanotube channel.[2,3] The latter has allowed us to develop a method for characterizing the opening efficiency of various methods, and fill the NTs with other molecules to create functional nanohybrids. Empty and filled NTs can be separated and the empty tubes allow enhanced diameter sorting by density gradient ultracentrifugation.[4] The pristine, closed and thus empty tubes obtained in this way possess superior optical properties.[5]

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

[2] W. Wenseleers et al. *Adv Mater* 19, 2274 (2007)

[3] S. Cambre et al. *PRL* 104, 207401 (2010)

[4] S. Cambre et al. *Angew Chem Int Ed* 50, 2764 (2011)

[5] S. Cambre et al. *ACS Nano* 6, 2649 (2012)

10:30**Non-dispersive D band in double-walled carbon nanotubes with ultrasmall diameter**Jeno Kürti¹, Balint Gyimesi¹, Janos Koltai¹, Viktor Zolyomi², Wolfgang Plank³, Xianjie Liu³, Alexander I.Chernov³, Lei Shi³, Thomas Pichler³, Hans Kuzmany³¹Department of Biological Physics, Eötvös University, Budapest, HU²Department of Physics, Lancaster University, Lancaster, UK³Faculty of Physics, University of Vienna, Vienna, A

Non-dispersive bands have been observed in the Raman spectrum of peapod grown double walled carbon nanotubes in the region of the D band. The appearance of these bands at 1246 cm^{-1} , 1273 cm^{-1} and 1360 cm^{-1} strongly depends on the preparation conditions. Changing the laser excitation frequency changes only the intensity of these bands but not their position. The excitation profile has its maximum for red laser excitation around 633 nm. The situation is similar to the observation of the non-dispersive Raman D band activated by well-ordered inter-layer interactions in rotationally stacked bilayer graphene (I band). We show that similarly to the case of bilayer graphene with rotated layers, the interaction between the inner and outer tubes with different chiralities is the mechanism for the appearance of the non-dispersive I band in double walled carbon nanotubes. Using DFT calculations we determined the perturbation potential due to the interaction between the two layers. The Fourier components of this potential determine the possible wave vectors in the double resonance process. In addition to that the effect of the Van Hove enhancement has to be taken into account.

11:00**Atomic configuration and properties of carbon-based heteroatomic nanostructures**Raul Arenal^{1,2}¹LMA-INA, Universidad de Zaragoza, Zaragoza, Spain²Fundacion ARAID, Zaragoza, Spain

Nanomaterials based on boron, carbon and/or nitrogen (C, B-C-, C-N-, B-C-N- and BN) have generated intense interest due to the versatility of the electronic properties of such systems, from photoluminescent materials in the visible range to wide band gap semiconductors, offering a wide range of fundamental and applicative perspectives [1-2]. For instance, heteroatomic nanotubes (NTs) based on the combination of these three elements (B, C, N) make them an attractive alternative to undoped carbon counterparts (C-NT) [1-2]. In this presentation, we will mainly focus on the study, by different advanced TEM techniques, of CN_x-NT. We will present the direct detection, via STEM-EELS measurements, of individual N atoms incorporated in SW-CNT [3]. Thus, the atomic configuration of these N atoms in the C network will be discussed. In addition, other EEL spectroscopic studies probing the optoelectronic properties of these nanostructures will be also presented.

[1] R. Arenal, X. Blase, A. Loiseau, *Advances in Physics*, 59, 101 (2010).

[2] P. Ayala, R. Arenal, A. Loiseau, A. Rubio, T. Pichler, *Rev. Mod. Phys.* 82, 1843 (2010).

[3] R. Arenal, M. Kociak, O. Stephan, submitted.

11:30

Graphene and atomically-thin BN examined by TEM and other probes

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¹Department of Physics, University of California at Berkeley, USA

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I will discuss our recent experimental investigations of the following topics:

Graphene can be sandwiched together with foreign species between the sheets. This new kind of intercalation allows tailor-made hybrid materials with desirable optical and thermodynamic properties. Nanoscale liquid droplets containing nanocrystal precursors can similarly be laminated in so-called Graphene Liquid Cells, which facilitates real-time TEM investigation of growth and dynamics of nanocrystals. Recent attempts have been made to induce specific defects into graphene and BN, and to manipulate the atomic-scale edge structure of these materials. Graphene and hBN can together be used to create analogs of ultra-heavy atomic nuclei, with highly unusual electronic structure.

18:30**CVD Growth of Self-Organized Micro-Honeycomb Network Structure of Single-Walled Carbon Nanotubes for Photovoltaic Devices**Shigeo Maruyama¹, Kehang Cui¹, Takaaki Chiba¹, Erik Einarsson¹, Shohei Chia-shi¹¹Department of Mechanical Engineering, The University of Tokyo, Tokyo

For photovoltaic devices, so far, spaghetti-like thin film of single-walled carbon nanotubes (SWNTs) known as bucky paper or vertically aligned SWNT (VA-SWNTs) have been examined for SWNT/Si heterojunction solar cells or counter electrode of dye-sensitized solar cells. Here, we propose a self-organized micro-honeycomb network structure of SWNTs obtained by water vapor treatment of as-synthesized VA-SWNTs for solar cell devices with higher performance.

The SWNT/n-Si heterojunction solar cell was built by placing the micro-honeycomb SWNTs network film on top of the substrate which has a 3 mm x 3 mm bare n-type silicon contact window in the center. Our preliminary tests showed that optimal photovoltaic conversion efficiency (PCE) under AM1.5 was 5.1%, with the fill factor of 46%. Furthermore, the superior performance of dye-sensitized solar cells with the micro-honeycomb SWNTs will be discussed.

Part of this work was financially supported by Grant-in-Aid for Scientific Research (22226006, 19054003), JSPS Core-to-Core Program, and Global COE Program 'Global Center for Excellence for Mechanical Systems Innovation'.

19:00**Application of Graphene-Based Nanostructures in Dye Sensitized Solar Cells**Ladislav Kavan¹, Jun-Ho Yum², Michael Graetzel²¹J. Heyrovsky Institute of Physical Chemistry, Dolejskova 3, CZ-18223 Prague 8, Czech Republic²Laboratory of Photonics and Interfaces, Institute of Chemical Sciences and Engineering, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland

The dye sensitized solar cell (DSC) is promising alternative to Si-based photovoltaics. The generic device is a photoelectrochemical DSC with sensitized TiO₂ photoanode, electrolyte solution, redox mediator and the counterelectrode. The latter is typically a layer of Pt nanoparticles on F-doped tin oxide (FTO). Graphene nanoplatelets (GNP) in the form of optically transparent films on FTO exhibit excellent electrocatalytic activity towards the state-of-art Co-based mediators. Dye-sensitized solar cell with GNP cathode is superior to that with Pt cathode particularly in fill factors and in the efficiency at higher illumination intensities. Graphene oxide (GO) shows almost no activity as DSC cathode, resembling the properties of HOPG. However, the activity of GO improves dramatically upon reduction with hydrazine and/or heat treatment. The reduced GO/GNP composite films are favored by good adhesion to FTO, smaller dark currents and by higher stability against aging.

19:30**Sense and Non Sense of ITO Replacement with CNT**Ivica Kolaric¹, Siegmur Roth²¹Head of Department Functional Materials, Fraunhofer IPA , Stuttgart, Germany²Sineurop Nanotech GmbH, München

ITO shortage is one of the great challenges for applications in the field of electronics and renewable energy. Especially in opto electronic applications such as LCD displays and touch elements ITO is used as transparent conductive electrode and one of the major cost drivers. As a result, researchers all over the world tried to replace ITO by nano carbons, such as CNT or Graphene, conductive polymers or nano metal wires. Even though those research results are getting continuously better, still no electronic company changed from ITO to the new alternatives. A critical analysis of those substitution materials, in context with the user's needs indicates ITO replacement is probably not a promising approach for ITO alternatives. However to amend ITO, it is.

By the utilisation of CNT for TCF applications we can generate and new generation of touch panels, which are flexible, environmental stable and sustainable.

THU 1**Charge sensing in carbon-based nanodevices**

Christoph Neumann^{1,2}, Christian Volk^{1,2}, Stephan Engels^{1,2}, Stefan Trellenkamp², Christoph Stampfer^{1,2}

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²Peter Grünberg Institute (PGI-8/9), Forschungszentrum Jülich, 52425 Jülich, Germany, EU

Carbon-based quantum devices, such as single electron transistors and quantum dots (QDs) implemented in graphene sheets and carbon nanotubes have received increasing attention over the last years. For example, graphene QDs have been suggested to be an interesting system for implementing spin qubits. Compared to the well-established GaAs-based QDs they exhibit intrinsic advantages such as small hyperfine interaction and reduced spin-orbit coupling, which promise more favorable spin coherence times. It has been shown that graphene nanoribbons can be used to detect the electronic charge states on QDs even when the current through the QD is below the detection limit, making them potentially valuable charge detectors (CDs) for future spin qubit devices. In the presented work we investigate the usability of graphene nanoribbon CDs implemented in all graphene as well as graphene-carbon nanotube hybrid quantum devices. The CDs are also successfully used in advanced experimental setups where high frequency pulses and magnetic fields are employed to manipulate the QD states. Moreover, back action effects from the CD onto the QDs are probed and investigated to optimize the working conditions.

THU 2**Langmuir and Langmuir-Blodgett films of the electron donor-acceptor dyad of Zn phthalocyanine bearing peripheral alkylether substituents and the C₆₀-imidazole adduct**

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An electron donor-acceptor dyad was formed in a CHCl₃ solution. It was composed of the donor of Zn(phthalocyanine) bearing peripheral ether substituents (tetrakis[2,9,16,23-tri{ethyleneglycol}monomethylether]phthalocyaninato)Zn(II), and the acceptor of the imidazole adduct of fullerene C₆₀, (2-[phenylimidazolyl]fullereno-

pyrrolidine). Langmuir films of the dyad and its components were prepared and characterized by simultaneous recording of isotherms of the surface pressure and surface potential vs. area per molecule and by imaging with BAM. Mono- and multi-layer Langmuir-Blodgett (LB) films of the dyad were transferred onto the FTO glass slides. Orientation of the dyad molecules in films, transferred at different surface pressures, with respect to the FTO surface was evaluated with the PM-IRRAS measurements. The presence of both dyad components in the LB films was confirmed with the UV-vis spectroscopy and cyclic voltammetry measurements. Morphology of the LB films was characterized by the AFM imaging. Preliminary photoelectrochemical measurements revealed generation of photovoltaic currents when the LB films-coated FTO electrode was used as the photocathode.

THU 3

Structural and optical properties of thin bismuth selenide crystals

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Last decade topological insulators have been intensively studied due to their unique electronic and magnetic properties. Recently optical characteristics of these materials attracted more attention. Here we present our results on modelling and experimental observation of dependence of the optical characteristics of topological insulator Bi₂Se₃ on crystal thickness. The calculated electron dispersion curves demonstrate that the conductive surface states disappear for crystals with the thickness less than 3 quintuple layers. The bandgap for a 1-layer thick Bi₂Se₃ becomes as large as 0.406 eV. In order to confirm these theoretical calculations, thin Bi₂Se₃ layers have been synthesized with a molecular beam epitaxy. AFM, SEM, optical absorption and Raman spectroscopy techniques have been employed to monitor the structural and optical characteristics of obtained samples. The interesting layered structures have been observed at the first steps of the crystal growth.

The work was supported by the grants of Russian Federation Ministry for Science and Education (11.G34.31.0061 and 16.513.11.3149) and by RFBR project 12-02-31637-mol-a.

THU 4

Bottom-up assembly of suspended single wall carbon nanotube and graphene devices

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The realisation of suspended single-wall carbon nanotube (SWCNTs) and graphene structures by a bottom up approach can lead to the fabrication of high density arrays, consisting of devices with superior performance compared to their supported counterparts. In addition, suspended structures are the building blocks towards devices like resonators, electromechanical switches etc that are not possible when there is a substrate in direct contact underneath them. This paper presents the fabrication of embedded electrodes into the silicon dioxide (SiO₂) using reactive ion etching and a metallisation step, prior to the deposition of the nanocarbons by alternating current (AC) dielectrophoresis (DEP). The devices are released from the substrate by HF etching. The resulting devices were characterized as field effect transistors and sensors and their potential for various applications is discussed.

THU 5

A Novel Ruthenium Oxide Contact-layer for Low-resistance CNT Via Interconnects Technology

Nozomi Okamoto¹, Takuya Suzuki¹, Tadashi Sakai², Yuji Awano¹

¹Department of Electronics and Electrical Engineering, Keio University

²LEAP

Carbon nanotube (CNT) is expected to be a promising candidate to replace conventional Cu interconnects because of various remarkable properties; highest current density, ballistic transport and high aspect ratio structure. For CNT via interconnects, Ti or TiN has been employed as a contact layer in order to lower contact resistance between CNT and Cu interconnects. However, Ti-related materials can be easily oxidized to TiO₂ by air, which leads high resistance. Ruthenium dioxide (RuO₂) exhibits metal-grade conductivity. In this paper, we propose RuO₂ as a contact layer alternative to TiN in order to lower the resistance of carbon nanotube via interconnects. We have succeeded, for the first time, in growing a forest of Multi-Walled CNTs from Co catalyst on a RuO₂ thin film. The structure of thin films at the bottom of CNTs consists of Co/ RuO₂ /TiN on Si substrate. RuO₂ is prepared in the following step; Ru is deposited by sputtering, then it is exposed to the air to oxidize to RuO₂. We also report measurements of contact resistance between RuO₂ and multilayer Graphene.

This work was performed as part of "Ultra-Low Voltage Device Project" funded and supported by NEDO and METI.

THU 6

Chemistry of perforated graphite: fluorination and bromination

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²CIC nanoGUNE Consolider, San Sebastian, Spain

Carbon material synthesized by reduction of graphite oxide in mineral acids at a temperature is above 200°C retains a layered structure and has a defects from etched holes with diameter of 1-2 nm in graphene sheets [1]. A chemical reactions that take place in this perforated graphite (PG) have a features associated with the large number of edge carbon atoms. The presence of vacancy defects leads to the reactions of covalent fictionalization. The Br-PG was obtained by bromination Br₂ during 2 days and F-PG was synthesized at 300°C by fluorination F₂. According to X-ray photoelectron spectroscopy data the formation of CF₂ groups at the edges of the holes are increase with fluorine content in the sample up to superstoichiometric CF_{1,2}. After the bromination of PG followed by vacuum drying and removing of intercalated Br₂ the resulting product has about 15% of bromine covalently bounded to carbon. Features of the C-Br bonding on the edges of the holes were studied by methods of quantum chemistry and possible models were discussed.

[1] A.V. Okotrub et. al., Perforation of graphite in boiling mineral acid, Phys. Status Solidi B, 249, (2012) P. 2620.

THU 7

Sorting of single walled carbon nanotubes by means of gel permeation chromatography

Frieder Ostermaier¹, Michael Mertig¹

¹Physikalische Chemie Mess- und Sensortechnik, TU Dresden, Germany

Due to their outstanding electronic properties single-walled carbon nanotubes (SW-CNT) are a promising material for future nanoelectronics. Metallic mSWCNT are suited for interconnections, and semiconducting scSWCNT can be used for field-effect transistors (FETs). For applications, it is necessary to provide SWCNT with defined electronic properties. Today there is no production method that yields only one electronic type. Hence post production sorting is mandatory for technical applications.

We used the scalable gel permeation chromatography to sort SWCNT from different production schemes according to their properties. We could show that the approach, that is known for SWCNT from the HiPCO process, can also be applied for the sorting of commercially available SWCNT from CVD methods.

We used UV-Vis for the quantitative characterization of the samples. This method allows a fast comparison of the mSWCNT and scSWCNT contents in a sample with only few preliminary information.

For further prove, we assembled FETs via dielectrophoresis. The measurement of the I-V curves of sorted scSWCNT approves the direct assembly of FETs. A selective burning step for metallic SWCNT can be omitted.

THU 8**Methods of Characterization of the Small Amounts of Residual Metal Catalyst in Purified Carbon Nanotubes**

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Our work presents the methods of detail physical analysis of partial steps leading to the removal of residual metal catalyst nanoparticles (NPs) from single walled carbon nanotubes (SWCNTs) and options of detecting negligible amount of metal in samples possessing diamagnetic response. The properties of remaining NPs after the multi-step purification (oxidation followed by mild acid treatment) and annealing both in static and dynamic vacuum have been investigated. Thermogravimetry, X-ray diffraction, static and dynamic magnetic property measurements and the Extended X-ray Absorption Fine Structure (EXAFS) experiments have been performed. The data provides information about the nature of the residual NPs in purified SWCNTs that is crucial for further understanding of the purification processes and their improvement. It has been demonstrated that even if all macroscopic methods indicate a high purity of treated sample, a non-negligible amount of the metal may still be present and the metal content has to be examined using local and elemental sensitive probes such as EXAFS.

THU 9**High pressure Raman response of graphene supported on Cu substrate**

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The unique structure and properties of graphene provide a broad field for fundamental research and applications. Raman spectroscopy has been proven to be

a valuable non-destructive tool in this emerging research area. We have studied the pressure evolution up to 6 GPa of the main graphene Raman bands (G and 2D) of CVD grown graphene films on $\approx 25 \mu\text{m}$ poly-Cu substrates. Mixtures of 4:1 methanol-ethanol and 1:1 FC70/FC77 fluorinert have been used as pressure transmitting media (PTM). The G and 2D Raman peaks of graphene exhibit similar pressure slopes (≈ 9 and $\approx 20 \text{ cm}^{-1}/\text{GPa}$, respectively) for both PTM, irrespectively of their frequencies and widths at ambient conditions (indicative of different initial doping/strain state). Furthermore, these values are similar to those earlier obtained from graphene on SiO₂/Si substrates using the 4:1 methanol/ethanol mixture as PTM. The similar results for polar and non-polar PTM as well as metallic or insulating substrates suggest that pressure-induced charge transfer effects do not contribute considerably in the pressure response of graphene that is mainly determined by its adhesion to the substrate and the elastic properties of the latter.

THU 10

Octagonal defect lines in graphene structures

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The subject of our study are graphene nanoribbons and carbon nanotubes containing defect lines built of successive octagons or octagons accompanied by pentagons. We show that such octagonal defects lines in graphene structures lead to state localization with energies at the Fermi level. We investigate the nature of these states and show that the localization is due to the zigzag shape of the edges of defect lines. The analysis of spin-up and spin-down bands splitting shows that such structures may reveal spontaneous magnetization. All the calculations are performed within the π -electron tight binding approximation, taking into account electron interaction effects by means of the Hubbard model. A Green function matching approach is used to obtain the local density of states (LDOS).

THU 11

Disentangling the nature of the metallic ground state in functionalised SW-CNT bundles.

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²AIST Tsukuba, Japan

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In this contribution we report on a comparative study of different metallicity sorted SWCNT-bucky papers functionalized by advanced filling reactions and p- and n-type intercalation. We will focus on the effect of charge transfer between the functional elements and semiconducting and metallic nanotubes yielding novel metallic SWCNT hybrids. From high resolution photoemission we study the nature of the metallic ground state in these SWCNT hybrids regarding a 1D Tomunaga-Luttinger liquid or Fermi liquid behaviour, respectively. This will be discussed especially regarding the charge transfer dependent modification of the van der Waals intertube interaction towards a metallic and weakly covalent crosslinking between the SWCNT within a bundle and the hybridisation between the encapsulated metal compounds and the SWCNT. Selected examples cover filling with organometallic compounds and metallofullerenes as well as intercalation by alkali metals and iron-trichloride.

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THU 12

Geometrical sensitivity of thermal expansion coefficients of helically coiled carbon nanotubes

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Helically coiled carbon nanotubes (HCCNTs) are parameterized by tubular radius, monomer length (tubular parameters), helical radius and helical step (helical parameters). On a local level, within our model, positive and negative Gaussian curvatures are obtained by incorporating pentagons and heptagons into the hexagonal carbon lattice. Global geometrical parameters and physical properties of HCCNTs depend on spatial distribution of pentagons and heptagons within the hexagonal carbon net: on their concentration, relative position and orientation, in particular. Temperature dependence of geometrical parameters are obtained by minimizing Helmholtz free energy at finite, fixed temperatures with implementation of line group symmetry and local harmonic approximation which made the calculations highly efficient. Geometrical sensitivity of thermal expansion coefficients of HCCNTs (for temperatures up to 1500 K) is shown.

THU 13

Properties of linear antenna microwave plasma and growth of various carbon nano-forms

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Recently linear antenna microwave plasma CVD processes are used for growth of

carbon allotropes. In the presented work we used such CVD system to grow various carbon forms (i.e. carbon nanotubes, carbon nano-walls/sheets, graphene or even diamond). A complex correlation between process parameters, plasma characteristics and the deposit is presented. Spatially resolved Langmuir probe measurements were done to calculate plasma temperature, density of species, plasma potentials, etc. We found that transformation from poly- to nanocrystalline diamond growth is significantly influenced by plasma temperature and density, especially for pressures lower than 50 Pa. Carbon nanotubes or nanowalls are controlled by substrate bias, and further decreasing of pressure down to 6 Pa was required to grow oriented carbon structures over large areas ($> 100\text{cm}^2$). A crucial technological parameter in the linear antenna CVD system is either using dc or rf substrate bias. A plasma treatment of carbon nanotubes or diamond to control their wetting properties in a such universal system will be further presented.

This work was financially supported by the research projects P205/12/0908 (GA-CR).

THU 14

Preparation of SnO₂ - TiO₂ / MWCNT composite photocatalysts with different synthesis method

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Photocatalytic activity of TiO₂ can be further improved by coupling it with other semiconductors or MWCNT and create a composite material. SnO₂-TiO₂ / MWCNT composite catalysts with different molar ratios were prepared and the photocatalytic activities of these samples were evaluated with methylene blue decomposition. The catalysts were synthesized by acid-catalysed sol-gel method. Two series of catalysts were made, one with co-precipitation and the other one with consecutive precipitation method. The samples were characterized by TEM, XRD, BET. These investigations revealed that the crystalline oxide nanoparticles were successfully bound onto the surface of MWCNTs. According to the photocatalytic measurements in the most cases MWCNT containing catalysts exhibited higher photocatalytic activity during the methylene blue decomposition. Photocatalytic reactions showed that SnO₂ enhances the efficiency of TiO₂. The best composites were made at the ratio of 25-75 (SnO₂-TiO₂ mole %). It can be concluded that the photocatalytic performance strongly depend on the synthesis method.

THU 15

Ultra-thin Al₂O₃ tunnel barriers grown by ALD for graphene devices

John Robertson¹, Bruno Dlubak¹, R S Weatherup¹, P B Kidambi¹, S Esconjauregui¹, S Hofmann¹

¹Cambridge University, , Cambridge

The growth of nm-thick dielectrics on graphene could further unlock graphene's potential for applications such as RF transistors [1] or lateral spin valves [2]. However both the lack of wetting of ultra-thin dielectrics and the impact on the graphene lattice are competing critical issues in developing high performance devices. While the wetting of films resulting from the soft ALD technique on graphene has been reported to be particularly low, we show here that the underlying substrate assistance through the atom-thick monolayer graphene sheet increases the nucleation density by at least 3 orders of magnitude [3]. Furthermore, transport measurements in complete devices reveal that ALD grown Al₂O₃ layers with thicknesses scaled down to 1 nm may be used as quality tunnelling contacts. These results highlight a promising pathway to the delicate integration of ultra-thin dielectrics with graphene.

[1] J. Robertson, Eur. Phys. J.: Appl. Phys. 291, 265 (2004)

[2] B. Dlubak et al., Nature Physics 8, 557 (2012)

[3] B. Dlubak et al., Appl. Phys. Lett. 100, 173113 (2012)

THU 16

Photoluminescence enhancement of Double-Walled Carbon Nanotubes filled with linear carbon chains

Philip Alexander Rohringer¹, Lei Shi¹, Thomas Pichler¹

¹Faculty of Physics, University of Vienna, Vienna

Double-Walled Carbon Nanotubes (DWNT) have come into focus of research due to their superior chemical and mechanical properties compared to Single-Walled Carbon Nanotubes (SWNT). However, their optical properties remain elusive, especially the capability of DWNT showing photoluminescence (PL) is subject to many discussions. Here we used CVD-grown DWNT that were subsequently annealed at high temperatures which leads to the growth of linear carbon chains (lcc) inside the hollow core of the inner tube [1]. Samples were solubilized using standard surfactants and normalized according to their optical densities. The pristine sample shows PL although the signal is overall weaker than for HiPco-SWNT. A strong enhancement of the DWNT-PL signal can be seen for inner tube species with optimal diameter for the formation of the carbon chains similar to the effect of filling SWNT with ferrocene [2]; also it is shown that this enhancement is depending strongly on the growth yield of the lcc. This gives further insight into tailoring the PL quantum yield by controlled filling reactions.

[1] L. Shi in preparation

[2] X. Liu et al., Adv. Funct. Mater., 22 (2012), 3202-3208

THU 17**Improvement of the Seebeck coefficient of thin single-walled carbon nanotube composite films through chemical treatment**Mingxing Piao¹, Urszula Dettlaff-Weglikowska¹, Siegmar Roth¹¹School of Electrical Engineering, Korea University, Seoul

Single walled carbon nanotube (SWCNT) networks, composed of semiconducting and metallic nanotubes are known for high electrical conductivity and a reasonable value of the Seebeck coefficient. We prepared and characterized thermoelectric materials based on thin films of SWCNT composites with polyvinylalcohol. While the pristine SWCNTs generated positive value of the Seebeck coefficient, the n-type chemical doping systematically increased the negative values of the Seebeck coefficient. As a result, the thermoelectric voltage as high as 92 μV per 1 K temperature gradient was measured for only one p/n junction of conducting composite films. That means an improvement by factor of 6 in comparison to the thermoelectric voltage of the recently published thermoelectric fabrics [1]. A combination of 10 electrically connected p-type and n-type layers demonstrated the addition of the individual thermopower contributions with a 25 mV voltage output, when a temperature difference of 50 K was applied.

[1] Corey A. Hewitt, Alan B. Kaiser, Siegmar Roth, Matt Craps, Richard Czerw, and David L. Carroll, Nano Lett. 2012 DOI: 1202161655234001

THU 18**Single-particle photoluminescence microscopy of carbon nanotubes under microfluidic and potentiostatic control**Nicolas Rühl¹¹Institute of Physical and Theoretical Chemistry Am Hubland, 97074 Würzburg

We describe the design and development of a microfluidic cell for single-particle spectroscopy of electrochemically controlled nanoparticles. The cell design allows for simultaneous control of electrochemical potential as well as of electrolyte-concentration and -type. We present first measurements of redox potentials of individual (6,5)-single-wall carbon nanotubes (SWNTs) using near infrared photoluminescence (PL) microscopy as a probe of electrochemical tube-doping.

We observed three potential ranges each with distinct dependence of photoluminescence emission intensity on the applied SWNT potential: a plateau with no significant PL change, the width of which is roughly given by the optical bandgap of the semiconducting carbon nanotube and two regions at larger negative or positive potentials characterized by a rapid decrease of the PL signal. We discuss how the data can be used to determine the redox potential of the observed individual carbon nanotube.

THU 19**Peculiarities of graphene CVD synthesis on nickel and copper foils**

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A chemical vapor deposition (CVD) method is a very prospective technique for graphene synthesis. Here we present a detailed investigation of parameters of this method providing the graphene fabrication onto both nickel and copper substrates. The home-made CVD equipment was used for synthesis. The foils were heated by an electric current running through the foil via Joule effect. The sample temperature was measured by pyrometer. A real time controlled synthesis is demonstrated in this work. Such synthesis parameters as a gas pressure, a partial content of different gases in a gas mixture and a temperature of substrate appeared to influence strongly to the quality of fabricated samples. The calibration curves have been obtained. As result we demonstrate a possibility to fabricate graphene film consisting of a desirable number of graphene layers (from one to tens) with a high quality and an extended covering area.

The work is supported by RFBR-12-02-31373 and by RAS research programs.

THU 20**Discerning the electronic properties of FeCl₃ intercalated metallicity sorted single-walled carbon nanotubes**

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Intercalation of atoms and molecules in graphitic systems such as SWCNTs is a matter constantly studied, from which several reports deal with n-type doping by alkali metals. Much less is reported on p-type doping. Recent studies on the intercalation with p-type dopants like FeCl₃ did not consider the influence of the SWCNT metallicity on the resulting characteristics. Therefore we investigated the electronic properties of SWCNTs intercalated with FeCl₃ using highly pure metallic and semiconducting nanotubes as a starting material produced by state of the art metallicity separation techniques. Here we report on a combined in-situ Raman valence band photoemission, XPS as well as XAS study to probe the p-type doping of FeCl₃ intercalated nanotubes as function of their metallic character. From in-situ Raman measurements and XPS we correlate the charge transfer to the Ra-

man response on an absolute scale. In addition the analysis of the valence band illustrates that semiconducting SWCNTs exhibit slightly higher doping at similar intercalation doses. This study provides an important step to the understanding of the charge transfer in metallicity sorted graphitic materials.

THU 21

Growth of Multilayer Graphene on Polycrystalline Ni Thin Film with Artificial Steps

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Multilayer graphene is one of the most attractive materials as an alternative to Cu LSI interconnects. There are reports on graphene growth by low-temperature (600°C and below) Plasma-Enhanced CVD. Among them is our report that indicates low-temperature growth is driven by "facet growth model", which suggests growth-starting points are fcc (110) and (100) facets of the metal catalyst (Co, Ni) [1]. However, we have not verified enough to conclude that graphene growth starts from these facets. In order to investigate whether graphene growth starts from these steps or not, we made 10-nm-height steps on polycrystalline Ni thin film by Ar milling and subsequently tried to grow multi-layered graphene on them by PECVD at 600°C. We found by SEM observations and Raman spectroscopy that within the distance of 5 μm from the step edge, almost all island formation of graphene takes place at, or very close to the artificially made steps, suggesting the graphene formation starts from the step edges.

This work was performed as part of "Ultra-Low Voltage Device Project" funded and supported by NEDO and METI.

[1] Y. Yamazaki et al., App. Phys. Exp. 5 (2012) 025101

THU 22

Analysis of quantum transport features in complex carbon nanotube structures

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³JARA – Fundamentals of Future Information Technologies

We have investigated a carbon nanotube (CNT) both in quantum transport and in the transmission electron microscope by means of a novel sample design. This enables us to determine the device structure unambiguously as a two-fold single-walled

CNT bundle. The corresponding low-temperature transport experiments are, to our knowledge, the first ones unambiguously conducted on this very system. The stability diagrams exhibit complex features as anti-crossings and Fano-shaped coulomb peaks. The origin of these characteristics is only found with the detailed knowledge about the atomic structure, which cannot be obtained with standard sample layouts. More precisely, we measure capacitive and molecular interactions between the various elements of the device and the environment. A more comprehensive control over the quantum dot can be obtained by manipulating the lead's opacity. This can be achieved by locally varying the tunnel probability to the dot. Therefore we present a fabrication process for top gate structures and show first measurements on top-gated CNTs.

THU 23

Controlling Growth and Diameter Distribution of Single-walled Carbon Nanotubes on Quartz

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Controlling the type (s or m), diameter, density and alignment of single-walled carbon nanotubes (SWNT) during chemical vapour deposition (CVD) growth is important for obtaining SWNT array field-effect transistors without percolation paths but still useful on/off ratios, high mobilities and possible near-infrared electroluminescence. Many parameters can be tuned during CVD growth but a fundamental understanding of the SWNT growth mechanism is still missing. We investigate the influence of different carbon sources, carbon feed rates and concentration of water during catalyst reduction and growth on the the nanotube diameter distribution and the ratio of semiconducting to metallic SWNT. Statistical analysis of Raman spectra (RBM peaks) over large sample areas using three different laser excitations allows for the reliable extraction of diameter distributions. Using the available growth parameters we can shift the diameter distribution from 1.27 nm to 1.57 nm and the semiconducting to metallic SWNT ratio from 50:50 to 85:15. We will discuss the influence of the different growth parameters and possible routes towards further improvements toward smaller diameters and fewer metallic SWNT.

THU 24

First-principles study of the stability and chemical reactivity of the graphene/SiC(0001) interface

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The interface between epitaxial graphene and SiC(0001) consists of a thin car-

bon "buffer" layer having the same topology of graphene, but with some C atoms forming covalent bonds to the Si atoms of the SiC surface. We use density functional theory and a set of model interfaces presenting very low graphene strains to study the energetic stability and chemical reactivity of the buffer layer. We find that the stability is proportional to the degree of structural corrugation, which is an indicator of the partial sp_2 to sp_3 rehybridization (pyramidalization) of the C atoms in the buffer layer. The relative stability of these model interfaces can in fact be explained through a local bond picture linking the local reactivity of the buffer layer to the pyramidalization angle of the Si-bonded C atoms. The remaining C atoms show a chemical reactivity significantly larger than in free-standing graphene, resulting in higher H-adsorption energies and lower barriers for H₂ splitting. We evaluate these quantities using a realistic model of the buffer layer having a low graphene strain and a graphene/SiC rotation angle close to the experimentally observed value of 30°.

THU 25

Growth of carbon nanotubes on carbon fibers

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Growing carbon nanotubes (CNTs) directly on carbon fibers is an interesting approach in order to integrate CNTs as nano-additives into carbon fiber-reinforced polymer composites. However, while growing CNTs in a catalytic CVD process carbon fiber surface gets damaged leading to degradation of its initial tensile strength. The origin of this damage is related to the high growth temperature used during the catalytic CVD process as well as the chemical interaction between the metal catalyst and the carbon fiber at the presence of highly reactive gases. In the present work, we studied systematically the growth of CNTs on PAN-based carbon fibers by varying the growth conditions. Traditional catalytic CVD process based on thermal decomposition of hydrocarbon as well as the recently reported equimolar C₂H₂-CO₂ reaction have been applied. The latter allows highly efficient CNT growth at much lower temperatures, which is favorable for the CNTs growth on carbon fibers. The mechanical properties of the carbon fibers have been monitored by single-fiber tests. CNT grafted carbon fibers are also impregnated with polymer and mechanically tested.

THU 26**Smart Compound Materials with Light-Controlled Properties**Antonio Setaro¹, Pascal Bluemmel¹, Stefanie Kreft¹, Stephanie Reich¹¹Physics Department, Freie Universität Berlin, Berlin

Here we show the results of our investigations on functionalization schemes, which confer additional element of control over the SWCNTs' properties, e.g., by decorating them with stimuli-responsive moieties. We focus on switches triggered by the light, which serves as one of the most advantageous external stimuli, due to its high spatiotemporal resolution and its non-invasive nature. We will highlight the relevance of the rational design of the morphology of the switch and how does it affect the properties of the complexes they form with carbon nanotubes. The effect of the tube-switch separation, their relative orientation and the structure of the moieties do impact the switching ability as well as the optical properties of the tubes themselves.

THU 27**Graphene replicating liquid molecules**N. Severin¹, P. Lange¹, V. Scenev¹, I.M. Sokolov¹, J. P. Rabe¹¹Institut für Physik, Physik von Makromolekülen, Humboldt-Universität zu Berlin, Berlin

Graphene can be regarded as the thinnest membrane known, highly flexible to follow the topography of a substrate with the precision down to single molecules, and impermeable to small molecules. We followed in-situ the wetting dynamics of monomolecular water films in a slit pore between mica and graphene with nanometer-scale lateral resolution by imaging the graphene topography conforming to the film. Furthermore, we demonstrate that the dynamics within a mixed monomolecular water-ethanol film confined between graphene and mica can be similarly followed. Water and ethanol, highly miscible in three dimensions are shown to nanophase separate within the monolayer. The growth dynamics of the domains allows to determine a lower bound for the two-dimensional diffusion constant of ethanol in water of $D \geq 2 \times 10^{-14} \text{ m}^2\text{s}^{-1}$. The lateral size of water and ethanol molecular domains becomes larger with the graphene thickness, which we attribute to the graphene bending energy. We account for stabilization of the heterogeneity by the counteraction of electrostatic repulsion of the charges doped in graphene by the molecules.

THU 28**Large control of surface carrier density by electrochemical gating with a novel polymer electrolyte solution**Kanudha Sharda¹, A. Sola¹, M. Tortello¹, D. Daghero¹, J.R. Nair¹, C. Gerbaldi¹, M. Bruna², R.S. Gonnelli¹

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By using a novel polymer electrolyte solution and a standard electrochemical-gating field-effect technique we recently succeeded in injecting surface charge densities up to more than 4×10^{15} charges/cm² in metallic thin films of Au, Ag and Cu. Relative variations of resistance up to 8%, 1.9% and 1.6% at room temperature in the three metals, respectively, and up to 10% at 4 K in Au films were observed. If the films are thick enough (> 25 nm), these results can be nicely explained within a free-electron model with parallel resistive channels. The injected surface charge was determined by a suitable modification of a classic method of electrochemistry called double-step chronocoulometry, but a validation by Hall-effect measurements was also carried out.

Preliminary experiments in multi-layer graphene devices (mainly from 3 to 5 layers) have been performed and surface charge densities exceeding 3×10^{14} charges/cm² can be inferred from the behavior of the Dirac curves. The large effects of this high carrier density on the resistivity of these devices as a function of temperature down to 2.7 K and on Kondo-like peaks appearing at $T < 30$ K will be discussed.

THU 29

High-yield preparation and resonance Raman studies of linear carbon chains inside double walled carbon nanotubes

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Linear carbon chains (LCCs), as one of the allotropes of carbon are increasingly getting attention due to their unique properties as a true 1D nanostructure. Encapsulating the LCCs into CNTs is an effective method to protect them from being damaged and decomposed. We have successfully synthesized and purified thin DWCNTs which are in part functionalized. We have then applied a heat treatment of the purified DWCNTs to grow LCCs inside the inner tubes under high vacuum conditions at high temperatures and different times. From Raman spectroscopy, we found that LCCs can be formed even at temperatures as low as 900°C. For the optimal growth conditions, which depend on doping, temperature and annealing time, the intensity of LC-band in the Raman response is as high as 150 % of the G-band, indicating a new record of the highest yield of LCCs insides DWCNTs prepared so far. The length dependence of the LCC's is revealed by a resonance Raman study of the fine structures of LC-band excited by different dye lasers. This gives a new insight into the growth mode of different functionalized 1D carbyne chains.

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THU 30

Fabrication of homogeneous thin films of single wall carbon nanotube towards even quality field effect transistors

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Due to the recent progress in the metal/semiconductor (m-/s-) separation of single wall carbon nanotubes (SWCNTs), thin film transistors (TFTs) using s-SWCNT solution have attracted a remarkable attention. However, the inhomogeneity of the thin film caused by coffee stain effect in the wet process induces uneven device characteristics for the TFTs on the same substrate. For example, a typical coefficient of variation (CV) of the on current is 130 % in the case of drop coating. To obtain homogeneous thin films, in this work, we focused on the dip coating method. Three different SWCNT concentrations, 0.1, 0.2, and 0.4 mg/ml, were prepared for four different sodium deoxycholate (DOC) concentrations, 0.1, 0.25, 0.5, and 1.0 wt. %. For the thin film formation, an aminopropyl triethoxysilane modified SiO₂/Si substrate was dipped in each solution for 24 h. All of them showed homogenous s-SWCNT networks, but detailed morphology and TFT performances were different. In the optimized condition, all 16 TFTs fabricated on the same substrate exhibited quite similar transfer characteristics and the CV was 20 % which is much improved from that of drop coating.

THU 31

Bilateral formation of mirrored carbon spirals

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Our research focuses on understanding and control of nanoscale shape formation via studies of novel synthesis routes to carbon nanostructures [1]. The process performed within a sealed vessel at elevated temperatures allows pressured ferrocene to react to form novel symmetric carbon nanostructures. The growth symmetry is determined at a given temperature and effective vapour pressure. In particular, at pressures that exceed 5 MPa bilateral carbon spirals are produced. A parametric plot of the surface geometry displays the fractal growth of the conical helix

made with the logarithmic spiral. Microscopy studies in a cross section along the spirals show graphitic flakes arranged in a herringbone structure, normal to which the defects propagate. Local-wave-pattern analysis reveals nano defect patterns of two-fold symmetry around the core. The data suggest that the bilateral growth originates from a globular cementite crystal with molten surfaces and the nano-defects shape emerging hexagonal carbon into a fractal structure.

[1] H. Shiozawa, et al. Nano Lett. 11, 160 (2011), H. Shiozawa, et al. Adv. Mater. 22, 3685 (2010), H. Shiozawa, et al. Phys. Rev. Lett. 102, 046804 (2009).

THU 32

Ultra low energy Raman Spectroscopy in MoS₂

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Molybdenum disulfide is a promising material for making two-dimensional crystals and flexible electronic and optoelectronic devices at the nanoscale. A fundamental requirement for such use is efficient thermal transport. Anharmonic phonon-phonon scattering is the dominant intrinsic limitation to thermal transport in insulators. Using appropriate samples, ultra-low energy Raman spectroscopy and first principles calculations, we provide a full experimental and theoretical description of compression and shear modes of few-layer MoS₂ and demonstrate that some of these are strongly anharmonic which is probably a general feature of nanolayered materials with weak interlayer coupling.

THU 33

On the spin-relaxation properties of graphene

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One of the prospective applications of graphene is in spintronics due to the expected long spin-relaxation time, τ_s . Yet, the experimental situation conflicts with the theoretical predictions as the measured τ_s is orders of magnitude shorter than expected. In addition, the appropriate theoretical model of spin-relaxation is unsettled. We outline the most general theoretical model of spin-relaxation in graphene and also study τ_s using ESR spectroscopy in alkali (Li, K, and Rb) doped graphite, which is thought to be a model system of strongly biased graphene. Results

of angular dependent ESR line-width and g -factor measurements on stage-I and II graphite intercalated compounds are presented and discussed in relation to the spin-relaxation in biased graphene.

Work supported by the ERC Starting Grant ERC-259374-Sylo, by the Swiss NSF, and by the Hungarian State Grants (OTKA) K72613, CNK80991, K73361, K101244, and K68807.

THU 34

Electrical transport properties of graphite oxide films reduced through various routes

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The main task of researchers nowadays is developing a preparation route for a large scale production of graphene enabling industrial applications. One of the directions is exfoliation of graphitic layers from graphite crystals by means of chemical oxidation. As a consequence of oxidation the material is electrically insulating. The conductivity is partially recovered by reducing the functional groups. A suspension of graphite oxide (GO) in water was either sprayed on quartz-glass substrates making optically transparent layers or free-standing papers were fabricated. Reduction of these GO samples was realized through chemical reactions or thermal annealing at various temperatures or through ion irradiation. The efficiency of different routes of reduction is compared through characterization by chemical analysis and IR and Raman spectroscopy suggesting that the thermal reduction recovers electrical conductivity to highest extent. The temperature dependencies of electrical conductivity were also measured down to low temperatures and charge transport mechanisms are discussed with respect to particular reduction routes.

THU 35

Electronic Properties of atomically precise Graphene Nanoribbons

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Its remarkable properties make graphene attractive for use in electronic devices. However, graphene is semimetallic and thus not directly suitable for most electronic or optoelectronic switching devices, which require a semiconductor with a specific, finite band gap. In armchair graphene nanoribbons (AGNRs), room tem-

perature application relevant band gaps open at widths smaller than 3 nm. We present recent results on the electronic properties of bottom-up fabricated 7-AGNRs. Scanning tunneling spectroscopy (STS) reveals a band gap of 2.3 eV for the ribbons adsorbed on Au(111) as well as a sensitive length dependence. Angle-resolved photoelectron spectroscopy (ARPES) and Fourier-transformed STS were used to determine the effective mass and energy-dependent charge carrier velocities for the frontier bands of 7-AGNRs. These results are compared to DFT simulations. Additionally, a combined computational and experimental investigation of the chemical structure of the GNR termini reveals important details about the length-critical polymerization step of the bottom-up fabrication process.

THU 36

Single walled carbon nanotubes at ultra-high pressure/stress.

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We report on the first study of single walled nanotubes (SWNTs) synthesized by HiPCO method at pressure/stress up to 70 GPa aimed at probing structural stability of small diameter SWCNTs and synthesis of new nanostructured carbon phases. Firstly, the material had been exposed to 25 GPa. Raman spectra of the recovered material exhibited extremely high defect density and evident recovery of the radial breathing mode (RBM) band with some intensity profile alteration. Secondly, the material was pressurized subsequently to about 70 GPa followed by a relatively fast pressure release. Raman characterization provides indications of materials' transformation to a new structural state as the result of the second pressure cycle. We discuss the structural evolution of the system enroute the final structure which is presumably comprised of deformed graphene nanoribbons and/or CNT polymers in addition to the smallest diameter SWCNTs survived ultra-high pressure/stress.

THU 37

Reversible NO_x chemisorption stimulated by synchrotron beam irradiation on ultra-pure SWCNTs surface

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Taking advantage of the great improvements in the purification and sorting of nanotubes of the last years, we have made use of ultra clean nanotube material and additional metallicity sorted samples in order to find the basic phenomena respon-

sible for the changes of the electronic properties of SWCNTs when used as sensors. Employing XPS and XAS we have analyzed the photo-induced effects on ultra-pure metallicity sorted SWCNTs upon a long exposure to synchrotron radiation.

After NO₂ dosing, fast photoemission measurements were performed in order to investigate time-dependent irradiation effects. We observed that synchrotron radiation induces the desorption of the physisorbed molecules on the SWCNTs, concomitant the remaining nitrogen compounds are weakly chemisorbed on defective sites of the tubes. No surface damage is detected and therefore, the process is fully reversible. The analysis of the radiation induced reactions plays a key role in the understanding the complex mechanism of NO₂ adsorption and desorption on the SWCNTs' sidewalls, which is the key to their future application in environmental sensing.

Work supported by FWF.

THU 38

Field Effect Transistors based on individual and localized Single Walled Carbon Nanotubes

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Electronic devices based on individual single walled carbon nanotubes remain at the prototype level. This is the consequence of the limited reliability of the growth processes (low yield and impurities) and the absence of control of the electrical properties of the SWNT obtained. The lack of specificity of the SWNT positioning is also a major limitation. To improve the location and narrow the electronic property distribution of the SWNTs, best strategy relies on the precise deposition of one single catalyst particle with controlled size. We have developed a method based on e-beam lithography. A negative tone resist is doped with Co. After patterning the resist, the metal is segregated at 800°C and the amorphous carbon generated by the decomposition of the resist is etched. At the end of the process, individual particles with a diameter of $1.5 \pm 0.2\text{nm}$ are localized within an area of 80nm^2 , corresponding to the lithographed surface. High-quality SWCNTs are grown with a diameter of $1.4 \pm 0.2\text{nm}$ from ethanol. The study performed for the catalyst deposition and SWNT growth process will be described. The performances of the fabricated field effect transistors will be presented.

THU 39

Graphene quantum dots on hexagonal boron nitride

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Graphene exhibits unique electronic and mechanical properties making it a promising material for future quantum-electronic applications. However, state of the art graphene quantum devices, such as graphene quantum dots fabricated on SiO₂ substrates suffer from their rather poor quality due to a large disorder potential. Recently, it has been shown that placing graphene on hexagonal boron nitride (hBN) substantially reduces the disorder potential due to its atomically-flat graphene-like hexagonal structure. Here, we present the fabrication and characterization of single-layer graphene quantum dots (QDs) on hBN substrates. In particular we show low-temperature transport measurements of quantum dots with various diameters. A systematic comparison of QDs on hBN with QDs on SiO₂ shows a significant difference in the Coulomb peak spacing statistics. This finding unfolds the role of the edge disorder in case of etched graphene QDs and points the way towards novel fabrication techniques making use of smooth confinement.

THU 40

Atomistic description of electron beam damage in nitrogen-doped graphene and carbon nanotubes

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By combining *ab initio* simulations with state-of-the-art electron microscopy and electron energy loss spectroscopy (EELS) [1], we study the mechanism of electron beam damage in nitrogen-doped graphene [2] and carbon nanotubes [3]. The incorporation of nitrogen atoms results in noticeable knock-on damage already at 80 kV. In the case of substitutional N, damage is initiated by the displacement of carbon atoms neighboring the dopants, leading to the conversion of substitutional dopant sites into pyridinic ones.

Although such events are relatively rare at 80 kV, they become significant at higher voltages typically used in EELS studies. Correspondingly, we measured an energy

loss spectrum time series at 100 kV that provides direct evidence for such conversions in N-SWCNTs, in good agreement with our theoretical prediction. Our improved understanding of the irradiation stability of these materials shows that structural changes cannot be neglected in their characterization using high-energy electrons.

- [1] T. Susi et al., ACS Nano 6 (2012) 8837
- [2] J.C. Meyer et al., Nature Mater. 10 (2011) 209
- [3] T. Susi et al., Chem Mater. 23 (2012) 8837

THU 41

Photocurrent generated by photosynthetic reaction centers bound to carbon nanotube/ITO layer structure

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Intensive studies have shown recently that photosynthetic proteins purified from plants (PS-I and PS-II) and from purple bacteria bind successfully to nanostructures while their functional activity is largely retained. Current researches are focusing on finding the best bio-nanocomposite sample preparations and experimental conditions for efficient energy conversion and for the stability of the systems. In our studies reaction center proteins (RC) purified from purple bacterium *Rhodospirillum rubrum* were bound successfully to amine- and carboxy-functionalized multi-walled carbon nanotubes (MWNTs) immobilized onto the surface of ITO by using specific silane. Structural (SEM, AFM) and functional (flash induced absorption change and conductivity) techniques have shown that RCs were bound effectively to the functionalized carbon nanotubes (CNT). An electrochemical cell with three electrodes was designed especially for measuring the photocurrent generated by this composite material. Several hundreds of nA photocurrent was measured with fully active RCs while the current was missing when the RC turnover was disrupted by depleting the electron acceptor quinones.

THU 42**Hummers and Brodie Graphite oxides: hydration, solvation and exfoliation.**Shujie You¹, Tamas Szabo², Serhiy Luzan¹, Alexandr V. Talyzin¹¹Department of Physics, Umea University, Umea²Department of Physical Chemistry and Materials Science, University of Szeged, Hungary

Graphite oxides (GO) synthesized by Brodie's and Hummers' methods are significantly different with respect to hydration, solvation and exfoliation properties. Hummers GO is stronger intercalated by liquid water and alcohols, exhibiting osmotic type of swelling. In contrast, Brodie GO shows crystalline swelling in alcohol solvents with step-like insertion of methanol or ethanol monolayers. Temperature dependent structural study of Hummers graphite oxide (H-GO) swelling in excess of liquid alcohols performed using synchrotron X-ray diffraction revealed effect of strong "negative thermal expansion". This phenomenon is strongly different compared solvation of Brodie graphite oxide (B-GO) which was found earlier to exhibit insertion of additional solvent monolayer at low temperatures as single step. However, the easier hydration and dispersion in water observed for Hummers GO do not correlate with better exfoliation properties. Higher surface area graphene powder was obtained by exfoliation of Brodie GO, while the temperature of its exfoliation is about 75°C higher than that for the studied sample of Hummers GO.

THU 43**High-throughput metal/semiconductor separation of single-wall carbon nanotubes; improvement in preparation of SWCNTs dispersion**Takeshi Tanaka^{1,2}, Satoshi Asano², Mariko Kubota², Kaori Makino², Shunjiro Fujii^{1,2}, Hiromichi Kataura^{1,2}¹Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Japan²Technology Research Association for Single Wall Carbon Nanotubes (TASC), Japan

For the electrical application of single-wall carbon nanotubes (SWCNTs), separation between metallic (M) and semiconducting (S) SWCNTs is required. We developed M/S separation method using agarose gel [1] and presented low-cost and high-throughput separation using pilot-scale chromatography at IWEPNM2012; however, the step of preparation for SWCNT dispersion restricted the throughput of M/S separation. Here we report the improvement of the preparation of SWCNT dispersion. The processes of dispersion by sonication and purification by ultracentrifugation restricted the throughput, so we changed the dispersion method from sonication to Nanomizer treatment and used continuous ultracentrifugation for the purification. We also scaled up the column size to 8.5 liter and finally achieved 2 g/day production of separated SWCNTs through the whole process including

dispersion, purification and separation. The result of thin film transistor using separated S-SWCNTs will be presented.

[1] Tanaka et al., Phys. Status Solidi RRL 5 (2011) 301.

THU 44

Strain-engineering sub-nanometer wavelength periodic ripples in graphene beyond the limits of continuum mechanics

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Atomic resolution STM investigations of graphene nanomembranes subjected to biaxial compressive strain reveal the smallest ripples ($\lambda = 0.7$ nm) ever developed in a membrane [1]. According to continuum mechanics, the thickness of a membrane that can support such structural ripples should be much smaller than the diameter of an atom; therefore, it should not exist. Microscopic modeling comprising the quantum mechanical nature of atomic bonds allows us to interpret the experimentally observed nanorippling mode. The reason for this is that in contrast to classical membranes the in- and out-of-plane deformations of a graphene sheet can be completely decoupled. This enables graphene to be at the same time the stiffest membrane for in-plane and the softest membrane for out-of-plane deformations. Spatially resolved tunneling spectroscopy measurements prove that structural graphene nanoripples induce a periodic modulation in the local charge density distribution on the same length-scale. This provides a novel and simple engineering method to control the atomic structure and electronic properties of graphene with an unmatched precision.

[1] L. Tapasztó et al. Nature Physics. 8, 739 (2012)

THU 45

Direct-write atomic layer deposition for the fabrication of carbon nanotube field-effect transistors

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Carbon nanotube field-effect transistors (CNTFETs) are conventionally fabricated "top-down" by electron beam lithography followed by evaporation of contacts.

Compatibility issues due to the use of resist films and lift-off chemicals motivate the development of a direct "bottom-up" fabrication method. Furthermore, an adhesion layer to prevent delamination of the contacts during lift-off may no longer be required in a bottom-up process.

We fabricated CNTFETs by direct-write atomic layer deposition (ALD) of Pt and Pd. In the direct-write ALD technique, the patterning capability of electron beam induced deposition (EBID) is combined with the material quality of ALD. First, thin seed layers (< 0.5 nm) are deposited by EBID in the desired pattern, after which a selective ALD process builds the seed layers into high-quality Pt contacts. This combined approach yields virtually 100% pure Pt (resistivity of $12 \mu\Omega\text{cm}$) with a resolution of 10 nm [1].

The fabricated CNTFETs display excellent p-type transfer characteristics, with a subthreshold swing down to 105 mV/dec and an on/off current ratio of approximately 10^6 .

[1] A.J.M. Mackus et al., *Nanoscale* 4, 4477 (2012)

THU 46

Carbon nanomembrane/graphene hybrids for electronic device applications

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Chemical functionalization of single-layer graphene (SLG) is of key importance for applications in functional electronic devices such as, e.g., field effect transistor (FET) based nanosensors. However, the electronic quality of graphene is typically destroyed after the functionalization, which significantly restricts the applications. Here, we present a route to non-destructive chemical functionalization of graphene via engineering of novel carbon nanomembrane (CNM)/SLG hybrids. We employ SLG, grown by methane CVD on Cu foils, and amino-terminated 1 nm thick CNMs, generated by electron-beam-induced crosslinking of aromatic self-assembled monolayers, to engineer hybrid CNM/SLG FETs on oxidized silicon wafers. Structural, chemical and electronic properties of the CNM/SLG hybrids are characterized by Raman spectroscopy, X-ray photoelectron spectroscopy and electrical transport measurements. We unambiguously show that the intrinsically high electronic quality of pristine SLG is preserved in the amino-functionalized hybrids opening broad avenues for their use as electrical transducers in graphene-based FETs.

THU 47

Production of Endohedral Fullerenes

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Endohedral fullerenes are fascinating compounds where an atom or a small molecule is trapped inside the fullerene cage. Due to their unusual properties they have several interesting applications (e.g., $\text{Gd@C}_{82}(\text{OH})_n$ can be used as a MRI contrast agent, $^{140}\text{La@C}_{82}$ as a radiotracer, N@C_{60} as a q -bit in a quantum computer).

There are several ways how to prepare them, but for endohedral metallofullerenes the most important method is the classical arc technique. The production yields, however, show a rather complicated pattern, some compounds can be easily prepared, for others only spectra could be recorded and some were never observed. In this contribution we show how these observations can be rationalized using *ab initio* calculations and statistical thermodynamics and the structural, electronic and thermodynamic properties of endohedral metallofullerenes can be successfully predicted.

THU 48

Design and investigation of properties of nanocrystalline diamond optical planar waveguides

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Synthetic polycrystalline diamond has remarkable properties comparable with natural diamond. Because of these properties it is a very promising material for many applications. In this paper we report about design, deposition and measurement of the properties of nanocrystalline diamond (NCD) optical planar waveguides (OPW). The design of the presented planar waveguides was realized on the bases of modified dispersion equation and was schemed for 632.8 nm, 964 nm, 1310 nm and 1550 nm wavelengths. The NCD OPW was deposited by MWPECVD and the structure of the deposited film was studied by SEM and Raman spectroscopy. Waveguiding properties were examined by prism coupling technique and it was found that the sample guided one fundamental mode. Values of the refractive indices of prepared NCD film measured at various wavelengths were almost the same as those of natural diamond. Moreover, the decrease of diamond surface roughness by a formation of composite structure will be pointed out.

This work was supported by the grants P108/11/0794, P108/12/0910, Purkyne Fellowship, FR-TI3/797, CTU no. SGS11/156/OHK3/3T/13, LH12186 and LH12236. This work occurred in frame of the LNSM infrastructure.

THU 49**Relation of strain and magnetic response of graphene@SPION nanostructures**

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We address correlation of the strain distribution in graphene (GN) to the magnetic response of ensemble of superparamagnetic (SPM) iron oxide nanoparticles (SPIONs) in a system composed of GN and a mono-layer of monodisperse SPIONs. The three types of nanostructures were synthesized on the Si/SiO₂ substrate: Si/SiO₂/SPIONs/GN(top), Si/SiO₂/GN/SPIONs and Si/SiO₂/GN/SPIONs/GN. The samples were investigated by AFM, SEM, EXAFS, Raman spectroscopy and SQUID magnetometry. The strain distribution, obtained by the analysis of the Raman signal maps was correlated to the SPION magnetic properties by means of the relaxation time, coercivity and blocking temperature. The sensitivity of the SPION magnetic response to the external magnetic field and inter-particle interactions, determined by their separation distance, opens possibility to detect intrinsic magnetic order and strain-induced pseudo-field in the GN.

THU 50**Effect of bundled content and defects on the optical limiting in aqueous suspensions of SWCNTs**

Anastasia Venediktova¹, A. Yu. Vlasov¹, I. M. Kislyakov², D.A. Videnichev², E. D. Obratsova³, E. A. Katz⁴, A.S. Pozharov³

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To date, a feasible scenario to devise an optical power limiting (OPL) material effectively protecting eyes and sensors against high-intensity laser irradiation is employing suspensions of single-wall carbon nanotubes (SWCNTs). The driving

mechanism behind the OPL in such systems is induced light scattering on the carbon plasma and solvent bubbles formed on the SWCNTs, both formations resulting from conversion of photo-excitation energy of nanoparticles into heat. Phenomena leading to this dissipation include direct energy scattering on phonons and preliminary scattering on the plasmon of SWCNTs. We report on a trial to determine relative contributions of the said phenomena into the gross manifestation of the OPL in aqueous suspensions of SWCNTs. It consisted in 1) varying the wavelength of the plasmon resonance through the use of various surfactant micro-environments around the SWCNTs and 2) checking impacts of the bundled content in the populace of nanoparticles and of the species containing defects. Characterization of suspensions was implemented via spectroscopy methods, cryo-TEM and HR TEM. The authors are grateful to RFBR 11-03-01106-a and RAS research projects.

THU 51

Separation and sorting of empty and water-filled carbon nanotubes using density gradient ultracentrifugation: in situ wavelength-dependent fluorescence-excitation and Raman spectroscopy

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Since the pioneering work of Arnold et al.[1], density gradient ultracentrifugation (DGU) has emerged as the most widely used and versatile technique for the structure sorting of carbon nanotubes (NTs), even though the mechanisms are not yet fully understood. For example, counter-intuitively it is found, in nearly all DGU studies, that increasing diameters possess increasing densities. This is due to the presence of water-filled NTs as we have shown in recent studies. The intact (and therefore empty) NTs can be isolated from the filled ones and follow the intuitive sorting order, moreover allowing an enhanced structure sorting by DGU.[2] Also the specific surfactant choice was found to have a significant effect on the diameter sorting.[2] We present 2D wavelength-dependent fluorescence-excitation and Raman spectra measured directly after DGU, in situ, as a function of height, in the centrifuge tube. As such, very detailed information on the chirality-density relation is obtained, allowing for optimizing the DGU sorting process.

[1] M.S. Arnold et al. Nature Nano 1, 60 (2006)

[2] S. Cambre et al. Angew Chem Int Ed 50, 2764 (2011)

THU 52

Direct Nano-writing of Biomimetic Lipid Membranes on Graphene

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²The University of Manchester

³Westfälische Wilhelms-Universität Münster

The integration and patterning of biological and biomimetic membranes on graphene has significant implications in biosensing, drug delivery and toxicology. Of these, lipid bilayers, which mimic cell membranes, are a model system for study. We demonstrate the assembly of lipid membranes of different compositions on graphene and graphene oxide using dip-pen nanolithography, a direct-write technique with sub-100 nm resolution. We show that lipid membranes assemble readily and uniformly on graphene, better than on silicon dioxide which represents the standard substrate for such membranes today. The optimisation of dip-pen writing conditions will be discussed. We also show that there is charge transfer interaction between the lipid membrane and graphene, through fluorescence quenching, Raman spectroscopy and electronic transport measurements. Finally, we are able to demonstrate the functionality of the membranes through protein binding assays.

THU 53

Hybrid Nanocomposite Material Consisting of Magnetic Nanoparticles in Nanocrystalline Diamond Matrix: Growth and Study of Properties

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We address a novel concept of hybrid nanocomposites constituted of nanocrystalline diamond (NCD) thin films incorporating magnetic nanoparticles (MNPs). NCD nanostructures attract a lot of interest due to their unique electrical, optical and mechanical properties, which make them widely suitable for applications in MEMS, diodes, biosensors, thermoelectric constituents, etc. Also the MNPs have been intensively investigated due to their applications in biomedicine, magnetic storage and separation. The NCD@MNPs composites combine functional properties of both these unique class of materials. NCD deposition technique using microwave plasma CVD, working at low pressure has been employed in the fabrication. Initially, the silicon substrates have been seeded by spin-coating using diamond and cobalt ferrite nanoparticles. For the NCD depositions a mixture H₂/CH₄/CO₂ at low temperatures was used. Morphology of the grown films was studied by AFM and SEM and the phase composition and the nanoparticles sizes were determined by the glancing-angle XRD. The nature of the carbon phase has been examined by

Raman spectroscopy. Magnetic response of the samples was studied using a SQUID magnetometer.

THU 54

Determination of Dopamine on a Nanostructured Boron-Doped Diamond Electrode

Marian Vojs^{1,2}, Miroslav Behul¹, Pavol Michniak¹, Vlastimil Rehacek¹, Robert Redhammer¹, Tibor Izak², Alexander Kromka²

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Boron-doped diamond electrodes (BDDE) are promising material for various applications in electrochemistry. In the present article, technological steps as growth of intrinsic nanodiamond (i-NCD)/BDD double layer, electrode fabrication and electrochemical response to dopamine (DA) are discussed. DA concentration was determined using the cyclic voltammetry and square-wave (SW) stripping voltammetry methods. The results show that the nano-structured electrodes exhibit a more ten times higher limit of detection than non-structured BDDE and strongly dependence of morphology i-NCD. Electrochemical oxidation of DA was carried out at BDDE, with which very stable and reproducible was observed within 4 h. The analytical detection limit nanostructured BDDE of anodic dopamine maximum (3xstandard deviation/slope) was determined to be SW: 1.7×10^{-6} M, adj. R square=0.998, and the maximum was shifted to 0.55 V vs. Ag/AgCl at the optimum conditions.

This work was financially supported by grants of SRDA No. APVV-0548-07, LPP-0094-09 and Slovak National Grant Agency No. 1/1102/11 and 1/1103/11 and GACR No. P108/12/G108.

THU 55

Theoretical investigation of carbon nanotube transistors used as strain sensors

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Acceleration sensors are first upcoming applications of carbon nanotubes (CNTs), where they are ideal candidates due to their mechanical strength and their outstanding piezoresistive response. Such acceleration sensors mostly need to be adjusted in

practice: Firstly, the intrinsic resistance of a semiconducting CNT might be too high and secondly, the Fermi level is shifted due to adsorbed molecules in experiment.

We propose different ways of tuning the characteristics of the CNTs while preserving the piezoresistive effect: One is the sub-monolayer decoration of CNTs with metal atoms which reduces the band gap in most cases and the other one is to adjust the drain-source voltage as well as the gate voltage. The gate voltage is assumed to be constant throughout the device.

The latter approach can be condensed in a fully parametric, analytical description, while for the first one, density functional calculations are still necessary. In both cases, the sensitivity of the sensor mostly remains unchanged while the sensing regime can be adjusted. Calculation results of ab-initio and analytical approaches are shown and compared systematically.

THU 56

Reliable manufacture of CVD graphene into electronic devices

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Graphene with its formidable electronic properties has a huge amount of applications. CVD of graphene is commonly used for electronic devices as it provides excellent process control and the produced large area films can be easily transferred and incorporated into devices using existing microprocessing technology. Most commonly graphene CVD takes place at very high temperatures ($>1000^{\circ}\text{C}$) on copper catalyst. However copper has a significant vapour pressure and contaminates the entire furnace and re-deposits on the graphene itself. Lowering the temperature of the process is imperative for better quality, reproducibility and cost. Using ethene it was possible to lower the process temperature to below 850°C . Using Raman spectroscopy, SEM and electrical measurements the graphene was characterised. It was found to be monolayered and of similar quality to most methane-based growths at $>1000^{\circ}\text{C}$. Also recently significant advances have been made in the field of ALD of Al_2O_3 on graphene. We explore some of the routes this technology has opened, including passivation and simple device fabrication.

THU 57

Electronic transport properties of metallic carbon nanotubes with metal contacts

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The electronic coupling between carbon nanotubes (CNTs) and metal electrodes

is of great importance for fundamental electron transport experiments as well as various applications, like in microelectronics.

In this theoretical work we compare quantum transport properties of metal–CNT–metal systems. Calculations are based on density functional theory and extended Hückel theory (comparing both) and the non-equilibrium Green’s function formalism in the limit of coherent transport.

The studied systems consist of metallic (6, 0) CNTs of different length, attached to Al, Cu, Pd, Pt, Ag, Au electrodes in an end-to-end configuration. The zero bias conductance shows length-dependent oscillations. Comparing the different metals, a ranking regarding their contact quality is found: $\text{Ag} \leq \text{Au} < \text{Cu} < \text{Pt} \leq \text{Pd} < \text{Al}$. This is discussed in terms of the metal’s work functions, contact distances and binding energies, where similar trends are observed.

For a chosen CNT length and Pd contacts, current voltage characteristics are in reasonable agreement with experimental work of Javey et al. [PNAS 101, 13408 (2004)].

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|---------------|--|
| 08:30 – 09:00 | X. Feng, Mainz <i>Atomically Precise Synthesis of Graphenes: A Bottom-up Approach</i> |
| 09:00 – 09:30 | M. Mayor, Basel <i>Single Molecule Junctions - from Structure Property Correlations and CNT Electrodes</i> |
| 09:30 – 10:00 | K. Franke, Berlin <i>Magnetic excitations of molecular spins on a superconductor</i> |
| 10:00 – 10:30 | Coffee break |
| 10:30 – 11:00 | R. R. Tykwinski, Erlangen <i>Assembly and properties of one-dimensional carbon chains</i> |
| 11:00 – 11:30 | E. Obraztsova, Moscow <i>Single-wall carbon nanotubes and graphene for lasers: from visible to mid-IR spectral range</i> |
| 11:30 – 12:00 | A. Penicaud, Bordeaux <i>Chemical exfoliation: reductive dissolution of graphene, nanotubes and other carbon nanoforms</i> |
| 12:00 – 17:00 | Mini-Workshops |
| 17:00 – 17:30 | L. Dunsch, Dresden <i>Clusterfullerenes: Exciting Nanostructures in Endohedral Electrochemistry and Magnetic States</i> |
| 17:30 – 18:00 | M. Orlita, Grenoble <i>Infrared magneto-spectroscopy of graphene-based systems</i> |
| 18:00 – 18:30 | H. Kataura, Tsukuba <i>Summary</i> |
| 18:30 – 20:00 | Break |
| 20:00 | Bauernbuffet – Farewell |

Friday, March 8th

Graphene/CNT chemistry, magnetic properties

08:30**Atomically Precise Synthesis of Graphenes: A Bottom-up Approach**Xinliang Feng¹¹Max Planck Institute for Polymer Research, Ackermannweg 10, Mainz

Graphene, a two-dimensional carbon allotrope, has demonstrated exceptional physical properties such as ultrahigh charge carrier mobility, quantum Hall effect, and good optical transparency, which make it a realistic candidate for a number of electronic applications. The future research and application of graphene calls for efficient synthesis at different length scales with high chemical definition.

Top-down production of graphene relies on peeling-off graphene layers from graphite in solution or on substrate. To open up the band gap of graphenes, a lateral confinement must be introduced, such as to cut graphene sheet into thin strips or unzipping carbon nanotubes into nanoribbons. In this presentation, a bottom-up synthetic route to nanographenes and graphene nanoribbons has been established, which provide an atomic precise synthesis of graphenes. This synthetic strategy is based upon the cyclodehydrogenation ("graphitization") of well-defined dendritic (3D) polyphenylene precursors. The advantage of this approach is obvious as the size, shape and edge control, structural perfection and processability (solution, melt, even gas phase) of graphene can be attained.

09:00**Single Molecule Junctions - from Structure Property Correlations and CNT Electrodes**Marcel Mayor¹¹Department of Chemistry, University of Basel, Basel

Molecules are the smallest objects still providing the structural diversity required to tune their properties in order to design their functions. Their minute sizes however make their integration and subsequent investigation challenging. In order to proof the single molecule nature of a junction series of molecules altering exclusively in a well controlled structural feature are of interest. With series of biphenylcyclophanes comprising different anchor groups their interring torsion angles were reflected in their transport features.

Also molecular junctions providing additional physical outputs complementing the current/voltage characteristics are of interest. Single walled carbon nanotubes (SWCNTs) are particular interesting electrode materials due to their reduced "quenching" characteristics compared to metals. A single molecule electroluminescence experiment became only possible using SWCNTs.

Recent attempts are geared towards selecting particular SWCNTs by tailor-made polymers with well defined dispersion properties.

09:30**Magnetic excitations of molecular spins on a superconductor**Katharina Franke¹¹Fachbereich Physik, Freie Universität Berlin, Berlin

Single magnetic molecules on a superconducting substrate present a model system to study the influence of a local magnetic moment on the superconducting state at the atomic scale. The magnetic moment of the adsorbate interacts with the Cooper pairs by exchange coupling and tends to break them apart. Signatures of this interaction are localized states in the superconducting gap, which can be probed by tunneling spectroscopy [1,2]. On the other hand, the quasi-free electrons in the substrate screen the localized spin via the Kondo effect. The delicate balance between these phenomena determines the resulting ground state of the system.

Using scanning tunneling spectroscopy, we show that the interaction of paramagnetic molecules with a superconducting lead surface is very sensitive to the details of the atomic scale surrounding [3]. Depending on the interaction strength the magnetic moment is able to interact with the Cooper pairs, or the superconducting state is unperturbed.

[1] A. Yazdani, et al. *Science* 275, 1767 (1997)

[2] S.-H. Ji, et al. *Phys. Rev. Lett.* 100, 226801 (2008)

[3] K. J. Franke, G. Schulze, J. I. Pascual, *Science* 332, 940 (2011)

10:30**Assembly and properties of one-dimensional carbon chains**Rik R. Tykwinski¹¹Department of Chemistry, Universität Erlangen-Nürnberg, Erlangen

The rigid and linear geometry of molecular chains composed sp-hybridized carbon provides an outstanding building block for the construction of conjugated scaffolds, and in particular, extended systems such as molecular wires. With this goal in mind, we have developed syntheses for a variety of molecules based on either a cumulene or acetylene structure and studied their molecular and materials properties. These studies include characterization of electronic structure by UV-Vis, Raman, and fluorescence spectroscopies, as well as analyses of geometry and structure by X-ray crystallography and computational methods. On the way to the practical integration of such molecules in functional devices, we are also exploring the use of mechanical bonds as a means to stabilize our molecular wires through the formation of rotaxanes. In this talk, some of our recent achievements toward forming sp-hybridized carbon materials, as well as the characterization of their electronic, optical, and structural properties, will be reviewed.

11:00**Single-wall carbon nanotubes and graphene for lasers: from visible to mid-IR spectral range**

Elena D. Obraztsova¹, Vladimir R. Sorochenko¹, Anton V. Tausenev¹, Petr A. Obraztsov¹, Maxim G. Rybin¹, Pavel S. Rusakov¹, Alexander I. Chernov¹, Pavel V. Fedotov¹

¹Natural Sciences Center, A.M. Prokhorov General Physics Institute, RAS, Moscow

Single-wall carbon nanotubes (SWNTs) and graphene serve as efficient, fast, working in a wide spectral range saturable absorbers for different types of lasers. Since first works [1] used the aqueous suspensions of SWNTs [1] a variety of different saturable absorbers based on nanotubes and graphene have been developed. One of the most popular type is a polymer film [2] with embedded SWNTs or graphene flakes. This work overviews the achievements in this field and discuss the new problems arising today. One of them is the extension of a working spectral range towards the mid-IR [3].

The work is supported by RFBR-11-02-92121 and RAS research projects.

1. N.N. Il'ichev, E.D. Obraztsova, et al. "1.54 mm nonlinear transmission of single-wall carbon nanotube suspension in D₂O; realization of self-mode-locking regime in Er³⁺-glass laser with nanotube-based Q-switcher", *Quantum Electronics* 34(2004)572
2. M. A. Solodyankin, E.D. Obraztsova, et al. "1.93 mm mode-locked thulium fiber laser with a carbon nanotube absorber", *Optics Letters* 33(2008)1336
3. V.R. Sorochenko, E.D. Obraztsova, et al., "Nonlinear transmission of CO₂-laser radiation by graphene", *Quantum Electronics* 42(2012)907.

11:30**Chemical exfoliation: reductive dissolution of graphene, nanotubes and other carbon nanoforms**Alain Penicaud¹¹Universite de Bordeaux - Centre de Recherche Paul Pascal, CNRS, Bordeaux

Despite the exceptional properties reported for individual nanotubes and graphene, dissolving graphite or nanotube soot in water or an organic solvent has proven a difficult task if not a challenge. Carbon nanotubes and graphite are insoluble in all media and require surfactants and/or sonication to obtain metastables suspensions. I will show that when electrically charged, e.g. as reduced carbon nanotube salts or graphite intercalation compounds, CNTs and graphene behave as polyelectrolytes and, as such, spontaneously dissolve in polar solvents without the need for any kind of additional energy, such as sonication or high shear mixing. These soluble species, either 1D- (nanotubes) or 2D- (graphene) form true polyelectrolyte solutions that behave as classical polyelectrolyte systems. Solutions of carbon nanotubes can be used to prepare conducting films, allowing for much improved conductivity/transparency ratio when compared to films prepared from suspensions with surfactants and sonication. Furthermore, these solutions can be used for controlled functionalization and nanoparticles decoration. The same technique can also be applied to other forms of carbon such as carbon nanohorns

17:00**Clusterfullerenes: Exciting Nanostructures in Endohedral Electrochemistry and Magnetic States**Lothar Dunsch¹¹Electrochemistry, IFW Dresden, Dresden

In endohedral metallofullerenes (EMF), the carbon cage plays a stabilizing role. In this way a variety of clusters can be used in nanostructures architecture starting with the most prominent type of nitride clusters. An overview is given on the variety of clusters available now in fullerenes and a special focus is laid on the mixed metal nitride clusters which make new properties of fullerenes available.

Thus by manipulation and tuning of the valence states of the endohedral cluster species an endohedral redox activity can be created for Sc, Ce, and Ti containing cluster fullerenes. The electron transfer makes the charge storage inside the fullerene cage possible and can switch the magnetic state of the cluster besides a variation of spin distributions.

By varying the composition of cluster fullerenes several magnetic metal ions can be used in a different arrangement to have different magnetic states inside the fullerene. The variation of the magnetic situation inside a fullerene is demonstrated for Gd-Sc clusterfullerenes. The encapsulation of Gd is of high interest for the application of endohedral fullerenes as contrast agents as shown for the so-called bio-shuttle application.

17:30**Infrared magneto-spectroscopy of graphene-based systems**Milan Orlita¹¹Laboratoire National des Champs Magnétiques Intenses, CNRS, Grenoble

The results of infrared magneto-spectroscopy measurements performed in LNCMI-Grenoble, CNRS, on various graphene-based materials will be reviewed. These systems involve multi- and mono-layers of epitaxial graphene, decoupled graphene flakes on the surface of graphite as well as bulk graphite. The magneto-optical methods, which mostly serve us as a tool of the Landau level spectroscopy, are employed to study the characteristic response due to massless or massive Dirac-type particles and, e.g., to distinguish materials with graphene layers exhibiting the rotational or Bernal stacking. The emphasis will be put on selected recent results, which are related to the following areas: the elastic and inelastic scattering of massless Dirac fermions in multilayer graphene, intrinsically induced confined magneto-plasmons in highly doped epitaxial graphene monolayer, the vicinity of the Lifshitz transition at the K point of bulk graphite, electron-phonon interaction in epitaxial graphene as well as the electron-electron sensitive Drude weight of massless Dirac particles.

18:00**IWEPNM 2013 Conference Summary**Hiromichi Kataura¹¹National Institute of Advanced Industrial Science and Technology (AIST), Japan

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