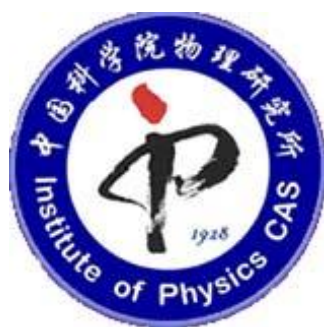


**2013 International Workshop on
Nanomaterials & Nanodevices**

July 2nd-8th, Beijing-Guilin, China



July 2nd-4th, 2013

Institute of Physics, Chinese Academy of Sciences, Beijing, China

July 5th-8th, 2013

Guilin University of Electronic Technology, Guilin, China

Institute of Physics, Chinese Academy of Sciences

Guilin University of Electronic Technology

中国科学院物理研究所纳米材料与器件国际研讨会
(北京部分)

International Workshop on Nanomaterials and Nanodevices
(Beijing Part, July 2nd-3rd, 2013)

Scientific Program

July 2nd, Tuesday, IOP Building D 212	
8: 30–8: 40	Opening Ceremony and Welcome Remarks Hongjun Gao (<i>Institute of Physics, CAS, China</i>)
8: 40–10: 35	Session 1 <i>Chair: Hrvoje Petek</i>
8: 40–9: 15	Peter Sutter (<i>Center for Functional Nanomaterials, USA</i>) “In-Situ Microscopy of 2D Materials: Growth, Processing, Properties”
9: 15–9: 50	Matthias Schreck (<i>Universität Augsburg, Germany</i>) “Wafer-Size Single-Crystal Metal Films on Silicon: a Powerful Substrate Structure for the Preparation of sp ² - and sp ³ -bonded Carbon Materials”
9: 50–10: 25	Thomas Greber (<i>University of Zurich, Switzerland</i>) “Sp ² Hybridized Single Layers: From Templates to Nanotents”
10: 25–10: 35	Coffee Break

10: 35–11: 45	Session 2 <i>Chair: Peter Sutter</i>
10: 35–11: 10	Hrvoje Petek (<i>University of Pittsburgh, USA</i>) “Transient Excitons at Metal Surfaces”
11: 10–11: 45	Jian Shen (<i>Fudan University, China</i>) “Electronic Nanofabrication of Complex Oxides”
11: 45	Lunch (IOP Restaurant)

Session 3	
<i>Chair: Wolf-Dieter Schneider</i>	
13: 30–15: 25	
13: 30–14: 05	Christian Teichert (<i>Institute of Physics, Montanuniversitaet Leoben, Austria</i>) “Diffusion Mechanisms in the Growth of Organic Semiconductor Nanostructures”
14: 05–14: 40	Karl-Heinz Ernst (<i>Empa, Switzerland</i>) “Shaking Hands in Flatland: Molecular Recognition among Chiral Molecules on Surfaces ”
14: 40–15: 15	Xincheng Xie (<i>Peking University, China</i>) “Dephasing Effect on the Helical Edge Excitations in Topological Insulators”
15: 15–15: 25	Coffee Break

Session 4	
<i>Chair: Christian Teichert</i>	
15: 25–17: 45	
15: 25–16: 00	Wolf-Dieter Schneider (<i>Institute of Condensed Matter Physics, Switzerland</i>) “Transport Properties and Electronic Structure of Individual Metallic Quantum Dots on Dielectric Supports: A Local View”
16: 00–16: 35	Min Ouyang (<i>University of Maryland</i>) “All Optical Spin Manipulation in Colloidal Nanostructures ”
16: 35–17: 10	Jiandi Zhang (<i>Louisiana State University, USA</i>) “Toward the Ultimate Critical Thickness of ‘Dead’ Oxide Layer”
17: 10–17: 45	Zheng Hu (<i>Nanjing University, China</i>) “Advanced Carbon-Based Nanotubes/Nanocages for Energy Conversion and Storage: Synthesis, Performance and Mechanism”

July 3rd, Wednesday, IOP Building D 212	
8: 30–10: 35	Session 5 <i>Chair: Shengbai Zhang</i>
8: 30–9: 05	Hans-Joachim Freund (<i>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany</i>) “Model Studies on Heterogeneous Catalysts at the Atomic Scale: From Supported Metal Particles to Two-dimensional Zeolites”
9: 05–9: 40	W. A. Hofer (<i>The University of Liverpool, UK</i>) “Efficient 3D-WKB STM Simulation Model ”
9: 40–10: 15	Chonglin Chen (<i>University of Texas at San Antonio, USA</i>) “Superfast Chemical Exchange Dynamics with Layer-by-Layer Exchange Diffusion of Oxygen and Hydrogen in Epitaxial Thin Films of Single-Crystalline Cobalt Double-Perovskites ”
10: 15–10: 35	Photo and Coffee Break

10: 35–12: 00	Session 6 <i>Chair: Xincheng Xie</i>
10: 35–11: 10	Shengbai Zhang (<i>Rensselaer Polytechnic Institute, USA</i>) “Carbon Kagome Lattice: a First-principles Prediction”
11: 10–11: 35	Yi Shi (<i>Nanjing University, China</i>) “Optoelectronic Devices based on Semiconductor Nanowires with Lateral Electrodes”
11: 35–12: 00	Xiaohui Qiu (<i>National Center for Nanoscience and Technology, China</i>) “Unraveling the Intra- and Inter-molecular Bonding Structures Using Atomic Force Microscopy”
12: 00	Lunch (IOP Restaurant)

Session 7	
<i>Chair: Matthias Schreck</i>	
13: 30–15: 50	
13: 30–14: 05	Rolf Möller (<i>University of Duisburg-Essen</i>) “Electronic Transport on the Nanoscale”
14: 05–14: 30	Hongjun Gao (<i>Institute of Physics, CAS, China</i>) “Intercalating Buffer Layers and Tuning Electronic Properties between Graphene and Metal hosts ”
14: 30–15: 05	Jing Tao (<i>Brookhaven National Laboratory, USA</i>) “Direct Observation of Nematicity and Topological Defects through Electronically Driven Phase Transitions in $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$ ”
15: 05–15: 40	Hongbin Yu (<i>Arizona State University, USA</i>) “Exploring Microwave Properties of Soft Magnetic Material ”
15: 40–15: 50	Coffee Break

Session 8	
<i>Chair: Rolf Möller</i>	
15: 50–17: 50	
15: 50–16: 25	Andrea C. Ferrari (<i>University of Cambridge, UK</i>) “Graphene Future Emerging Technology”
16: 25–16: 50	Guangyu Zhang (<i>Institute of Physics, CAS, China</i>) “Graphene on Hexagonal Boron Nitride: Epitaxial Growth and 2D Superlattice Behaviors”
16: 50–17: 25	Ileana Rau (<i>Almaden Research Center, USA</i>) “Magnetic Atoms on Thin MgO Films”
Closed Remark: Hans-Joachim Freund	

**中国科学院物理研究所纳米材料与器件国际研讨会
(桂林部分)**

International Workshop on Nanomaterials and Nanodevices

(Guilin Part, July 5th, 2013)

Scientific Program

8: 30— 8: 40	Opening Ceremony and Welcome Remarks
8: 30—8: 40	Huaiying Zhou (<i>Guilin University of Electronic Technology, China</i>) Lixian Sun (<i>Guilin University of Electronic Technology, China</i>)
8: 40—10: 40	Session 1 <i>Chair: Xincheng Xie</i>
8: 40—9: 05	Lixian Sun (<i>Guilin University of Electronic Technology, China</i>) “New Materials for Energy Storage, Bio/fuel Cells and Bio/chemical Sensors”
9: 05—9: 30	Matthias Schreck (<i>Universit ät Augsburg, Germany</i>) “Heteroepitaxial Diamond on Ir/YSZ/Si: a Versatile Material Platform for Applications Ranging from Neutron Scattering to Quantum Optics”
9: 30—9: 55	Feng Liu (<i>Utha university, USA</i>) “Organic Topological Insulators in Organometallic Lattices”
9: 55—10: 20	Wolf-Dieter Schneider (<i>Institute of Condensed Matter Physics, Switzerland</i>) “Transport Properties and Electronic Structure of Individual Metallic Quantum Dots on Dielectric Supports: A Local View”
10: 20—10: 40	Photo and Coffee Break

10: 40—11: 55	Session 2 <i>Chair: Chonglin Chen</i>
10: 40—11: 05	W. A. Hofer (<i>The University of Liverpool, UK</i>) “Efficient 3D-WKB STM Simulation Model”
11: 05—11: 30	Shengbai Zhang (<i>Rensselaer Polytechnic Institute, USA</i>) “Atomistic Mechanism for Oxygen Evolution Reaction at TiO ₂ (110)/bulk Water Interface: The Role of Photohole-assisted O-O Bond Formation”

11: 30–11: 55	Jing Tao (<i>Brookhaven National Laboratory, USA</i>) “Direct Observation of Nematicity and Topological Defects through Electronically Driven Phase Transitions in $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$ ”
11: 55	Lunch

13: 30–14: 55	Session 3 <i>Chair: Jiandi Zhang</i>
13: 30–13: 55	Hrvoje Petek (<i>University of Pittsburgh, USA</i>) “A multi-State Molecular Switch Based on STM Tunneling Electron-induced Enantiomerization of an Endohedral Fullerene $\text{Sc}_3\text{N}@C_{80}$ ”
13: 55–14: 20	Karl-Heinz Ernst (<i>Empa, Switzerland</i>) “Electrically Driven Molecular Machines at Surfaces”
14: 20–14: 45	Siu-Wai Chan (<i>Columbia University, USA</i>) “Nanoparticles of Ceria: their Microstructure and Impedance Response”
14: 45–14: 55	Coffee Break

14: 55–16: 20	Session 4 <i>Chair: Hongbin Yu</i>
14: 55–15: 20	Peter Sutter (<i>Center for Functional Nanomaterials, USA</i>) “In-Situ Microscopy of 2D Materials: Growth, Processing, Properties”
15: 20–15: 45	Rolf Müller (<i>University of Duisburg-Essen</i>) “Electronic Transport on the Nanoscale”
15: 45–16: 10	Christian Teichert (<i>Institute of Physics, Montanuniversitaet Leoben, Austria</i>) “AFM based Characterization of ZnO Nanostructures”
16: 10–16: 35	Thomas Greber (<i>University of Zurich, Switzerland</i>) “Endohedral Single Molecule Magnets 123”
16: 35–17: 00	Wende Xiao (<i>Institute of Physics, CAS, China</i>) “Reversible Spin Control of Individual Magnetic Molecule by Hydrogen Atom Adsorption”
<i>Closing Remarks: Feng Liu, Guanghui Rao</i>	

Beijing Part

In-Situ Microscopy of 2D Materials: Growth, Processing, Properties

Peter Sutter

Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973

psutter@bnl.gov

Two-dimensional (2D) crystals, such as graphene, hexagonal boron nitride, and several metal dichalcogenides, represent a new class of functional materials with a wealth of interesting physical and chemical properties. While initial studies on these systems have been enabled primarily by monolayer sheets isolated from layered bulk crystals, broader fundamental investigations and potential applications require reliable and scalable methods for fabricating and processing high-quality 2D membranes.

I will discuss recent advances in understanding the synthesis and processing of 2D materials on metal substrates, derived primarily from real-time observations by surface electron microscopy complemented by high-resolution scanning probe microscopy and in-situ spectroscopy methods. Real-time low-energy electron microscopy and associated analytical methods provide insight into the fundamental growth mechanisms of 2D crystals, their interaction with a metal substrate, as well as processes that modify the substrate coupling and may be harnessed for the bottom-up assembly of functioning devices. Going beyond homogeneous 2D crystals, heterostructures that combine different 2D materials in layer stacks or as several tightly interfaced components in a single, atomically thin membrane promise tunable properties and greatly extended functionality, and raise fundamental questions on interface formation, intermixing, strain, and polarity in a new context at reduced dimensionality. I will demonstrate pathways to overcoming the formidable challenges involved in the controlled fabrication of such novel materials. Our combined findings establish a powerful toolset for the scalable fabrication of 2D materials and their heterostructures for research and applications.

Acknowledgments: Work performed under the auspices of the U.S. Department of Energy under contract No. DE-AC02-98CH10886.

**Wafer-Size Single-Crystal Metal Films on Silicon:
a Powerful Substrate Structure for the Preparation of sp^2 - and sp^3 -bonded
Carbon Materials**

Matthias Schreck

Institute of Physics, University of Augsburg (Germany)

matthias.schreck@physik.uni-augsburg.de

The ability of carbon's four valence electrons to form different states of hybridization gives rise to a variety of allotropes with extreme and often contrary physical properties. C-atoms with sp^2 -hybridization and a planar trigonal arrangement of the binding orbitals are the basic building blocks for graphite, graphene, nanotubes and fullerenes. The 1D and 2D sp^2 -carbon structures excel in ultimate tensile strength and highest charge carrier mobility.

On the contrary, diamond, the crystalline modification of sp^3 -carbon, is electrically a wide band gap semiconductor, i.e. in the un-doped state a perfect insulator. In the 3D structure built up by strong σ -bonds the carbon atoms have the highest atomic density of all solid materials. Diamond combines a unique selection of unsurpassed material properties like the ultimate hardness, Young's modulus, thermal conductivity and a high optical transparency over a wide wavelength range. Insertion of impurities can cause p- or n-type conductivity. In addition, the diamond crystal lattice is a perfect host for single photon emitters.

The scientific work in our research group is focused on the synthesis of graphene and diamond by chemical vapor deposition (CVD) techniques with the aim to develop wafer size materials with highest structural quality. In the case of diamond, iridium surfaces have turned out to provide a unique template for subsequent heteroepitaxial diamond growth. In the case of graphene, heteroepitaxy on various metals has currently the highest potential for ultimate quality graphene combined with a realistic option for the transfer to an industrial technology.

My two presentations describe the development of metal layers with single crystal structure on silicon and their application as substrates for the deposition of graphene and diamond.

The first talk comprises:

- preparation and structural properties of single crystal metal films on silicon via

yttria-stabilized zirconia (YSZ) buffer layers

- CVD growth of graphene on metal/YSZ/Si(111)

-metal/YSZ/Si(111) as substrates for alternative low-dimensional systems: h-BN, ZnO nanopillars

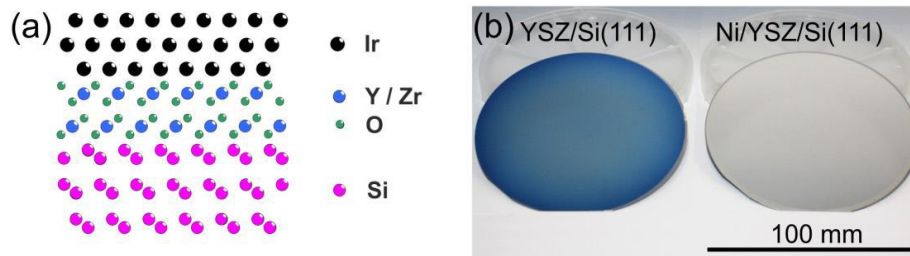


Fig 1: (a) Schema of the layer structure $Ir/YSZ/Si(111)$. Iridium can be replaced by other metals like Ru , Rh , Ni , Pt , ...

(b) Optical image of 4" $YSZ/Si(111)$ and $Ni/YSZ/Si(111)$ wafers.

sp² Hybridized Single Layers: From Templates to Nanotents

Thomas Greber

University of Zurich, Switzerland

greber@physik.uzh.ch

The properties of single layers of carbon or boron nitride on transition metals enable new functionalities ^[1]. I will give a short overview of its use as templates for molecules, and its application as intercalating materials.

Finally, a recent development on immobilization of single atoms beneath a single layer of h-BN will be discussed ^[2]. The atoms display like sitting in "nanotents" where the single layer forms the "rainfly", which protects the implanted atoms.

[1] Graphene and Boron Nitride Single Layers, Chapter 18 in CRC Handbook of Nanophysics Vol. 5 (2011), ED. Klaus Sattler, Taylor and Francis, or:

http://www.physik.uzh.ch/groups/grouposterwalder/kospace/Graphene_and_Boron_Nitride_Greber.pdf

[2] Immobilizing Individual Atoms beneath a Corrugated Single Layer of Boron Nitride, Cun et al., Nano Letters 13 (2013) 2098.

Transient excitons at metal surfaces

Hrvoje Petek

Department of Physics and Astronomy, University of Pittsburgh

petek@pitt.edu

On account of high electron density, the Coulomb interaction in metals is efficiently screened on the length scale of interatomic distance and the time scale of inverse plasma frequency, i.e., on Ångstrom and attosecond scales. Nevertheless, transient excitonic interactions have been invoked in the interpretation of optical spectra and electron dynamics in noble metals. We explore the surface electronic structure of silver and copper surfaces by four-dimensional (photoelectron density, energy, momentum, and time) multiphoton photoemission. Features observed in the near-resonant multi-photon photoemission spectra cannot be understood from the joint density of occupied and unoccupied states that are coupled by optical transitions and a Fermi Golden Rule transition rate formalism, suggesting that quasiparticle correlations, for example, transient excitonic interactions can play an important role. We study photoexcited electron and hole propagating in the occupied and unoccupied surface states, and how their mutual Coulomb interaction affects the transition amplitudes, as well as photoelectron energy and momentum distributions in multi-photon photoemission spectra. Photoelectron energy-momentum distributions provide clear evidence for electron-hole pair correlation, local field effects, and related excitonic and plasmonic interactions, on the time scales for screening in noble metals.

Electronic Nanofabrication of Complex Oxides

Jian Shen

Department of Physics, Fudan University, Shanghai 200433, China

shenj5494@fudan.edu.cn

The development of nanofabrication methods has been the key to success of nanoscience and nanotechnology. Conventional nanofabrication is accomplished by spatial confining structures into nanoscale following the designed patterns. In stark contrast, electronic nanofabrication is done by patterning electronic states of a material system in real space without actual removal of materials. This can only be applied to strongly correlated systems which energetically favor co-existence of electronic phases. In this work, we show that ferromagnetic metallic domains can be patterned in antiferromagnetic insulating matrix in manganites systems using localized magnetic and electric fields. This approach allows us to control the global physical properties of the system in a desired manner.

Diffusion Mechanisms in the Growth of Organic Semiconductor Nanostructures

Christian Teichert,

Institute of Physics, Montanuniversität Leoben, Franz Josef Str. 18, A-8700 Leoben, Austria

teichert@unileoben.ac.at

Crystalline films of conjugated organic semiconductors offer attractive potential for optoelectronic and electronic applications on flexible substrates. Due to the complexity and anisotropy of the molecular building blocks, novel growth mechanisms can occur as is demonstrated for the growth of the rod-like oligophenylene molecule parasexiphenyl (6P) on mica surfaces and graphene substrates^[1].

On clean mica(001), the self-organization of crystallites into one-dimensional chains is observed on a wetting layer where the 6P molecules lie almost flat on the surface^[2]. On an ion bombarded mica surface, the formation of terraced mounds composed by almost upright standing molecules is due to an active Ehrlich Schwoebel barrier for step-edge crossing. Quantitative analysis of the mound morphology together with transition state theory calculations revealed the existence of molecule bending during step edge crossing and level dependent step edge barriers^[3]. Analyzing temperature and rate dependent growth experiments for the same system, we determined also the size of the critical nucleus to be significantly larger than one^[4] and the subtle interplay of intra- and interlayer diffusion - resulting in elongated hexagonal second-layer islands - has been explored.

Low Energy Electron Microscopy (LEEM), micro Low Energy Electron Diffraction (μ LEED), and atomic force microscopy (AFM) have been employed to study the initial growth of 6P on graphene which offers the potential to be used as a transparent flexible electrode. Due to the structural similarity between substrate and 6P, one can expect that the molecules lie flat on the substrate. On Ir(111) supported graphene at 240 K, indeed layer-by-layer growth of lying molecules is observed as it is desired for OLEDs^[5]. The nucleation of the 6P islands occurs at wrinkles in the metal supported graphene layer. Larger islands composed of flat-lying molecules detach from the original nucleation sites and move rapidly as entities across wrinkle free substrate areas^[6]. In addition, μ LEED reveals the surface unit cells in the different growth stages and at various substrate temperatures. At temperatures above room temperature, again crystalline needles appear on a

molecular wetting layer ^[7] which is in agreement with AFM observations for 6P grown on exfoliated graphene transferred to silicon oxide ^[8].

Contributions by G. Hlawacek, M. Kratzer, S. Lorbek, Q. Shen, S. Klima, P. Puschnig, D. Nabok, G. Biddau, C. Draxl (Leoben), P. Frank, T. Potocar, A. Winkler (Graz), F. S. Khokhar, R. van Gastel, H. Zandvliet, B. Poelsema (Enschede), and B. Vasić, R. Gajić (Belgrade) are acknowledged.

[1] G. Hlawacek, C. Teichert, *J. Phys.: Condens. Matter* **25** (2013) 143202.

[2] C. Teichert, et al., *Appl. Phys. A* **82** (2006) 665.

[3] G. Hlawacek, et al., *Science* **321** (2008) 108.

[4] T. Potocar, et al., *Phys. Rev. B* **83** (2011) 075423.

[5] G. Hlawacek, et al., *Nano Lett.* **11** (2011) 333.

[6] G. Hlawacek, et al., *IBM J. Res. Devel.* **55** (2011) 15:1.

[7] F. S. Khokhar, et al., *Surf. Sci.* **606** (2012) 47.

[8] M. Kratzer, et al., submitted to *J. Vac. Sci. Technol. B* 2013.

Shaking Hands in Flatland:

Molecular Recognition Among Chiral Molecules on Surfaces

Karl-Heinz Ernst^{1,2,}*

¹ *Nanoscale Materials Science, Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland*

² *Department of Chemistry, University of Zurich, Winterthurerstr. 190, CH-8057 Zürich, Switzerland*

Karl-Heinz.Ernst@empa.ch

Molecular recognition among chiral molecules on surfaces is of paramount importance in biomineralization, enantioselective heterogeneous catalysis, and for the separation of chiral molecules into their two mirror-image isomers (enantiomers) via crystallization or chromatography. Understanding the principles of molecular recognition in general, however, is a difficult task and calls for investigation of appropriate model systems. One popular approach is thereby studying intermolecular interactions on well defined solid surfaces. This allows in particular the use of scanning tunneling microscopy (STM). We present an elucidation of chiral recognition of helical hydrocarbons at the single molecule level, in monolayers and in up to the multi-layer. This includes lateral separation of the molecules that constitute a dimer with a modified STM tip and the subsequent determination of their handedness with a non-modified tip. We will show that a preference between homochiral and heterochiral recognition among molecules depends strongly on substrate symmetry, but may switch with increasing coverage within the monolayer or from saturated monolayer to multilayer.

Financial support by the Swiss National Science Foundation (SNSF), the Swiss Secretary for Education and Research (SER) and the Swiss Sino Science and Technology Cooperation (SSSTC) is gratefully acknowledged.

*Coauthors of parts of the results presented in this talk are: Johannes Seibel,¹ Manfred Parschau,¹ Quirin Stöckl,¹ Laura Zoppi,² Oliver Allemann,² Jay Siegel,² Susanne Baumann, Christopher Lutz, Andreas Heinrich (IBM ARC).

Dephasing Effect on the Helical Edge Excitations in Topological Insulators.

Xincheng Xie

Peking University, China

xcxie@pku.edu.cn

The topological insulator (TI) is a novel quantum state with metallic surface (edge) states, which is characterized by linear gapless dispersion and protected by the time-reversal symmetry. We show how normal dephasing effect can cause dramatic changes to the transport properties of TI surface (edge) states. For three-dimensional TI surfaces states, we find the dephasing effect can cause extremely large backscattering behavior under charge impurities. For two-dimensional TI systems, we find the combination of dephasing effect and Rashba spin-orbital coupling can destroy the helical edges states. These results can explain some recent experimental findings.

Transport Properties and Electronic Structure of Individual metallic Quantum Dots on Dielectric Supports: A Local View

Wolf-Dieter Schneider

Institute of Condensed Matter Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL),

CH-1015 Lausanne, Switzerland

and

Fritz-Haber-Institute of the Max-Planck-Society, D-14195 Berlin, Germany

wolf-dieter.schneider@epfl.ch

Contacts between metallic nanostructures and semiconducting or dielectric supports are expected to constitute the basic building blocks of future nanoscale electronics and nanocatalysts. We investigate with low-temperature scanning probe techniques the transport properties and the local electronic structure of individual nanocontacts formed between flat metallic islands and their supporting substrates. In the first example, Pb on HOPG, on h-BN/Ni(111), and on NaCl/Ag(111), the observed differential conductance spectra reveal a suppression at small bias voltages characteristic for the presence of dynamical Coulomb blockade (DCB) phenomena. By increasing the thickness of the dielectric NaCl film from 2 to 3 monolayers, we observe a transition from the DCB regime to the orthodox Coulomb staircase (CBS) regime. A comparison with calculations based on the theory of environmentally assisted tunneling and on the orthodox theory for a double barrier junction allows us to determine the capacitances and resistances of the contacts, which depend systematically on the island-substrate contact area^[1]. In the second example, tunneling spectroscopy on two-dimensional Li-islands on CaO/Mo(001) reveals a standing wave pattern which indicates the metallic character of these monolayer nanoislands. Moreover, depending on the capacitances and resistances of the metal-oxide junction, also here DCB as well as CBS phenomena are observed. In addition, an unoccupied gap state below the CaO conduction band, which originates from Li-O hybridization across the metal-oxide interface is detected. With increasing diameter of the Li islands, this state shifts towards the Fermi level, reflecting the decreasing workfunction at higher Li coverage^[2]. These findings facilitate quantitative investigations of the local electronic structure of metallic quantum dots. They are important for future studies of the

physical and chemical properties of supported nanostructures in relation to superconductivity [3], magnetism, and catalysis.

Support from the Swiss National Science Foundation and the DFG Excellence-Initiative ‘Unicat’ is gratefully acknowledged.

[1] C. Brun, K.-H. Müller, I. P. Hong, F. Patthey, C. Flindt, and W.-D. Schneider, Phys. Rev. Lett. **108**, 126802 (2012).

[2] X. Shao, Y. Cui, W.-D. Schneider, N. Nilius, H.-J. Freund, J. Phys. Chem. C **116**, 17980 (2012).

[3] C. Brun, I.-P. Hong, F. Patthey, I. Yu. Sklyadneva, R. Heid, P. M. Echenique, K. P. Bohnen, E. V. Chulkov, and W.-D. Schneider, Phys. Rev. Lett. **102**, 207002 (2009).

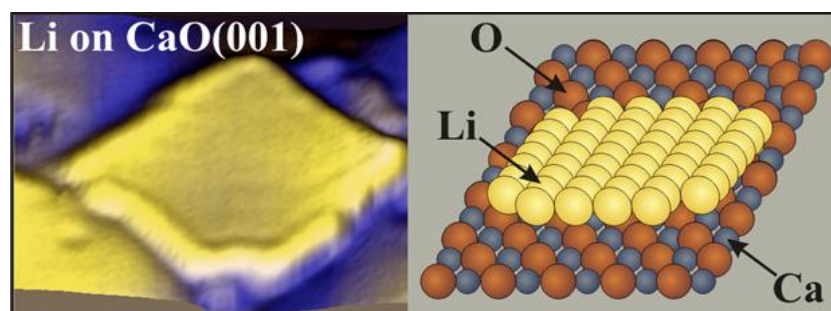


Figure 1. Topographic image (STM) of a large Li island on CaO/Mo(001) ($25 \times 25 \text{ nm}^2$, 2.0 V) and atomic visualization^[2].

All Optical Spin Manipulation in Colloidal Nanostructures

Min Ouyang

University of Maryland – College Park

mouyang@umd.edu

In this talk I will present a few recent advances from my research group, centering on coherent manipulation of spin dynamics in precisely engineered colloidal hybrid nanostructures by ultrafast all optical technique. Ultrafast optical spectroscopy not only offers a unique tool to probe spin dynamics with extremely high sensitivity but also allows precise control of fundamental quantum processes at the nanoscale. For example, enabled by its fine temporal resolution, plasmon enhanced coherent spin manipulation has been demonstrated in semiconductor quantum structures through plasmon-exciton coupling. All optical spin echo has been achieved for the first time in colloidal nanostructures with manifestation of intrinsic long spin lifetime that should provide valuable opportunity to reveal nature of quantum spin couplings at the nanoscale.

Toward the Ultimate Critical Thickness of “Dead” Oxide Layer*

Jiandi Zhang

Louisiana State University

jiandiz@lsu.edu

In contrast with the metallic or even superconducting phenomenon emerging at the interface of two insulating oxides such as LaAlO₃/SrTiO₃, several ultrathin films of metallic oxides exhibit nonmetallic behavior, challenging our understanding of these materials at interface and possible technological application. For such “dead layer” phenomena, the central question is: is this an intrinsic effect caused by dimensional confinement, or caused by strain, interface, segregation, impurity, or stoichiometry. We have systematically studied the thickness-dependence of structure/properties for La_{2/3}Sr_{1/3}MnO₃ (LSMO) on SrTiO₃(001) by using in-situ growth of laser MBE and characterization such as LEED, XPS and STM, and ex-situ transport measurements. With optimized growth conditions to minimize the oxygen deficiency (oxygen non-stoichiometry), we were able to focus on the other intrinsic effects associated with the dead layer. In this talk, I will summarize our recent results on the dead layer of LSMO by showing that the dimensionality/structure effects play key role in determining the dead layer. With this optimized quality of ultrathin films, new critical behaviors emerge, such as the non-monotonic structure relaxation with thickness, the enhanced magnetoresistance effect and extreme sensitivity to strain at the critical thickness at ~ 6 unit cells. In particular, the ultimate critical thickness of 4 u.c can be reached when the film is grown on strain-free substrate. These behaviors are proposed to correlate with subtle balance of different competing effects.

* Supported by US Department of Energy.

Advanced Carbon-based Nanotubes/Nanocages for Energy Conversion and Storage: Synthesis, Performance and Mechanism

Lijun Yang, Qiang Wu, Xizhang Wang, Zheng Hu

Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

Fuel cells, supercapacitors and lithium-ion batteries are the typical energy conversion and storage devices of great significance in which carbon-based nanostructures could play irreplaceable role. The functionalized carbon-based nanotubes/nanocages (CNTs/CNCs) could be applied to fuel cells to lower Pt loading by highly dispersing and immobilizing Pt-based nanoparticles, or to totally get rid of Pt with the metal-free electrocatalytic ability themselves. The abundant nanostructures and morphologies, tunable compositions, high surface area, good conductivity, small volume expansion, as well as the low cost and environmental benignity make the CNTs/CNCs have great potential as electrode materials of supercapacitors and lithium-ion batteries. In this talk I will give a brief introduction to the progressive advancements in our group about the synthesis^[1,2], performance^[3-7] and mechanism^[7,8] of the CNTs/CNCs for this kind of energy conversion and storage. Special attention will be paid to the materials design by doping the CNTs/CNCs with electron-rich N^[3-5], electron-deficient B^[7], and the both^[8] to elucidate the correlation of the performance with the doping microstructures, which is a general interesting issue in developing the advanced carbon-based energy materials.

References

1. C. Y. He, X. Z. Wang, Q. Wu, Z. Hu*, Y. W. Ma, J. J. Fu and Y. Chen, "Phase-equilibrium-dominated vapor-liquid-solid growth mechanism" *J. Am. Chem. Soc.* **132** (2010)4843
2. Y. J. Tian, Z. Hu*, Y. Yang, X. Z. Wang, X. Chen, H. Xu, Q. Wu, W. J. Ji and Y. Chen, "In situ TA-MS study on the six-membered-ring-based growth of carbon nanotubes with benzene precursor" *J. Am. Chem. Soc.* **126** (2004)1180
3. S. Chen, J. Y. Bi, Y. Zhao, L. J. Yang, C. Zhang, Y. W. Ma, Q. Wu, X. Z. Wang, and Z. Hu*, "Nitrogen-doped carbon nanocages as efficient metal-free electrocatalyst for oxygen reduction reaction" *Adv. Mater.* **24** (2012) 5593
4. S. J. Jiang, Y. W. Ma, G. Q. Jian, H. S. Tao, X. Z. Wang, Y. N. Fan, Y. N. Lu, Z. Hu* and Y. Chen, "Facile construction of Pt-Co/CN_x nanotube electrocatalysts and their application to oxygen reduction reaction" *Adv. Mater.* **21** (2009) 4953
5. Y.W. Ma, S. J. Jiang, G.Q. Jian, H.S. Tao, L.S. Yu, X.B. Wang, X.Z. Wang, J.M. Zhu, Z. Hu* and Y. Chen, "CN_x nanofibers converted from polypyrrole nanowires as platinum support for methanol oxidation" *Energy Environ. Sci.* **2** (2009)224
6. K. Xie, X. T. Qin, X. Z. Wang, Y. N. Wang, H. S. Tao, Q. Wu, L. J. Yang, and Z. Hu*, "Carbon nanocages as supercapacitor electrode materials" *Adv. Mater.* **24** (2012)347
7. L. J. Yang, S. J. Jiang, Y. Zhao, L. Zhu, S. Chen, X. Z. Wang, Q. Wu, J. Ma, Y. W. Ma, Z. Hu*, "Boron-doped carbon nanotubes as metal-free electrocatalysts for oxygen reduction reaction" *Angew. Chem. Int. Ed.* **50**(2011)7132
8. Y. Zhao, L. J. Yang, S. Chen, X. Z. Wang, Y. W. Ma, Q. Wu, Y. F. Jiang, W. J. Qian, and Z. Hu*, "Can boron and nitrogen codoping improve oxygen reduction reaction activity of carbon nanotubes" *J. Am. Chem. Soc.* **135** (2013)1201

Model Studies on Heterogeneous Catalysts at the Atomic Scale: From Supported Metal Particles to Two-dimensional Zeolites

Hans-Joachim Freund

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

freund@fhi-berlin.mpg.de

Understanding catalysis, and in particular heterogeneous catalysis, has been based on the investigation of model systems. The enormous success of metal single crystal model surface chemistry, pioneered by physical chemists, is an outstanding example. Increasing the complexity of the models towards supported nano particles, resembling a real disperse metal catalyst, allows on to catch in the model some of the important aspects that cannot be covered by single crystals alone. One of the more important aspects is the support particle interface. We have developed strategies to prepare such model systems based on single crystalline oxide films which are used as supports for metal and oxide nano particles, whose geometric structure, morphology, electronic structure, as well as interaction and reaction with molecules from the gas phase may be studied at the atomic level.

After a general introduction to model studies in catalysis, a selection of results from different research areas are presented: a) adsorption and reaction on nano particles supported on thin oxide films; b) 2D-3D-morphology, geometric, and electronic structure of supported metal nano particles partially in relation to doping of the support; c) strong metal support interaction (SMSI); and d) adsorption and reaction on two-dimensional silicates and alumino-silicates in ordered and vitreous phases.

Efficient 3D-WKB STM simulation model

K. Palotás, G. Mándi, W. A. Hofer

The University of Liverpool, UK

Whofer@liverpool.ac.uk

We review the recently developed three-dimensional (3D) atom-superposition approach for simulating scanning tunneling microscopy (STM) and spectroscopy (STS) based on ab initio electronic structure data. In the method, contributions from individual electron tunneling transitions between the tip apex atom and each of the sample surface atoms are summed up assuming the one-dimensional (1D) Wentzel-Kramers-Brillouin (WKB) approximation in all these transitions. This 3D WKB tunneling model is extremely suitable to simulate spin-polarized STM and STS on surfaces exhibiting a complex noncollinear magnetic structure, i.e., without a global spin quantization axis, at very low computational cost. The tip electronic structure from first principles can also be incorporated into the model, that is often assumed to be constant in energy in the vast majority of the related literature, which could lead to a misinterpretation of experimental findings. Using this approach, we highlight some of the electron tunneling features on a prototype frustrated hexagonal antiferromagnetic Cr monolayer on Ag(111) surface. We obtain useful theoretical insights into the simulated quantities that is expected to help the correct evaluation of experimental results. By extending the method to incorporate a simple orbital dependent electron tunneling transmission, we reinvestigate the bias voltage- and tip-dependent contrast inversion effect on the W(110) surface. STM images calculated using this orbital dependent model agree reasonably well with Tersoff-Hamann and Bardeen results. The computational efficiency of the model is remarkable as the k-point samplings of the surface and tip Brillouin zones do not affect the computational time, in contrast to the Bardeen method. In a certain case we obtain a relative computational time gain of 8500 compared to the Bardeen calculation, without the loss of quality. We discuss the advantages and limitations of the 3D WKB method, and show further ways to improve and extend it.

**Superfast Chemical Exchange Dynamics with Layer-by-Layer Exchange
Diffusion of Oxygen and Hydrogen in Epitaxial Thin Films of Single-Crystalline
Cobalt Double-Perovskites**

Chonglin Chen

University of Texas San Antonio, Texas 78249, USA

cl.chen@utsa.edu

Superfast chemical exchange dynamic behavior were discovered on the surfaces of the highly epitaxial thin films of single-crystalline cobalt double-perovskites (LnBCO) (Ln = Er, Pr; $0.0 < x < 0.5$). The exchange diffusion of oxygen and hydrogen through these films were examined by measuring their resistance R under a switching flow of oxidizing gas (O₂) and reducing gas (H₂) in the temperature range of 250~800 °C. These films were found to exhibit ultrafast oxygen/hydrogen diffusivity and high sensitivity to redox environments. Their resistance R changes by three to four orders of magnitude in less than 0.1 s. When measured as a function of the gas flow time t, these LnBCO films show fast oscillations in the R vs. t plots with time period shorter than 1 s during the oxidation cycle under O₂. This unprecedented oscillation phenomenon provides the first direct experimental evidence that oxygen/hydrogen atoms diffuse through the LnBCO thin films layer by layer via the oxygen-vacancy-exchange mechanism. The excellent chemical dynamics and ultrafast layer-by-layer oxygen vacancy exchange diffusion suggest that the as-grown LnBCO can be an excellent candidate for energy harvest and chemical sensor developments.

Carbon Kagome Lattice: a First-Principles Prediction

Yuanping Chen, Yiyang Sun, Han Wang, Damien West, and S. B. Zhang

Department of Physics, Applied Physics & Astronomy, Rensselaer Polytechnic Institute, Troy, New York 12180,

USA

zhangs9@rpi.edu

The study of two-dimensional (2D) carbon allotropes is a never ending pursue for their extraordinary physical properties and structural richness. In a separate and unrelated front, recently 2D Kagome lattice has attracted considerable attention for its exceptional physical properties. Here, we consider a Kagome lattice made of pure carbon chains. The resulting carbon Kagome lattice (CKL) is a three-dimensional solid with theoretical hardness approaching that of cubic BN. Despite the triangular ring structure, CKL has exceptional stability comparable to C₆₀. The CKL is also a direct gap elementary semiconductor- 3.4 eV by hybrid functional HSE calculation. Band-edge optical transition of the CKL is electrical-dipole allowed with the imaginary part of the dielectric function comparable to GaN and ZnO. The effective masses of the electrons and holes are, on the other hand, comparable to those of silicon, making the CKL an exceptional contender for monolithic integration of high-power electronics with short-wave-length optoelectronics.

Optoelectronic Devices based on Semiconductor Nanowires with Lateral Electrodes

Yi Shi

School of Electronic Science and Engineering, Nanjing University, Nanjing 210093, China

yshi@nju.edu.cn

Optoelectronic devices based on semiconductor nanowire have attracted intense interests, concerning the advantages of nanowire growth, fabrication, architecture, functionality, etc. A large amount of prototypes, such as nanowire photodetectors, solar cells, light emitting diodes, lasers, have been developed. In this talk, the progress of nanowire optoelectronic devices is shortly surveyed, and our related results are reported, including the ZnO nanowire non-catalyst growth, lateral electrode fabrication, photodetection, interfacial transport and optical resonances.

A method of fabricating the lateral electrodes on nanowires is developed, which provides a large contact area, a short transport path in diameter and compatibility for varied building-block geometries. Furthermore, a Schottky-type and a MIS-type UV photodetectors are constructed based on the lateral electrode architecture. The Schottky photodetector, where Au serves as the semi-transparent top electrode, exhibits a on/off ratio of 6000, a cut-off wavelength near 380 nm and zero-bias photoresponse. The photoresponse originates from the enhanced transport because of the interfacial-state related barrier reduction. The interfacial transport inhomogeneity is investigated in a nanowire ensemble device with the discrete structure and instantaneous interfacial state. A modification of the ultra-thin Al₂O₃ insertion is introduced to construct a MIS photodetector. Stable and rapid photoresponse is achieved, with a high on/off ratio. The homogeneous tunneling across the uniform and conformal insertion layer contributes to the improvement, which is analyzed by direct and Fowler - Nordheim tunneling models.

Polarization photodetection is integrated in the nanowire photodetector, with 50% enhancement of polarization ratio. The optical resonances in the metal - nanowire cavities is analyzed by FDTD simulation. The photocurrent varied with the angle between excitation polarization and nanowire orientation. The optical absorption is related to Fabry - Perot resonance under TE and the surface plasmon resonance under TM. The electric field distribution and the Poynting vector certify the relationship of polarization photodetection and the optical resonances, calculated with varied incident wavelength and diametrical geometries.

Unraveling the Intra- and Inter-Molecular Bonding Structures Using Atomic Force Microscopy

Xiaohui Qiu

National Center for Nanoscience and Technology, China, Beijing 100190

xhqu@nanoctr.cn

The atomic force microscope (AFM) has evolved into an instrument with spatial resolution fine enough to image atomic features. It has been recently demonstrated that in the short-range regime of forces, Pauli repulsive interactions between the CO-terminated AFM tip and the electron density in the proximity of the sample enable the achievement of image contrast of atoms and bonds in the chemical structures of individual molecules. Here we used a state-of-the-art AFM with a qPlus sensor to visualize in real-space the formation of hydrogen bonding between molecules (8-hydroxyquinoline, 8-hq) on metal substrate. The atomically resolved molecular structures with unprecedented details enable a precise determination of the characteristics of the hydrogen bonds, including bonding sites, orientations and lengths. The observed bond contrast was interpreted by ab initio density functional calculations that indicate the electron density contribution from the hybridized electronic state of hydrogen bond. We also identified intermolecular coordination between the dehydrogenated 8-hq and Cu adatoms. The direct identification of local bonding configurations, especially hydrogen bonding, by AFM would advance the understanding of intermolecular interactions in complex molecules with multiple active sites or conformationally flexible biological molecules. The observation of hydrogen bonding in real-space would also be an interesting subject for theoretical chemistry.

Electronic Transport on the Nanoscale

Rolf Möller

Faculty of Physics, University of Duisburg-Essen

rolf.moeller@uni.due-de

To study the transport through objects at the nanoscale a scanning tunneling microscope with several tips is used. Two different configurations will be discussed. The lateral transport of electrons may be studied by using two tips to drive a current parallel to the surface. A third tip enables to map the corresponding electrochemical potential. Measurements for a 2D conducting layer will be discussed^[1]. The measurements are complemented by the analysis of the density of states, e.g. revealing the scattering of surface state electrons by steps and defects on the Bi(111) surface^[2]. To analyze the transport perpendicular to the surface, a thin metallic layer is placed on a semiconducting surface. At the interface a Schottky barrier is formed, which can only be overcome by electrons of sufficient energy. This may be used to split the current of electrons coming from the tip of the microscope into two parts, the ballistic electrons and the electrons which have been scattered. This technique has been applied to study the ballistic transport of electrons through individual molecules^[3]. On the other hand inelastic processes may be revealed by analyzing the fluctuations in the tunneling current observed at different positions of the tunneling tip above an adsorbed molecule^[4].

- [1] J. Homoth, M. Wenderoth, T. Druga, L. Winking, R.G. Ulbrich, C.A. Bobisch, B. Weyers, A. Bannani, E. Zubkov, A.M. Bernhart, M.R. Kaspers, R. Möller, *Nano Letters* 9, 1588 (2009)
- [2] M. C. Cottin, C. A. Bobisch, J. Schaffert, G. Jnawali, A. Sonntag, G. Bihlmayer, and R. Möller, *Appl. Phys. Lett.* 98, 022108 (2011).
- [3] A. Bannani, Ch. Bobisch, R. Möller, *Science* 315, 1824 (2007)
- [4] J. Schaffert, M.C. Cottin, A. Sonntag, H. Karacuban, C.A. Bobisch, N. Lorente, J.-P. Gauyacq, R.Möller, *Nature Materials* 12, 223–227 (2013)

Intercalating Buffer Layers and Tuning Electronic Properties between Graphene and Metal hosts*

Hong-Jun GAO (高鸿钧)

Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

hjgao@iphy.ac.cn

Graphene is being considered as a contender as the reference material with extraordinary properties for a post-CMOS technology. The availability of high quality and large scale single crystal graphene is fundamental for it to fulfill its promise in electronic applications. Graphene is usually grown on a metallic substrate from which it has to be transferred before it can be used. However, uncontrolled shear and strain, associated with the transfer and the presence of extended domains, lead to unavoidable tearing, rendering it useless for scalable production. We propose a way to overcome this bottleneck and produce high quality, free standing graphene by intercalating Si or Hf in graphene (G) epitaxially grown on metals, like Ru(0001) & Ir(111). This G/Si/metal architecture, produced by the silicon-layer intercalation approach (SIA), was characterized by scanning tunneling microscopy /spectroscopy (STM/STS), Raman, and angle resolved electron photoemission spectroscopy (ARPES) and proves the high structural and electronic qualities of the new composite. The SIA eliminates the need for the graphene transfer and also allows for an atomic control of the distance between the graphene and the metal.

1. Jinhai Mao, Li Huang, and Hong-Jun Gao *et al.*, **Appl. Phys. Lett.** **100**, 093101 (2012) (Cover Story).
2. Lei Meng, Rongting Wu, Haitao Zhou, Geng Li, Yi Zhang, Linfei Li, Yeliang Wang, and H.-J. Gao, **Appl. Phys. Lett.** **100**, 083101 (2012).
3. Linfei Li, Yeliang Wang, Lei Meng, Rong-ting Wu, and H.-J. Gao, **Appl. Phys. Lett.** **102**, 093106 (2013).

* In collaboration with Yeliang Wang¹, Junfeng He¹, Shixuan Du¹, Xingjiang Zhou¹, A. H. Castro Neto².
¹*Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China;* ²*Graphene Research Center, Singapore National University.*

Direct Observation of Nematicity and Topological Defects through Electronically Driven Phase Transitions in $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$

Jing Tao

Brookhaven National Laboratory, USA

jtao@bnl.gov

Competing degrees of freedom in strongly correlated systems give rise to a variety of electronic phases and phase transitions as a function of temperature, doping levels, magnetic field and pressure, etc. Symmetry and symmetry breaking have been considered to play a key role in the electronic structures in many correlated materials, particularly in doped transition metal oxides. Recent researches have demonstrated that nematic and smectic states, with certain broken symmetry, are essential in understanding materials properties such as high- T_c superconductivity. Here we report direct observations of electronic nematicity in doped manganites $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$, which is a 3D system with superstructure modulation at low temperatures resulted from competing spin, charge, orbital and lattice. Both the electron diffraction results and HRTEM images obtained from single crystal domain of $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$ clearly show a C4 to C2 symmetry breaking in the superstructures at intermediate temperature range upon cooling. Upon cooling the electronic nematicity persists in the electronic structure until long-range ordering forms as a stripe phase at low temperatures. During warming process, we identified topological defects and their formation and evolution in the superstructures, indicating that the phase transition is through proliferation of dislocations which is a center mechanism of electronic liquid crystal transition. Theoretical simulations will also be provided for better interpretation of the underlying physics in the phenomena.

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Exploring Microwave Properties of Soft Magnetic Material

Hongbin Yu

Arizona State University, USA

Hongbin.Yu@asu.edu

Soft magnetic materials, such as permalloy(NiFe) and others, have widely been studied for many current and potential future applications, ranging from hard disk drive, sensors, magnetic random access memory, spintronics and power delivery. The fundamental properties of these materials in the form of bulk and very thin films and nanostructures have attracted many interests and have been investigated extensively. Here we show using microwave device structure, one can conveniently study many properties of soft magnetic materials, especially in the form of patterned structures, in the microwave range such as ferromagnetic resonance frequency and its shift as a function of external bias field, pattern's geometry and its dependence on the film thickness. In particular, a special form of microwave device, on-chip inductors that incorporate various soft magnetic alloys as cores, will be discussed in the context of their magnetic materials and structure optimization, as well as the increasing interests in RF devices and on-chip power delivery applications in advanced computation chips.

Graphene on Hexagonal Boron Nitride: Epitaxial Growth and 2D Superlattice Behaviors

Guangyu Zhang

Institute of Physics, CAS, Beijing, China

gyzhang@iphy.ac.cn

Hexagonal boron nitride has recently emerged as an excellent substrate for graphene, owing to its atomically flat surface and its potential to engineer graphene's electronic structure. So far, graphene/h-BN hetero-structures have been obtained only through a transfer process, which introduces structural uncertainties due to the random stacking between graphene and h-BN substrate. In this talk, I introduce our recent progress on epitaxial growth of single-domain graphene on h-BN by a remote-plasma assisted deposition technique. Large-area graphene single crystals were successfully grown for the first time on h-BN with a fixed stacking orientation. The macroscopic epitaxial graphene is in principle limited only by the size of the h-BN substrate and our synthesis method is potentially applicable on other flat surfaces. The epitaxial graphene on h-BN is of high quality with a typical carrier mobility of $\sim 5,000\text{-}20,000\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. More interestingly, we found that graphene on h-BN is a typical 2D superlattice structure induced by a trigonal moiré pattern with a period of $\sim 15\text{ nm}$, which was observed by atomic force microscopy. Transport measurements reveal a additional sets of Dirac points as a result of the superlattice potential. Quantum Hall effect is also observed with the 2D-superlattice-related feature developed in the fan diagram of longitudinal and Hall resistance, while the Dirac fermion physics near the original Dirac point is unperturbed.

Guilin Part

New Materials for Energy Storage, Bio/fuel Cells and Bio/chemical Sensors

*Li-Xian Sun**, Fen Xu, Huai-Ying Zhou, Hai-Liang Chu, Huan-Zhi Zhang, Yong-Jin Zou, Cui-Li Xiang,
Shu-Jun Qiu, Shu-Sheng Liu

*Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, 1 Jinji Road,
Guilin 541004, China; E-mail: lxsun@dicp.ac.cn*

Studies of economic, highly efficient and safe hydrogen storage materials (HSMs) play an important role in the development of fuel cells in vehicles. The application of phase change materials (PCMs) for solar thermal-energy storage has received considerable attention in recent years due to their high storage density. Furthermore, bio/fuel cells and bio/chemical sensors based on nano-materials are of great importance for environment protection and clinic analysis.

In recent years, studies on HSMs (including Ni-H battery), PCMs bio/fuel cells and bio/chemical sensors were performed in our lab.. In this report, the following aspects will be introduced:

The promising materials for HSMs studied in our laboratory including MHx: M= Mg, La, Ni, etc., alanate, borohydride and MOF;

A series of microencapsulated PCMs like Octadecane with good performance synthesized through in-situ polymerization and their applications in thermal regulation of gypsum boards;

The bio/fuel cells and bio/chemical sensors based on carbon/MOFs materials etc. for electricity generation and hydrogen/CO₂/glucose sensors.

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References

- [1] S. Liu, L.X.Sun, F. Xu, et al., Nanosized Cu-MOFs induced by graphene oxide and enhanced gas storage capacity, *Energy and Environmental Science*, 6(2013) 818-823.
- [2] X. L. Si, L.X.Sun, F. Xu, et al., High and selective CO₂ uptake, H₂ storage and methanol sensing on the amine-decorated 12-connected MOF CAU-1, *Energy and Environmental Science*, 4(2011)4522-4527.
- [3] T. Jiang, L. X. Sun, W. X. Li. First-principles study of hydrogen absorption on Mg(0001) and formation of magnesium hydride. *Physical Review B*, 81 (2010) 035416.
- [4] H.Z. Zhang, L.X. Sun, F. Xu et al., Preparation and thermal performance of gypsum boards incorporated with microencapsulated phase change materials for thermal regulation, *Solar Energy Materials And Solar Cells*,102(2012) 93-102.
- [5] Y.J. Zou, C.L. Xiang, L.N. Yang, L.X.Sun, F. XU, Z. Cao, A mediatorless microbial fuel cell using polypyrrole coated carbon nanotubes composite as anode material, *Int. J. Hydrog. Energy*, 33 (2008) 4856-4862
- [6] Y.J. Zou, C.L. Xiang, L.N. Yang, L.X.Sun, F. XU, Glucose biosensor based on electrodeposition of platinum nanoparticles onto carbon nanotubes and immobilizing enzyme with chitosan-SiO₂ sol-gel. *Biosensors & Bioelectronics*, 23 (2008) 1010-1016.

**Heteroepitaxial Diamond on Ir/YSZ/Si:
a Versatile Material Platform for Applications Ranging from
Neutron Scattering to Quantum Optics**

Matthias Schreck

Institute of Physics, University of Augsburg (Germany)

matthias.schreck@physik.uni-augsburg.de

Full benefit of diamond's unique properties in various fields of technology requires single crystal material with minimum defect density. In the high pressure high temperature (HPHT) process diamond is synthesized close to thermodynamic equilibrium. The maximum size of crystals is limited to about 1 cm³. The kinetically controlled low pressure synthesis by CVD methods represents an alternative concept with higher scalability. Surfaces of approx. 1 m² have already been coated with polycrystalline films using the hot filament method.

High purity crystals are grown by plasma (preferentially microwave plasma) techniques. To obtain single crystals with technologically relevant dimensions, heteroepitaxy on foreign materials is currently the most promising approach. In the present talk the development and current state of the art of diamond heteroepitaxy will be summarized. Additionally, some prominent examples for applications of our samples will be given.

In detail, the following topics will be discussed:

- iridium, the ideal growth surface for the nucleation of oriented diamond with unmatched epitaxial alignment¹
- the transition of highly oriented diamond grains on Ir to a real single crystal²
- Ir/YSZ/Si(001) multilayer substrates - the key to single crystal diamond wafers³
- photonic crystal structures in heteroepitaxial diamond⁴
- SiV centers in epitaxial diamond nano-islands: a host for single photon sources⁵
- diamond mosaic crystals as ultimate neutron monochromator material⁶

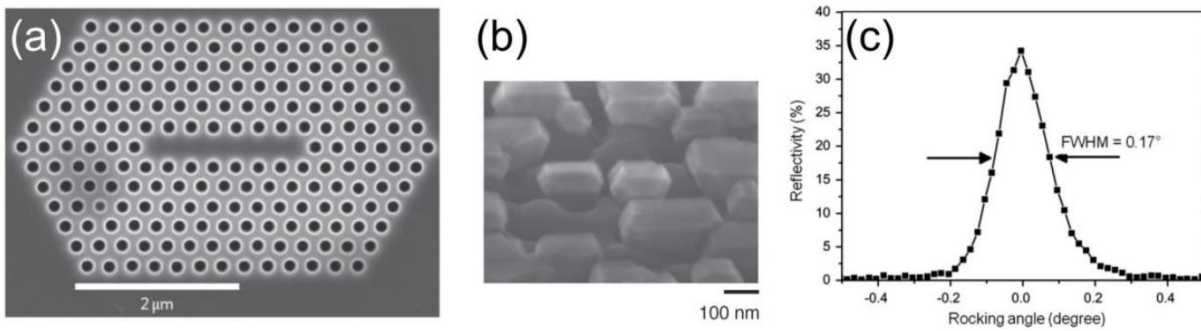


Fig.: 1: (a) Photonic crystal structure in diamond/Ir/YSZ/Si(001)⁴
 (b) epitaxial diamond nano-islands containing single SiV centres⁵
 (c) neutron reflectivity of a 1-mm thick diamond mosaic crystal⁶.

[1] M. Schreck, H. Roll, B. Stritzker, Appl. Phys. Lett. 74 (1999) 650.

[2] M. Schreck, F. Hürmann, H. Roll, J.K.N. Lindner, B. Stritzker, Appl. Phys. Lett. 78 (2001) 192.

[3] S. Gsell, T. Bauer, J. Goldfuß, M. Schreck, B. Stritzker, Appl. Phys. Lett. 84 (2004) 4541.

[4] J. Riedrich-Möller, L. Kipfstuhl, C. Hepp, E. Neu, C. Pauly, F. Mücklich, A. Baur, M. Wandt, S. Wolff, M. Fischer, S. Gsell, M. Schreck, C. Becher; Nature Nanotechnology 7 (2012) 69:

[5] E. Neu, M. Fischer, S. Gsell, M. Schreck, C. Becher, Phys. Rev. B 84 (2011) 205211.

[6] A. K. Freund, S. Gsell, M. Fischer, M. Schreck, K.H. Andersen, P. Courtois, G. Borchert, M. Skoulatos, Nucl. Instrum. Methods A 634 (2011) S28.

Organic Topological Insulators in Organometallic Lattices

Feng Liu

Department of Materials Science and Engineering, University of Utah,

Salt Lake City, UT 84112, USA

fliu@eng.utah.edu

Topological insulators (TIs) are a recently discovered class of materials having insulating bulk electronic states but conducting boundary states distinguished by nontrivial topology. So far, several generations of TIs have been theoretically predicted and experimentally confirmed, all based on inorganic materials. In this talk, I will present our recent study of a family of two-dimensional organic TIs made of organometallic lattices ^[1-4], based on first-principles calculations and tight-binding model analyses. Designed by assembling molecular building blocks of organometallic compounds with strong spin-orbit coupling into a hexagonal and Kagome lattices, these new classes of organic TIs are shown to exhibit nontrivial topological edge states in both Dirac bands and flat Chern bands ^[1,2], which are robust against significant lattice strain. Realization of anomalous quantum Hall effect in magnetic organic TIs with the inclusion of transition metal elements will also be discussed ^[3,4]. We envision that organic topological materials will greatly broaden the scientific and technological impact of topological materials.

[1] Z. F. Wang, Zheng Liu and Feng Liu, "Organic topological insulators in organometallic lattices", *Nature Commun.*4, 1471 (2013).

[2] Z. Liu, Z. F. Wang, J.-W. Mei, Y. Wu and Feng Liu, "Flat Chern Band in a Two-Dimensional Organometallic Framework", *Phys. Rev. Lett.*110, 106804 (2013).

[3] Z. F. Wang, Z. Liu and Feng Liu, "Quantum anomalous Hall effect in 2D organic topological insulator", *Phys. Rev. Lett.* 110, 196801 (2013).

[4] Z. F. Wang, N. Su and Feng Liu, "Prediction of a Two-Dimensional Organic Topological Insulator", *Nano Letters*, 13, 2842 (2013).

Transport Properties and Electronic Structure of Individual metallic Quantum Dots on Dielectric Supports: A Local View

Wolf-Dieter Schneider

Institute of Condensed Matter Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL),

CH-1015 Lausanne, Switzerland

and

Fritz-Haber-Institute of the Max-Planck-Society, D-14195 Berlin, Germany

wolf-dieter.schneider@epfl.ch

Contacts between metallic nanostructures and semiconducting or dielectric supports are expected to constitute the basic building blocks of future nanoscale electronics and nanocatalysts. We investigate with low-temperature scanning probe techniques the transport properties and the local electronic structure of individual nanocontacts formed between flat metallic islands and their supporting substrates. In the first example, Pb on HOPG, on *h*-BN/Ni(111), and on NaCl/Ag(111), the observed differential conductance spectra reveal a suppression at small bias voltages characteristic for the presence of dynamical Coulomb blockade (DCB) phenomena. By increasing the thickness of the dielectric NaCl film from 2 to 3 monolayers, we observe a transition from the DCB regime to the orthodox Coulomb staircase (CBS) regime. A comparison with calculations based on the theory of environmentally assisted tunneling and on the orthodox theory for a double barrier junction allows us to determine the capacitances and resistances of the contacts, which depend systematically on the island-substrate contact area ^[1]. In the second example, tunneling spectroscopy on two-dimensional Li-islands on CaO/Mo(001) reveals a standing wave pattern which indicates the metallic character of these monolayer nanoislands. Moreover, depending on the capacitances and resistances of the metal-oxide junction, also here DCB as well as CBS phenomena are observed. In addition, an unoccupied gap state below the CaO conduction band, which originates from Li-O hybridization across the metal-oxide interface is detected. With increasing diameter of the Li islands, this state shifts towards the Fermi level, reflecting the decreasing workfunction at higher Li coverage ^[2]. These findings facilitate quantitative investigations of the local electronic structure of metallic quantum dots. They are important for future studies of the physical and chemical properties of supported nanostructures in relation to superconductivity ^[3], magnetism, and catalysis.

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[1] C. Brun, K.-H. Müller, I. P. Hong, F. Patthey, C. Flindt, and W.-D. Schneider, Phys. Rev. Lett. **108**, 126802 (2012).

[2] X. Shao, Y. Cui, W.-D. Schneider, N. Nilius, H.-J. Freund, J. Phys. Chem. C **116**, 17980 (2012).

- [3] C. Brun, I.-P. Hong, F. Patthey, I. Yu. Sklyadneva, R. Heid, P. M. Echenique, K. P. Bohnen, E. V. Chulkov, and W.-D. Schneider, Phys. Rev.Lett. **102**, 207002 (2009).

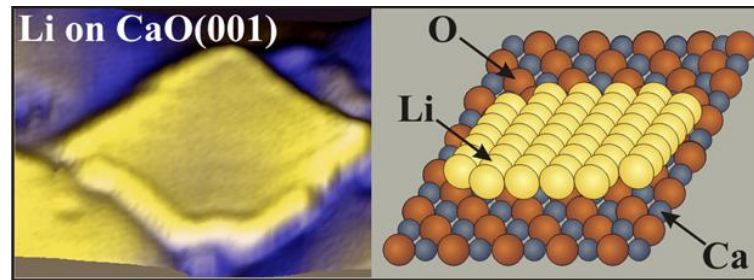


Figure 1. Topographic image (STM) of a large Li island on CaO/Mo(001) ($25 \times 25 \text{ nm}^2$, 2.0 V) and atomicvisualization^[2].

Atomistic Mechanism for Oxygen Evolution Reaction at TiO₂(110)/bulk Water Interface: The Role of Photohole-Assisted O-O Bond Formation

M. Lucking, Yiyang Sun, Damien West, and [Shengbai Zhang](#)

Department of Physics, Applied Physics & Astronomy, Rensselaer Polytechnic Institute, Troy,

New York 12180, USA

zhangs9@rpi.edu

Despite the vast literatures on water splitting at TiO₂/water interfaces, a quantum mechanical atomistic mechanism appears lacking, due largely to the difficulty in theorizing and modeling solid/liquid interfaces. Here, we postulate how to model the kinetic barriers for the reduction of water molecules, based on which we propose an atomistic mechanism for photocatalytic oxygen evolution reaction on the TiO₂ surface in aqueous environment. Our first-principles calculations reveal the crucial role of photogenerated holes in the process. In particular, the formation of an O₂ molecule requires the transformation of a pair of occupied O dangling bond states below TiO₂ valence band edge into a high-energy antibonding O₂ $\sigma^*(2p)$ state above the TiO₂ conduction band edge. Occupying the high-lying state makes the reaction barrier prohibitively high. Introducing two photoholes in the process, however, can eliminate the occupation of the high-energy state during the formation of O₂ and hence reduces the reaction barrier to about 0.9 eV. It suggests measurable reaction at room temperature in qualitative agreement with experiments.

Efficient 3D-WKB STM Simulation Model

K. Palotás, G. Mándi, W. A. Hofer

The University of Liverpool, UK

Whofer@liverpool.ac.uk

We review the recently developed three-dimensional (3D) atom-superposition approach for simulating scanning tunneling microscopy (STM) and spectroscopy (STS) based on ab initio electronic structure data. In the method, contributions from individual electron tunneling transitions between the tip apex atom and each of the sample surface atoms are summed up assuming the one-dimensional (1D) Wentzel-Kramers-Brillouin (WKB) approximation in all these transitions. This 3D WKB tunneling model is extremely suitable to simulate spin-polarized STM and STS on surfaces exhibiting a complex noncollinear magnetic structure, i.e., without a global spin quantization axis, at very low computational cost. The tip electronic structure from first principles can also be incorporated into the model, that is often assumed to be constant in energy in the vast majority of the related literature, which could lead to a misinterpretation of experimental findings. Using this approach, we highlight some of the electron tunneling features on a prototype frustrated hexagonal antiferromagnetic Cr monolayer on Ag(111) surface. We obtain useful theoretical insights into the simulated quantities that is expected to help the correct evaluation of experimental results. By extending the method to incorporate a simple orbital dependent electron tunneling transmission, we reinvestigate the bias voltage- and tip-dependent contrast inversion effect on the W(110) surface. STM images calculated using this orbital dependent model agree reasonably well with Tersoff-Hamann and Bardeen results. The computational efficiency of the model is remarkable as the k-point samplings of the surface and tip Brillouin zones do not affect the computational time, in contrast to the Bardeen method. In a certain case we obtain a relative computational time gain of 8500 compared to the Bardeen calculation, without the loss of quality. We discuss the advantages and limitations of the 3D WKB method, and show further ways to improve and extend it.

Direct Observation of Nematicity and Topological Defects through Electronically Driven Phase Transitions in $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$

Jing Tao

Brookhaven National Laboratory, USA

jtao@bnl.gov

Competing degrees of freedom in strongly correlated systems give rise to a variety of electronic phases and phase transitions as a function of temperature, doping levels, magnetic field and pressure, etc. Symmetry and symmetry breaking have been considered to play a key role in the electronic structures in many correlated materials, particularly in doped transition metal oxides. Recent researches have demonstrated that nematic and smectic states, with certain broken symmetry, are essential in understanding materials properties such as high- T_c superconductivity. Here we report direct observations of electronic nematicity in doped manganites $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$, which is a 3D system with superstructure modulation at low temperatures resulted from competing spin, charge, orbital and lattice. Both the electron diffraction results and HRTEM images obtained from single crystal domain of $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$ clearly show a C4 to C2 symmetry breaking in the superstructures at intermediate temperature range upon cooling. Upon cooling the electronic nematicity persists in the electronic structure until long-range ordering forms as a stripe phase at low temperatures. During warming process, we identified topological defects and their formation and evolution in the superstructures, indicating that the phase transition is through proliferation of dislocations which is a center mechanism of electronic liquid crystal transition. Theoretical simulations will also be provided for better interpretation of the underlying physics in the phenomena.

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A Multi-State Molecular Switch Based on STM Tunneling Electron-Induced Enantiomerization of an Endohedral Fullerene Sc₃N@C₈₀

Hrvoje Petek

Department of Physics and Astronomy, University of Pittsburgh

petek@pitt.edu

Single molecule switches represent the ultimate miniaturization of electronic devices. Living organisms employ single molecule isomerization for transduction of energy and sensing of light. We demonstrate a single molecule switch based on rotation of Sc₃N cluster within C₈₀ fullerene cage among three distinct sets of stable enantiomeric configurations. Scanning tunneling microscopy imaging of the switching amplitude modulation within single molecules, together with ab initio theory, identify the rotation and axis switching isomerization pathways. Bias-dependent action spectra and modeling implicate the antisymmetric stretch vibration of Sc₃N cluster as the dominant pathway for the energy transfer from tunneling electrons to cluster rotation. Switching of the molecular conductivity through internal cluster motion, without altering the molecular shape, offers substantial advantage for the integration of endohedral fullerene-based single-molecule devices.

Electrically Driven Molecular Machines at Surfaces

Karl-Heinz Ernst^{1,2,*}

¹ *Nanoscale Materials Science, Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland*

² *Department of Chemistry, University of Zurich, Winterthurerstr. 190, CH-8057 Zürich, Switzerland*

Karl-Heinz.Ernst@empa.ch

Molecular recognition among chiral molecules on surfaces is of paramount importance in Directional motion at the nanoscale is an intrinsic feature of nature's biological motors and machines. For instance, in living cells motor proteins fueled by the hydrolysis of ATP move along microtubules in order to support several essential cellular functions. Fueled translational motion along a surface by employing entirely synthetic systems remains an extremely challenging goal and will be the key to the artificial molecular transporters that offer fascinating opportunities for future technologies. We present here the design of an artificial molecular four-wheel drive machine, based on chiral overcrowded systems, and demonstrate that the concerted action of molecular rotary motors integrated in this system can be used to induce translational motion across a metal surface^[1]. Excitation with tunneling electrons emanating from the tip of a scanning tunneling microscope (STM) results in rotational movement of the motor units, which, in turn, leads to translational movement of the entire molecular machine. Changing the unidirectional nature of the rotary motion of individual motor units tunes the self-propelling machine to either follow random or preferentially linear trajectories on the surface. Without the need for (solution phase) chemical fuels, this self-propulsion system offers bright prospects for designing complex nanomachinery for transport and assembly.

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[1] T. Kudernac, N. Ruangsapichat, M. Parschau, B. Maciá N. Katsonis, S. R. Harutyunyan, K.-H. Ernst, B. L. Feringa, *Nature* **479** 208 (2011).

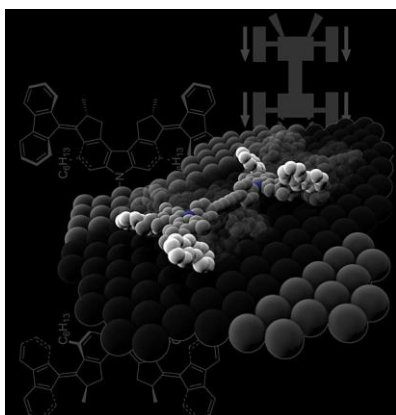


Figure 1: Sketch of a molecule with four unidirectional rotors (light grey) whose electronic and vibronic excitation results in linear propulsion on a surface.

Nanoparticles of Ceria: Their Microstructure and Impedance Response

¹ *Siu-Wai Chan*, ^{1,2} *Chunyan Tian*, ^{1,3} *Apisak Meesrisom*, ^{1,4} *Palm Ng*, and

¹ *Joan M. Raitano*

¹ *Materials Science and Engineering program, Department of Applied Physics and Applied Mathematics,*

Henry Krumb School of Mines, Columbia University, New York, NY 10027, USA

² *IBM East Fishkill, New York, NY*, ³ *Air Force Research Laboratory, XX, MA*

⁴ *Bayside High School, Queens, New York, NY*

sc174@columbia.edu

Ceria, which Prof. Arthur Nowick studied for many years, has been used in automobile catalytic convertors to abate gas pollutants, in fuel cell electrodes and in gas sensors. The non-stoichiometry and defect chemistry of ceria, as well the fundamentals of grain boundary resistance to ionic transport, was thoroughly investigated by his former graduate students, Drs. Tuller, Wang and Gerhardt. With the present availability of mono-dispersed nanoparticles of ceria, there exist a new opportunity to explore and investigate the solid state chemistry of nano-ceria, compared to the bulk form, as a model system for nano-oxides. We report on our recent impedance spectroscopy measurements of nano ceria doped with Pd, one of the metal catalysts used in automobile catalytic convertors. We review how different heat-treatments can significantly change the transport properties and the effects of these treatments on grain boundary impedance. Whenever appropriate, we compare these with earlier results obtained from ceria thin films.

AFM Based Characterization of ZnO Nanostructures

Christian Teichert,

Institute of Physics, Montanuniversität Leoben, Franz Josef Str. 18, A-8700 Leoben, Austria

teichert@unileoben.ac.at

ZnO is a versatile and multifunctional material with potential applications in photovoltaics and electronics as well as actuators.

In the first part, we report on atomic-force microscopy (AFM) based investigations to study the morphological, electrical, and optoelectric properties of arrays of upright standing ZnO nanorods. We have demonstrated that - against the intuition - AFM is applicable to study the morphology of individual freestanding ZnO nanorods ^[1], and conductive atomic-force microscopy (C-AFM) allows to characterize the electric properties of these nanostructures ^[2]. C-AFM measurements under simultaneous light irradiation - so called photoconductive AFM reveals a persistent photoconductivity which can be addressed to photo-excitation of charge carriers localized at defect states ^[3].

In the second part, we study polycrystalline ZnO multilayer varistors. C-AFM ^[4] and scanning surface potential microscopy (SSPM) ^[5] have been employed to explore the electrical properties of the ZnO grain boundaries which are indispensable for the varistor effect. The results are complemented by electron backscatter diffraction and micro four-point probe measurements.

Contributions by A. Andreev, I. Beinik, G. Brauer, X.Y. Chen, A. Djurišić, M. Hofstätter, Y. Hou, Y. F. Hsu, M. Kratzer, A. Nevsad, M. Schloffer, M. Hofstaetter, and P. Supancic are acknowledged.

- [1] G. Brauer, et al., *Nanotechnology* **18** (2007) 195301.
- [2] I. Beinik, et al., *J. Appl. Phys.* **110** (2011) 052005.
- [3] I. Beinik, et al., *Beilstein J. Nanotechnol.* **4** (2013) 208.
- [4] M. Schloffer et al., *J. Eur. Ceram. Soc.* **30** (2010) 1761.
- [5] A. Nevsad, et al., *Proc. SPIE* **8626** (2013) 862618-1-8.

In-Situ Microscopy of 2D Materials: Growth, Processing, Properties

Peter Sutter

Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973

psutter@bnl.gov

Two-dimensional (2D) crystals, such as graphene, hexagonal boron nitride, and several metal dichalcogenides, represent a new class of functional materials with a wealth of interesting physical and chemical properties. While initial studies on these systems have been enabled primarily by monolayer sheets isolated from layered bulk crystals, broader fundamental investigations and potential applications require reliable and scalable methods for fabricating and processing high-quality 2D membranes.

I will discuss recent advances in understanding the synthesis and processing of 2D materials on metal substrates, derived primarily from real-time observations by surface electron microscopy complemented by high-resolution scanning probe microscopy and in-situ spectroscopy methods. Real-time low-energy electron microscopy and associated analytical methods provide insight into the fundamental growth mechanisms of 2D crystals, their interaction with a metal substrate, as well as processes that modify the substrate coupling and may be harnessed for the bottom-up assembly of functioning devices. Going beyond homogeneous 2D crystals, heterostructures that combine different 2D materials in layer stacks or as several tightly interfaced components in a single, atomically thin membrane promise tunable properties and greatly extended functionality, and raise fundamental questions on interface formation, intermixing, strain, and polarity in a new context at reduced dimensionality. I will demonstrate pathways to overcoming the formidable challenges involved in the controlled fabrication of such novel materials. Our combined findings establish a powerful toolset for the scalable fabrication of 2D materials and their heterostructures for research and applications.

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Electronic Transport on the Nanoscale

Rolf Möller

Faculty of Physics, University of Duisburg-Essen

rolf.moeller@uni.due-de

To study the transport through objects at the nanoscale a scanning tunneling microscope with several tips is used. Two different configurations will be discussed. The lateral transport of electrons may be studied by using two tips to drive a current parallel to the surface. A third tip enables to map the corresponding electrochemical potential. Measurements for a 2D conducting layer will be discussed^[1]. The measurements are complemented by the analysis of the density of states, e.g. revealing the scattering of surface state electrons by steps and defects on the Bi(111) surface^[2]. To analyze the transport perpendicular to the surface, a thin metallic layer is placed on a semiconducting surface. At the interface a Schottky barrier is formed, which can only be overcome by electrons of sufficient energy. This may be used to split the current of electrons coming from the tip of the microscope into two parts, the ballistic electrons and the electrons which have been scattered. This technique has been applied to study the ballistic transport of electrons through individual molecules^[3]. On the other hand inelastic processes may be revealed by analyzing the fluctuations in the tunneling current observed at different positions of the tunneling tip above an adsorbed molecule^[4].

[1] J. Homoth, M. Wenderoth, T. Druga, L. Winking, R.G. Ulbrich, C.A. Bobisch, B. Weyers, A. Bannani,

E. Zubkov, A.M. Bernhart, M.R. Kaspers, R. Möller, *Nano Letters* 9, 1588 (2009)

[2] M. C. Cottin, C. A. Bobisch, J. Schaffert, G. Jnawali, A. Sonntag, G. Bihlmayer, and R. Möller,

Appl. Phys. Lett. 98, 022108 (2011).

[3] A. Bannani, Ch. Bobisch, R. Möller, *Science* 315, 1824 (2007)

[4] J. Schaffert, M.C. Cottin, A. Sonntag, H. Karacuban, C.A. Bobisch, N. Lorente, J.-P. Gauyacq,

R. Möller, *Nature Materials* 12, 223–227 (2013)

Endohedral Single Molecule Magnets 123

Thomas Greber

University of Zurich, Switzerland

greber@physik.uzh.ch

In an anisotropic environment paramagnetic atoms may be stabilized in a given magnetic doublet, where the magnetic moment is parallel or antiparallel to a fixed axis in space.

This also holds inside a carbon nano-sphere like C80 ^[1]. If more than one Dy atom are placed in DySc₃-nN@C80 (n=1,2,3), then the magnetic interactions between the n paramagnetic centers lead to peculiar ground states that are reflected in the hysteresis curves of the different molecules.

[1] An Endohedral Single-Molecule Magnet with Long Relaxation Times: DySc₂N@C80, Westerström et al., J. Am. Chem. Soc. 134 (2012) 9840.

Reversible Spin Control of Individual Magnetic Molecule by Hydrogen Atom Adsorption

Wende Xiao

Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100190, China.

wdxiao@iphy.ac.cn

Control over charge and spin states at the single molecule level is crucial not only for a fundamental understanding of charge and spin interactions but also represents a prerequisite for development of molecular electronics and spintronics. While charge manipulation has been demonstrated by gas adsorption and atomic manipulation, the reversible control of a single spin of an atom or a molecule has been challenging. Typically, atomic or molecular spin can be probed as a Kondo effect that manifests itself as a conductance anomaly at the Fermi level when it is coupled to a metallic system. However, an effective method to manipulate molecular spin both individually and ensemble has been limited. Herein we demonstrate that the Kondo resonance of manganese phthalocyanine molecules on a Au(111) substrate can be reversibly switched off and on via a robust route through attachment and detachment of single hydrogen atom to the magnetic core of the molecule. As further revealed by density functional theory calculations, even though the total number of electrons of the Mn ion remains almost the same in the process, gaining one single hydrogen atom can lead to redistribution of charges within 3d orbitals with a reduction of the molecular spin state from $S = 3/2$ to $S = 1$ that directly contributes to the disappearance of the Kondo resonance. This process can be reversed by a local voltage pulse or thermal annealing to desorb the hydrogen atom, accompanied by a recovery of the molecular Kondo resonance.