Committee:
Prof. Dr. Hans-Peter Steinrück, U Erlangen-Nürnberg, Erlangen (Chairman)
Prof. Dr. Hans-Joachim Freund, Fritz-Haber-Institut, Berlin
Prof. Dr. Eberhard Umbach, KIT, Karlsruhe
Prof. Dr. Horst Niehus, HU Berlin
Prof. Dr. Waldemar A. A. Macedo, CDTN, Belo Horizonte (Vicechair)
Prof. Dr. Fernando Lázaro Freire Jr., PUC-Rio, Rio de Janeiro
Prof. Dr. André Avelino Pasa, UFSC, Florianópolis
The workshop is the eighth meeting of scientists in surface science and nanoscience from Brazil and Germany stimulated by the successful previous editions.

Main topics are fundamental problems (theory and experiment) in surface science and nanoscience as well as corresponding applications, with special emphasis to the areas of nanostructured materials, thin films, polymers, devices and catalysis. All of these represent active areas in both countries, with promising perspectives for the future.

Location:
Welcome Kongresshotel
Mußstraße 7
96047 Bamberg

Contact:
Prof. Dr. Hans-Peter Steinrück (Chair)
Friedrich-Alexander-Universität
Erlangen-Nürnberg (FAU)

Prof. Dr. Waldemar A. A. Macedo (Vicechair)
Centro de Desenvolvimento da Tecnologia Nuclear (CDTN), Belo Horizonte

www.8gbw.org
Conference Site:
Welcome Kongresshotel Bamberg
Mußstraße 7 |
96047 Bamberg
Tel: +49 951 7000-0

Conference Office:
Sunday: 15:00 – 22:00
Monday: 08:30 – 16:30

Special Events:
Sunday evening (19:00):
  ➔ Welcome dinner
Tuesday evening (18:00):
  ➔ Short guided tour through Bamberg and Franconian dinner
Wednesday afternoon and evening (Departure: 13:30):
  ➔ Excursion to Franconian cultural sites, including conference dinner

Oral presentations:
Please bring your own computer or arrange with a colleague. In case of problems, please approach the local organizers at the beginning of the meeting.
Invited talks: 35 min + 10 min discussion
Contributed talks: 15 min + 5 min discussion
!! All speakers are urgently requested to stay in time to leave ample time for discussions !!

Posters:
There are two Poster Sessions (Tuesday and Thursday); at both sessions all posters will be presented.
Poster size: A0, vertical

Contacts
Prof. Dr. Hans-Peter Steinrück         Dr. Andreas Bayer
  ➔ hans-peter.steinruack@fau.de        ➔ andreas.bayer@fau.de
  ➔ Tel: +49 179 240 1255              ➔ Tel: +49 160 9144 2373
### Monday, 16.9.2013

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<tr>
<th>Time</th>
<th>Speaker</th>
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<tr>
<td>9:30</td>
<td><strong>Prof. Dr. Hans-Peter Steinrück</strong></td>
<td>opening</td>
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<tr>
<td>9:45</td>
<td><strong>Prof. Dr. Roberto Bechara Muniz, UFF, Niterói</strong></td>
<td>&quot;Spin dynamics of itinerant electron ferromagnetic nanostructures&quot;.</td>
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<tr>
<td>10:30</td>
<td>COFFEE</td>
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<tr>
<td>11:00</td>
<td><strong>Prof. Dr. Karsten Horn, Fritz-Haber-Institut, Berlin</strong></td>
<td>&quot;Epitaxial graphene and its electronic structure&quot;.</td>
</tr>
<tr>
<td>11:45</td>
<td><strong>Prof. Dr. Abner de Siervo, UNICAMP, Campinas</strong></td>
<td>&quot;On the electronic and magnetic properties of Co on Graphene/SiC(0001)&quot;.</td>
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<tr>
<td>12:30</td>
<td>LUNCH</td>
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<tr>
<td>14:15</td>
<td><strong>Prof. Dietrich Menzel, TU München</strong></td>
<td>&quot;Ultrafast charge transfer at graphene monolayers on differently coupled substrates&quot;.</td>
</tr>
<tr>
<td>14:35</td>
<td><strong>Prof. Dr. Edmar Avellar Soares, UFMG, Belo Horizonte</strong></td>
<td>“Structural and electronic properties of Graphene-covered metal monolayers on Ni(111)(1x1)“.</td>
</tr>
<tr>
<td>14:55</td>
<td><strong>Prof. Dr. Martin Weinelt, Freie Universität Berlin</strong></td>
<td>&quot;Femtomagnetism of lanthanide thin films&quot;.</td>
</tr>
<tr>
<td>15:40</td>
<td><strong>Mrs. Kenia Novakoski Fischer, MPI of Microstructure Physics, Halle</strong></td>
<td>&quot;Epitaxial growth of Fe on Ag(001) revisited: Stress signatures of interfacial intermixing and epitaxial film growth&quot;.</td>
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<td>16:00</td>
<td>COFFEE</td>
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<tr>
<td>16:35</td>
<td><strong>Prof. Dr. Gabriel Vieira Soares, UFRGS, Porto Alegre</strong></td>
<td>&quot;Thermal stability of dielectrics on germanium: role of the substrate&quot;.</td>
</tr>
<tr>
<td>17:20</td>
<td><strong>Prof. Dr. Michael Grunze, Universität Heidelberg</strong></td>
<td>&quot;Melanosomes in real and Fourier space: biointerphase science at the resolution limit&quot;.</td>
</tr>
<tr>
<td>18:05</td>
<td><strong>Mr. Diogo Reis, UFMG, Belo Horizonte</strong></td>
<td>“Determination of the Surface Atomic Structure of the Topological Insulators Bi$_2$Se$_3$ and Bi$_2$Te$_3$ by Low Energy Electron Diffraction&quot;.</td>
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**Tuesday, 17.9.2013**

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<th>Time</th>
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<tr>
<td>9:00</td>
<td><strong>Prof. Dr. Luiza Rocco, UFRJ, Rio de Janeiro</strong></td>
<td>&quot;Ultrafast charge transfer in poly(thiophene) probed by resonant Auger spectroscopy&quot;.</td>
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<tr>
<td>9:45</td>
<td><strong>Prof. Dr. Christof Wöll, Karlsruhe Institute of Technology (KIT)</strong></td>
<td>&quot;Interfacial Systems Chemistry: Surface templated assembly of three-dimensional functional frameworks&quot;.</td>
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<tr>
<td>11:00</td>
<td><strong>Mr. Shadi Fatayer, UNICAMP, Campinas</strong></td>
<td>&quot;Metal-Tetraphenyl porphyrins in vicinal gold: a STM and XPS study“.</td>
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</table>
| 11:20 | **Dr. Hubertus Marbach, Universität Erlangen-Nürnberg.** | “Towards room temperature switching of individual molecules“.
| 11:40 | **Prof. Dr. Roberto Paniago, UFMG, Belo Horizonte** | "Structure and magnetism of ultra-thin Fe$_3$O$_4$ investigated by surface science techniques". |
| 12:30 | LUNCH                           |                                                                      |
| 14:15 | **Dr. Andreas Heinrich, IBM, San Jose, CA, USA** | "The quantum and classical properties of spins on surfaces". |
| 15:00 | **Prof. Dr. Jürgen Kirschner, MPI für Mikrostrukturphysik, Halle** | "Experiments on the exchange-correlation hole in the near-surface region". |
| 15:45 | **Dr. Thomas Stempel Pereira, SPECS Surface Nano Analysis GmbH** | “State-of-the art ARPES: new concepts for analyzers and excitation sources“.
| 16:05 | COFFEE & POSTER SESSION         |                                                                      |
| 18:00 | **SHORT GUIDED TOUR THROUGH BAMBERG & FRANCONIAN DINNER** | |
### Wednesday, 18.9.2013

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<tr>
<th>Time</th>
<th>Speaker and Affiliation</th>
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<tr>
<td>9:00</td>
<td>Prof. Dr. Paulo B. Miranda, USP, São Carlos</td>
<td>&quot;Nonlinear vibrational spectroscopy of interfaces: applications to electrocatalysis and Layer-by-Layer polymer films&quot;.</td>
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<tr>
<td>9:45</td>
<td>Prof. Dr. Timo Jacob, Universität Ulm</td>
<td>&quot;Modeling Electrochemical Systems: From Fundamentals to Batteries&quot;.</td>
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<td>10:30</td>
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<tr>
<td>11:00</td>
<td>Mr. Eduardo Pitthan, UFRGS, Porto Alegre</td>
<td>&quot;SiO₂ films on 4H-SiC: reducing interface electrical degradation due to thermal oxidation&quot;.</td>
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<tr>
<td>11:20</td>
<td>Dr. Sergey Levchenko, Fritz-Haber-Institut der MPG</td>
<td>&quot;Multiscale modeling of point defects at metal-oxide surfaces: Case study of MgO (100)&quot;.</td>
</tr>
<tr>
<td>11:40</td>
<td>Prof. Dr. Carlos F. O. Graeff, UNESP, Bauru</td>
<td>&quot;Electrically Detected Magnetic Resonance – basic concepts and applications&quot;.</td>
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<tr>
<td>12:30</td>
<td>LUNCH</td>
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<tr>
<td>13:30</td>
<td>CONFERENCE EXCURSION &amp; CONFERENCE DINNER</td>
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### Thursday, 19.9.2013

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<tr>
<th>Time</th>
<th>Speaker and Affiliation</th>
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<tr>
<td>9:00</td>
<td>Prof. Dr. Katharina Al Shamery, Universität Oldenburg</td>
<td>&quot;Elementary processes at nanostructured (photo)catalysts&quot;.</td>
</tr>
<tr>
<td>9:45</td>
<td>Prof. Dr. Daniela Zanchet, UNICAMP, Campinas</td>
<td>&quot;In situ characterization of catalysts for hydrogen production&quot;.</td>
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<td>10:30</td>
<td>COFFEE</td>
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<tr>
<td>11:00</td>
<td>Prof. Fabiano Bernardi, UFRGS, Porto Alegre</td>
<td>&quot;H₂ reduction reaction of CuₓNi₁₋ₓ / CeO₂ (x=0, 0.5, 1) nanoparticles&quot;.</td>
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<tr>
<td>11:20</td>
<td>Mr. Christopher Penschke, Humboldt-Universität Berlin</td>
<td>&quot;Au adsorption on oxygen defective CeO₂(111) studied by density functional theory&quot;.</td>
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<tr>
<td>11:40</td>
<td>Dr. Katrin Winkler, DFG (German Science Foundation)</td>
<td>&quot;Information on DFG and DAAD programs concerning Brazilian-German projects&quot;.</td>
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<td>12:30</td>
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<tr>
<td>14:15</td>
<td>Prof. Dr. Martin Stutzmann, Walter Schottky Institut, TU München</td>
<td>&quot;Electronic control of catalysis on wide-gap semiconductors&quot;.</td>
</tr>
<tr>
<td>15:00</td>
<td>Prof. Dr. Ado Jório, UFMG, Belo Horizonte</td>
<td>&quot;Raman Spectroscopy Analysis of Graphene-Related Systems&quot;.</td>
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<tr>
<td>15:45</td>
<td>Dr. Fernando Stavale, CBPF, Rio de Janeiro</td>
<td>&quot;Revealing the optical properties of intrinsic defects in crystalline ZnO films&quot;.</td>
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<tr>
<td>16:05</td>
<td>COFFEE &amp; POSTER SESSION</td>
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<td>19:00</td>
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### Friday, 20.9.2013

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<tr>
<th>Time</th>
<th>Speaker and Affiliation</th>
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<tr>
<td>9:00</td>
<td>Prof. Dr. Jürgen Behm, Universität Ulm</td>
<td>&quot;Bimetallic Catalysis: Trends in the Chemistry of Bimetallic Surfaces&quot;.</td>
</tr>
<tr>
<td>9:45</td>
<td>Jeison Fischer, MPI of Microstructure Physics, Halle</td>
<td>&quot;Superparamagnetic Response of Fe-coated W Tips in Spin-polarized Scanning Tunneling Microscopy&quot;.</td>
</tr>
<tr>
<td>10:05</td>
<td>Dr. Christian Papp, Universität Erlangen-Nürnberg</td>
<td>&quot;Growth and Doping of Graphene&quot;.</td>
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<td>10:30</td>
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<tr>
<td>11:00</td>
<td>Prof. Dr. Waldemar A. A. Macedo, CDTN, Belo Horizonte</td>
<td>&quot;Influence of magnetic annealing and interdiffusion on the exchange bias of CoFe/IrMn layered nanostructures&quot;.</td>
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<tr>
<td>11:20</td>
<td>Prof. Dr. Hans-Joachim Freund, Fritz-Haber-Institut, Berlin</td>
<td>&quot;From pure metal supported oxide films to two-dimensional zeolite films&quot;.</td>
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<tr>
<td>12:05</td>
<td>Prof. Dr. Hans-Peter Steinrück – concluding remarks</td>
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<td>12:30</td>
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Abstracts
of
invited talks and contributed talks
We review our theoretical studies of spin dynamics in ferromagnetic nanostructures adsorbed on metallic substrates. Our approach is based on a realistic description of the electronic structure for the substrate/adsorbate combination, and ferromagnetism in the film is driven by on site Coulomb interaction between the d electrons treated in mean field theory. Spin excitations are described by the transverse spin dynamic susceptibility, which is calculated within the random phase approximation. We discuss the influence of spin-orbit coupling on the spin dynamics of ultrathin films of Fe adsorbed onto W(110), with especial attention given to the spin current that propagates through the metallic substrate when the magnetization of the ferromagnetic nanostructure is set into precession.
Epitaxial graphene and its electronic structure
Karsten Horn1,*
(1) Department of Physical Chemistry, Fritz Haber Institute of the Max Planck Society, Berlin, Germany
e-mail: horn@fhi-berlin.mpg.de

With all the excitement about the “wonder material” graphene, one may well ask whether this is just publicity and media hype, or what the real merits of this “old and new” material really are. It is certainly clear that the discovery of graphene, a material that exhibits most unusual properties and promises some interesting applications, has opened a new chapter in solid state physics. Materials science, surface and “nano”-science, solid state physics and even quantum electrodynamics meet in a most surprising way in graphene research. It is also sign of the maturity of these fields (with surface science being particularly important in this “thinnest material conceivable”) and their experimental and theoretical methods that so much has been learnt in such a short time since the discovery of graphene’s unique electronic properties in 2005.
In the talk I will cover the band structure of single and bilayer/multilayer graphene, with particular emphasis on the shape of the bands at the Dirac point, both for graphene on semiconductors and metals. An important aspect in these studies is the possibility to induce ambipolar doping by chemical means, to change the position of the Fermi level over a wide range. Emphasis will be laid on the analysis of the spectral function of graphene in terms of the coupling of the photohole to elementary excitations such as phonons and plasmons, and the effect of defects (such as small rotational domains) on the shape of the Fermi surface and scattering rate. A wealth of new graphene-related system can be prepared by intercalating different metals in between graphene and a substrate. The interaction with ferromagnetic metals will also be covered; these systems have received particular attention because of a possible use of graphene as a spin filter. Thus while time will show whether many of the envisaged applications of graphene can be realized, the analysis of such experiments shows that graphene is ideally suited to study solid state physics in a true 2D material, and an abatement of the storm of activities around this material is not expected any time soon.
On the electronic and magnetic properties of Co on Graphene/SiC(0001)

Luis H. de Lima, Richard Landers, and Abner de Siervo*

(1) Department of Applied Physics, Institute of Physics “Gleb Wataghin”, State University of Campinas, 13083-859, Campinas, SP, Brazil

e-mail: asiervo@ifi.unicamp.br

Fabrication of monodispersed and uniform-sized nanoclusters on substrates is currently a challenging subject that has received great interest. Monodispersed metal nanoclusters on insulating or semiconducting substrates have a wide range of applications in heterogeneous catalysis, as well as prototypes for magnetic medias with ultrahigh-density recording [1]. A promising route to fabricate nanostructures arrays is the self-assembly of atoms and molecules induced by surface nanotemplates (atomically well-defined surfaces) that are naturally or artificially patterned at the nanoscale [2]. In this work, cobalt nanoparticles were grown on graphene/SiC(0001)[3]. The graphene was obtained by heating a SiC(0001) surface to temperatures of about 1150°C in ultrahigh vacuum and Co was directly deposited on this surface at room temperature by electron-beam evaporation and various sessions of evaporation were done with different deposition rates and times, monitored by X-Ray Photoelectron Spectroscopy (XPS) and Scanning Tunneling Microscopy (STM). Basically, the cobalt clusters prefer to form on the defects sites, in the border between different regions of the substrate. XPS shows that the cobalt peak agrees with metallic cobalt, which indicates that there is no cobalt silicide/carbide formation. The magnetic properties of nanoparticles were investigated with X-Ray Magnetic Circular Dichroism (XMCD) at PGM beamline of the Brazilian Synchrotron Light Laboratory. The XMCD results (L2,3 edge at 20K) show an enhancement of the orbital moment with an apparent in-plane anisotropy, indicating that the spin density are spherically symmetric.

Ultrafast charge transfer at graphene monolayers on differently coupled substrates

Dietrich Menzel1,*, Paolo Lacovig2, Rosanna Larciprete3, Matteo Dalmiglio2, Krassimir Kostov4, and Silvano Lizzit2

(1) Physik-Dept. E20, Techn. Univ. Muenchen, 85748 Garching, Germany, and Fritz Haber-Institut der MPG, 14195 Berlin, Germany
(2) Sincrotrone Trieste, S.S. 14 Km 163.5, 34149 Trieste, Italy
(3) CNR Institute for Complex Systems, 00133 Roma, Italy
(4) Inst. of Gen. and Inorg. Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

e-mail: dietrich.menzel@ph.tum.de

While the unique electronic properties of graphene (Gr) are being investigated vividly with all methods of surface science, the dynamics of excited states remote from the Dirac cone range are still not well known. We have therefore used the well established core-hole-clock method with adsorbed argon [1] to investigate the ultrafast charge transfer of atomically localized excited electrons to Gr monolayers (Gr-ml) on substrates with strongly varying coupling. The substrates ranged from the strongly bound, regularly buckled Gr-ml on Ru(0001) with valleys and hills and the strongly bound but unbuckled - due to good lattice match - Gr-ml on Ni(111), via the more weakly bound but still buckled Gr/Ir(111) and the flat Gr/Pt(111), to three decoupled, quasi-lifted off Gr-ml (on SiC, on O/Ru(0001), and on SiO2/Ru(0001)). Part of the results have just been accepted for publication [2]. The CT times vary widely, and by and large follow the expected correlation with the coupling strength and 2D vs. 3D final states; for the buckled layers clear differentiation of "valleys" and "hills" results. But some unexpected results are found: CT is faster than expected on weakly coupled metals and slower on Gr/Ni, and there is a specific slowdown on the decoupled layers which we interpret in terms of local charge accumulation (similar to dynamical Coulomb blockade [3]). These results will be discussed in detail.

Our results are not only interesting for the understanding of ultrafast electron dynamics on Gr but should also be important for photochemistry on Gr and for contact formation in electrochemistry.

In the present work, we report new experimental and theoretical results on graphene on Ni(111)(1x1) and on the metal intercalation on graphene on Ni(111). The experiments were performed on an ultra-high-vacuum system with a base pressure of 1 x 10^{-10} mbar and equipped with the standard facilities for sample preparation (cleaning, heating and deposition) and analysis (XPS, LEED, Mossbauer, etc). The metal intercalation was produced by evaporating monolayers of Fe, Rh and Au on the previously prepared graphene/Ni(111) and. The structural properties were investigated by using low energy electron diffraction (LEED) and photoelectron diffraction (PED) and x-ray photoelectron spectroscopy was used to probe the electronic properties. First principle calculations were performed in the framework of the SIESTA implementation. A comparison between the results obtained for the three systems will be made pointing out the main differences.

We acknowledge financial supporting from LNLS, FAPEMIG, CNPq and INCT of Carbon Nanomaterials.
Femtomagnetism is an active research field in thin film and surface magnetism, which promises magnetic writing speeds three orders faster than current technology. Investigations in this area comprise the spin and magnetization dynamics in ferro- and ferrimagnetic samples driven by femtosecond laser pulses. In the first two picoseconds after optical excitation the electronic system and the underlying lattice and spin subsystems of a ferromagnet are not in equilibrium. It remains controversial, which microscopic processes are responsible for the change of the magnetization within a few hundred femtoseconds: direct interaction with the laser field, scattering among electrons, phonons and magnons, and/or spin-transport?

To approach these problems we perform time- and angle-resolved photoemission (TR-ARPES) with lasers and high-order harmonics VUV sources. We have studied ultrafast demagnetization for the local-moment ferromagnets Gadolinium and Terbium, prepared as epitaxial films of 10 nm thickness on a W(110) substrate. In the lanthanides equilibration of the excited state involves more than one timescale, because the optical excitation occurs in the valence band but the magnetic moment is dominated by the localized 4f electrons. Following excitation by an intense infrared pulse, TR-ARPES with VUV radiation allows us to directly map the transient exchange splitting of the $\Delta_2$-like $\Sigma$ valence bands near the center of the bulk Brillouin zone [1]. In addition we probe linear magnetic dichroism in 4f photoemission [2]. While the minority valence band reacts immediately, the response of the majority counterpart is delayed by 1 ps and is only half as fast. Comparing ultrafast de- and thermal re-magnetization we conclude that the exchange splitting and the binding energy of the majority and minority spin valence bands map the true magnetization dynamics. Optical excitation drives the valence band-structure out of magnetic equilibrium, which constitutes a key ingredients for ultrafast magnetic switching.


Epitaxial growth of Fe on Ag(001) revisited: Stress signatures of interfacial intermixing and epitaxial film growth

K. Novakosi Fischer 1,2,* , D. Sander 1 , A.A. Pasa 2 and J. Kirschner 1

(1) Max Planck of Microstructure Physics, Halle, Germany
(2) Laboratório de Filmes Finos e Superfície, Universidade Federal de Santa Catarina, Florianópolis, Brazil

e-mail: kfischer@mpi-halle.mpg.de

The seemingly simple epitaxial system Fe/Ag(001) shows a complex growth behavior for the deposition of the first atomic layers Fe, where simple layer-by-layer growth has been ruled out. Instead, island growth and surface alloying, leading to a rough surface morphology were proposed [1]. A recent study suggests that the evaporation rate at room temperature is a decisive factor for the resulting Fe-Ag interface structure, where a low rate promotes layer-by-layer growth (10min/ML) [2]. We perform stress measurements by the crystal curvature technique [3] to quantify the contributions of surface stress changes and epitaxial misfit of the Fe/Ag system. We find a non-monotonic change of stress in the first 2-3 layers for growth at 300 K for a deposition rate of 1.2 min/ML. A surprisingly large tensile stress of +7.3 GPa is observed during the deposition of the first 0.5 layer Fe, which is followed by a compressive stress of -0.73 GPa from 0.5 to 1.5 layer, which levels off and changes sign to tensile stress around 2.5 layer. Then a tensile stress sets in, which leads to an average film stress of +2 GPa in a 10 layer Fe film. This unexpected complex stress variation in the monolayer range rules out simple layer-by-layer growth of an epitaxially strained Fe film, which would lead to a constant tensile epitaxial misfit stress of +1.7 GPa, in contrast to our observation. The non-monotonic stress variation of the initial growth gets less prominent for growth below 300 K, and a compressive stress regime is not observed at 225 and 150 K. We ascribe the initial strong tensile stress and the following non-monotonic stress change up to a thickness of 2-3 layers for deposition at 300 K to Fe-induced surface stress changes of Ag and to atomic intermixing, respectively. The magnitude of intermixing induced stress change is largest for the highest temperature of 300 K, and is of opposite sign as compared to the epitaxial misfit stress.

There is a current research effort to investigate high-mobility semiconductors due to their potential applications in future high performance metal-oxide–semiconductors field effect transistors (MOSFET). Germanium (Ge) is of particular interest since it presents electron and hole mobilities higher than those of Si, being a promising candidate for next generation devices[1]. However, the formation of a stable, chemical and electrical passivating layer on Ge surfaces with a low density of electrically active defects is still a challenge. Many high-k dielectrics have been proposed as possible gate insulators for Ge-based devices such as HfO$_2$, Al$_2$O$_3$, TiO$_2$, and La$_2$O$_3$ [2]. An adequate high-k material must fulfill many requirements like thermal and chemical stability with Ge. It has been reported that HfO$_2$ films on Ge can react during the deposition process and/or during post-deposition annealing. However, beneficial effects of this reaction were observed, such as the increase of the HfO$_2$ permittivity and decrease of oxygen diffusion in the film, but deleterious effects in the electrical characteristics of the interface also took place. In this way, it is mandatory to understand the atomic transport of different species during the deposition process and/or annealing steps in order to achieve acceptable low density of interface states. In the present work, we investigated the effect of thermal annealing on the physico-chemical properties of dielectrics films deposited on p-type Ge(100) and Si(001) wafers. After deposition, samples were submitted to annealing steps in different atmospheres using gases enriched in rare isotopes, which enabled us to identify species incorporated due to thermal annealing or to air exposure. The amount and depth distribution of $^{18}$O, $^2$H and $^{15}$N were determined by nuclear reaction analyses (NRA). The chemical ambient and the surface atomic composition were determined by X-ray photoelectron spectroscopy and low energy ion scattering, respectively. The total amounts of heavy elements were determined by Rutherford Backscattering spectrometry and the microstructure of the films was observed by transmission electron microscopy. Constraining differences concerning thermal stability were observed for films deposited on Si and Ge. Mechanisms of Ge and O diffusion and reaction based on the observed results will be discussed.

Melanosomes are about 500 nm small, melanocyte-based organelles in the iris cell, which produce and store the pigment melanin. Melanosomes shield their iris host cells from harmful ultra-violet radiation and sequester redox-active metal ions. In general, melanosomal malfunctions cause diseases like skin cancer, albinism, and -of particular interest here- glaucoma, a disease in which the optic nerve is damaged leading to impaired vision and blindness. The biomedical hypothesis is that structurally altered melanosomes are the trigger for the ocular affection pigmentary glaucoma. To test this hypothesis, we studied the structure and chemical composition of murine organelles from the healthy wild type C57BL/6J (B6) in comparison to organelles from the mutant DBA/2J (D2), which develops glaucoma spontaneously with synchrotron based methods. In order to avoid any artifacts due to sample preparation or radiation damage, small-angle X-ray scattering experiments (SAXS) have been performed on suspended and vitrified melanosomes. To be able to correlate the results of different methods, a cryo-stage for an optical microscope has been designed. The correlation of optical cryo-micrographs with scanning transmission X-ray images supplemented the interpretation of SAXS data with hard X-rays. The analysis showed that B6 organelles exhibit a smooth surface. They are made up of densely packed subunits with a radius of gyration $R_{B6} = (22.6 \pm 6.0)$ nm. D2 organelles feature a rough surface and show a granular substructure with constituents of $R_{D2} = (31.3 \pm 2.0)$ nm. Both phenotypes show different elemental and molecular composition in the melanosomes. The synchrotron studies, which support the hypothesis on the cause for pigmentary glaucoma, will be discussed with reference to the biomedical literature.
Surface Atomic Structure of the Topological Insulators Bi$_2$Se$_3$ and Bi$_2$Te$_3$ by Low Energy Electron Diffraction

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It is found recently that some materials exhibit a new electronic phase called topological insulator, being these materials insulators into the bulk and conductors in its edges by surface states that are topologically protected. In this way, there is a great interest in these materials to be used in spintronics [1,2]. Once the properties of the topological insulators are surface effects, a detailed knowledge of the surface structure is of great significance for a complete understanding of these properties.

In this work we present a detailed investigation of the atomic structure of the Bi$_2$Se$_3$ (0001) and Bi$_2$Te$_3$ (0001) surfaces carried out by in-situ Low Energy Electron Diffraction (LEED). The relaxations of the first six atomic layers including the first Van der Waals gap as well as the surface termination investigation will be discussed. Also, an Angle Resolved Photoemission Spectroscopy measurement will be presented.

Ultrafast charge transfer in poly(thiophene) probed by resonant Auger spectroscopy

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Ultrafast electron dynamics in the low-femtosecond regime was evaluated for poly(thiophene) by resonant Auger spectroscopy using the core-hole clock method [1]. Sulfur KLL 2,3L2,3 Auger decay spectra were measured as a function of the photon energy. Remarkable changes developed by tuning the photon energy along the sulphur 1s absorption edge, depending on the nature of the intermediate core excited states. Features characteristics of the Auger Resonant Raman effect were observed. Competition between core hole decay and delocalization of the photoexcited electron was monitored. Branching ratios of Raman (spectator) and normal Auger channels were calculated and electron delocalization times derived.

Supramolecular chemistry holds unique prospects for the fabrication of novel functional materials. Precisely defined, nanometer-sized molecular subunits which may already be rather complex self-assemble to form even more complex structures which exhibit functionalities not provided by the individual building blocks.

Here we extend the fabrication of surface-anchored networks beyond the formation of planar, two-dimensional adlayers by demonstrating the synthesis of highly-ordered, three-dimensional porous metal-organic frameworks (MOFs) nucleated on organic surfaces exposed by different types of self-assembled thiolate-based monolayers (SAMs). We will demonstrate the principle of liquid phase epitaxy [1] for the case of $\text{[Cu}_3\text{(BTC)}_2\text{(H}_2\text{O})_n\text{]}$ (HKUST-1) grown on COOH- and OH-terminated SAMs. XRD data reveal the formation of highly ordered crystalline MOF thin-films, or SURMOF, with a structure identical to that observed in the bulk on both SAMs. AFM characterization of patterned substrates by micro-contact printing ($\mu$Cp) shows clearly the selective and homogeneous deposition of the frameworks.

The availability of SURMOFs [2], opens the prospect of adding additional functionality to these ultrathin surface coatings [3] by placing nanoobjects inside the pores within the MOFs, e.g. metal clusters or dye molecules, and then characterizing their properties using electrochemistry.

Metal-Tetraphenyl porphyrins in vicinal gold: a STM and XPS study

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Systems of low dimensions, for instance periodic nanostructures at surfaces, are of great technological interest and present exciting scientific challenges. The formation of nanostructured systems, ordered with long range periodicity can be obtained by self-assembling methods. In particular, metallorganic systems in the scale of few nanometers may be efficiently synthesized by the SAM (Self-assembling of Monolayers) method [1].

Organometallic molecules of porphyrinic groups are interesting for technological applications because it is feasible through the SAM method to produce devices in order to act as organic light emitting diodes, optoelectronic systems and sensors for different applications [2].

In the present research we have investigated the electronic and morphological properties of CoTPP and NiTPP (Cobalt and Nickel Tetraphenyl Porphyrin) self-assembled on an Au(788) surface. The TPP films were deposited under UHV on an Au(788) single crystal at room temperature using a homemade Knudsen cell with a quartz crucible. The main results are based on UHV Scanning Tunneling Microscopy (STM) and X-Ray Photoelectron Spectroscopy (XPS).

The STM images showed the existence of two distinct domains at the surface as a consequence of the intermolecular interaction between the MTPP. NiTPP and CoTPP form a “nearly-square” lattice in the vicinal substrate. The growth of the Metal TPP was found to begin at the step edge of the Au(788) since were not observed “free-islands” of the molecules through the images. Using XPS analysis, we explored the chemical stability of Metal-TPP on Au(788) and the possibilities of charge transfer to the substrate.

Towards room temperature switching of individual molecules

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The STM investigation of large organic molecules on surfaces has become a vivid field in science with the vista to engineer functional devices. One important example is the application of switchable molecular building blocks in information storage. Herein, we report the observation of a supramolecular ordered phase of 2H-5,10,15,20-Tetrakis(3,5-di-tert-butyl)-phenylporphyrin (2HTTBPP) on Cu(111) by scanning tunneling microscopy (STM) in ultra-high vacuum around room temperature (RT). In this surface confined supramolecular structure, the 2HTTBPP molecules are arranged in alternating rows with intrinsically different intramolecular conformations, i.e. a concave and a convex appearance in STM. This particular system was chosen due to the expected strong molecule-substrate interactions¹,² on the one hand and the well-known conformational flexibility of the specific porphyrin derivative on the other.³ Interestingly, individual 2HTTBPP molecules spontaneously switch between these two conformations at RT. Detailed analysis of the temperature dependence of the switching behavior allows to extract the thermodynamic potentials of the thermally induced molecular switching process, and to distinguish the enthalpic and entropic contributions. In addition, we demonstrate tip-induced switching of individual molecules at 200 K.

In summary, we report a novel type of molecular switching and gained fundamental insight into the mechanism. In particular, we found evidence that entropic effects are crucial for the observed supramolecular structure and the switching mechanism at RT. Furthermore, we were able to demonstrate controlled switching of individual molecules with an STM tip close to room temperature.

Structure and magnetism of ultra-thin Fe$_3$O$_4$
investigated by surface science techniques

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The anisotropy created by the low dimensionality in ultra-thin films can promote changes in their physical properties which can be employed from the technological point of view to develop devices and materials for specific applications. The magnetic and structural properties of iron oxides in the ultra-thin limit (few atomic layers) are still poorly understood. The magnetic characterization of ultra-thin magnetite (Fe$_3$O$_4$) is important for understanding a series of phenomena such as spin polarization, metal-insulator transition and superparamagnetism. While structural determination can be achieved employing electron diffraction techniques like LEED (Low Energy Electron Diffraction) and PED (Photoelectron Diffraction), the suitable \textit{in-situ} surface science methods for magnetic characterization are XMCD (X-ray magnetic circular dichroism) and MOKE (magneto-optical Kerr effect). We employ as additional technique the Mössbauer Effect in the surface sensitive mode (CEMS).

We present a series of results of well ordered ultra-thin iron oxide on top of selected substrates such as Pd(100) and Pd(111). Samples were prepared at various thicknesses by evaporating ultra-pure Fe and dosing O$_2$ in ultra high vacuum. The XMCD and XPD studies were done at the Brazilian Synchrotron Light Laboratory (LNLS- Brazil) at the PGM and SGM beam lines respectively. LEED, MOKE and Mössbauer investigations were performed in a multi-technique surface science facility at the Department of Physics in UFMG. The goal in our work is to correlate surface structure and magnetic response as a function of film thickness using the above mentioned methods. Through XMCD for example we have determined for several films the population of Fe$^{2+}$ and Fe$^{3+}$ in the tetrahedral and octahedral sites of the magnetite structure (inverted spinel). We have established the critical thickness of magnetite formation and the transition from FeO (antiferromagnetic) to Fe$_3$O$_4$ (ferrimagnetic) in the thickness range between 0.9 and 1.2nm. Magnetic properties like anisotropy, coercitivity, field strength, and superparamagnetism obtained from MOKE and CEMS results are discussed.

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The quantum and classical properties of spins on surfaces

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The scanning tunneling microscope has been an extremely successful experimental tool because of its atomic-scale spatial resolution. In recent years this has been combined with the use of low temperatures, culminating in precise atom manipulation and spectroscopy with microvolt energy resolution. In this talk I will review recent developments in investigating the electronic and magnetic properties of atoms and small clusters of atoms on surfaces. A particular focus will be on the use of magnetic materials for future device applications in the IT industries.

A large enough cluster of magnetic atoms on a surface behaves similar to a macroscopic magnetic particle: it's magnetization points along an easy-axis direction in space and magnetization reversal requires sufficient thermal energy to overcome a barrier. How many atoms does it take to create such a magnet? What are the size limits of stable magnetic nanoparticles? Those are important questions for future technologies as well as for basic understanding of materials.

When the number of atoms in a cluster becomes small, quantum tunneling of magnetization can take place and hence quantum mechanics can no longer be ignored but rather takes center stage. Single atoms that are slightly decoupled from conducting substrates often show such intriguing quantum effects. These quantum systems can be studied with inelastic tunneling spectroscopy, a technique we coined spin-excitation spectroscopy. With this approach it is possible to measure the energy eigenstates of the spin Hamiltonian that describes spins on surfaces with high precision.
The exchange correlation hole is of fundamental importance in solid state physics. The basic concept was developed in the 1930s, but explicit experimental studies started only in the last decade. They employ two-electron scattering from surfaces detected in coincidence in vacuum.

We present a joint experimental and theoretical study of correlated electron pair emission from a ferromagnetic Fe(001) surface induced by spin-polarized low-energy electrons. Spin-dependent angular and energy distribution of the emitted pairs have been measured and calculated. They are analyzed with the aid of the spin-, momentum-, symmetry-, and layer-resolved valence electron density of states, which we obtained by an ab-initio density functional theory calculation. The observed spectra are found to arise almost completely from only the first three surface layers. Momentum distributions for parallel spins of the emitted electrons exhibit an exchange-correlation hole, which is larger than the correlation hole in the antiparallel spin case. By comparing experimental antiparallel-spin pair spectra with their theoretical counterparts we determine an effective screening strength of the Coulomb interaction in the surface region.
State-of-the art ARPES: new concepts for analyzers and excitation sources

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Novel materials like graphene or topological insulators show intriguing structural and electronic properties. Topological insulators, for example, are characterized by their particular electronic structure which enables metallic like charge conduction at surfaces of an otherwise insulating material. Angular resolved photoemission spectroscopy (ARPES) is the obvious choice for studying the electronic structure of surfaces, and technological developments in the field of electron spectrometers and laboratory light sources have led to new possibilities in electronic structure determination.

The PHOIBOS series of hemispherical energy analyzers with 100, 150 and 225mm mean radius sets a new standard with the highest resolution and transmission. The modular power supply and detector concept makes them suitable for every aspect of electron spectroscopy: from laser based ARPES measurements at low kinetic energies starting at virtually zero kinetic energy, to quantitative XPS and high energy photoemission spectroscopy. The multi-element transfer lens of the hemispherical analyser PHOIBOS is optimized for ultimate energy and angular resolution up to highest kinetic energies and can be used for angular or spatially resolved studies. The acceptance angle can be extended with additional pre-lenses to +/- 30°. Different 2D detector concepts are available: a 2D-CCD detector with a Peltier cooled camera, a 2D-DLD detector (one time and two lateral dimensions), and combined 2D/SPIN detectors.

The THEMIS time-of-flight spectrometer series complements the SPECS photoemission spectrometer line and adds a new dimension the ARPES. Here, the combination of the PHOIBOS analyzer series lens design and the proven 2D-DLD detector technology enables most flexible operation, detecting large angular emission cone and energy windows simultaneously. The raw data from the detector (position and flight time for each electron) is precisely transformed into emission angle and energy coordinates in real time.
Surfaces and interfaces play a fundamental role in many aspects of science and technology, such as adsorption, electrochemical reactions, wettability and interactions with biological membranes. In this talk we will briefly describe two powerful and versatile techniques for studying interfaces: electronic and vibrational surface spectroscopy by second-harmonic generation (SHG) and sum-frequency generation (SFG).[1] As second-order nonlinear optical processes, SHG and SFG are forbidden in media with inversion symmetry and may occur only at interfaces between centrosymmetric media such as gases, liquids and amorphous solids. This makes these techniques intrinsically surface specific. Besides the spectral information, which is usually related to the structure of the interface, both techniques are sensitive to molecular orientation at interfaces. We will then present our application of SFG spectroscopy to the study of Layer-by-Layer (LbL) polyelectrolyte films,[2] where we have investigated the molecular arrangement at all steps of film fabrication (adsorption, rinsing and drying). Two important conclusions are: i) the polyelectrolyte conformation of each layer is affected by the adsorption of subsequent layers, and ii) the drying step may introduce macroscopic inhomogeneity in the films. Our findings have important consequences for the applications of LbL films, such as in biosensors. Another recent investigation employed SFG spectroscopy to identify adsorbed reaction intermediates for the ethanol electro-oxidation reaction on polycrystalline Pt electrodes in acidic medium.[3] It was found that many possible adsorbates coexist at the electrode surface, even at low potentials. These results indicate that the platinum surface is much more reactive, and the reaction mechanism for ethanol electro-oxidation is considerably more complex than previously considered. This might be also true for many other molecule-catalyst systems.

The characterization of solid-liquid interfaces is of broad interest to electrochemistry since it is the place where electrochemical reactions occur. Several factors are influencing the nature of a given electrode/electrolyte interface such as the chosen metallic electrode, the solvent, the electrode potential, or the electrolyte. Also co-adsorbates from the electrolyte affect the physicochemical processes, e.g. adsorption and desorption, metal deposition, corrosion, and the kinetics of electrochemical reactions.

In this talk we will discuss how theoretical investigations that combine methods describing different length- and time-scales can be useful in determining the interfacial morphology and composition as well as ongoing electrocatalytic processes. In the first part, examples will be presented where ab initio studies combined with thermodynamic considerations helped in revealing the nature of the electrode under reaction conditions. Afterwards, electrode processes such as the electrochemical oxygen reduction reaction and the formic acid oxidation will be considered [1,2]. Based on extensive first principles-based calculations on the reaction intermediates and transition states, we will discuss the ORR mechanism on Pt(111) electrodes. After benchmarking our QM calculations to experimental data, we report a multi-pathway electrochemical ORR mechanism that is sensitive to reaction conditions, and specifically to the applied electrode potential. A simple analysis based on calculated rate constants remarkably reproduces experimentally known factors concerning the electrocatalytic ORR.

Finally, I will discuss our recently formulated continuum approach to investigate an all-solid-state lithium-ion battery [3], consisting of transport equations and intercalation reactions.

SiO\textsubscript{2} films on 4H-SiC: reducing interface electrical degradation due to thermal oxidation

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Silicon Carbide (SiC) is an alternative semiconductor to substitute silicon (Si) in device applications that require high-power, high-frequency, and/or high-temperature. In addition, a SiO\textsubscript{2} film can be thermally grown on SiC in a similar way to that on Si, allowing the technology used to produce Si MOS (metal-oxide-semiconductor) devices to be adapted to the case of SiC [1]. However, the oxidation of SiC leads to a higher interface state density in the SiO\textsubscript{2}/SiC interface, as compared to SiO\textsubscript{2}/Si. Such interfacial defects were indicated as the main causes of the low channel mobilities of SiC transistors [2]. A better understanding of the thermal oxidation of SiC should lead to answers on how to thermally grow SiO\textsubscript{2} layers minimizing the interface electrical degradation. Concerning oxidation parameters, it is already known that longer oxidation times lead to a larger electrical degradation of the SiO\textsubscript{2}/SiC structure [3]. In this work, we present an attempt to minimize the electrical degradation in the SiO\textsubscript{2}/SiC interfacial region by oxidizing SiC substrates in a minimal oxidation time, using \textsuperscript{18}O\textsubscript{2}, aiming to form stoichiometric SiO\textsubscript{2} on SiC. X-ray photoelectron spectroscopy (XPS) was used to monitor the formation of this stoichiometric SiO\textsubscript{2} film. To obtain a thicker oxide film, a SiO\textsubscript{2} layer was deposited by sputtering as a further step. The formed structure presented improved properties compared to deposited and to thermally grown SiO\textsubscript{2} films on SiC. Effects of a post-deposition annealing (PDA) in Ar as an attempt to improve the quality of the formed structures were also investigated. Capacitance-voltage and current-voltage measurements in Al/SiO\textsubscript{2}/4H-SiC MOS structures were performed to investigate the electrical properties. Amounts and distribution of \textsuperscript{18}O in the samples were determined by nuclear reaction analyses and related to the electrical modifications induced by the PDA in Ar and will be also presented.

Multiscale modeling of point defects at metal-oxide surfaces: Case study of MgO (100)

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Doping greatly influence s electronic and chemical properties of oxide materials and can occur both intentionally and unintentionally. Impurities, defects, and their complexes introduce new electronic states, converting an insulator to either electron (n-type) or hole (p-type) conductor. The problem we address in this work is how the charge carriers (electrons or holes) in the doped oxide bulk material influence charge state and concentration of oxygen vacancies (also called F centers) at the surface. As a particular example, we consider F centers at the MgO (100) surface. Our approach employs density-functional theory (DFT), combined with \textit{ab initio} atomistic thermodynamics [1]. We demonstrate that standard LDA and GGA exchange-correlation (xc) functionals fail to correctly describe charged defect formation energies due to the self-interaction error. Therefore, we carefully analyze the performance of a family of hybrid xc functionals, and choose one according to a fundamental condition on DFT ionization energies. The functional is further validated by CCSD(T) calculations for embedded clusters. We find that doping is as important thermodynamic variable as temperature and pressure. The charge carrier transfer to surface defects results in a depletion of the charge carriers and creation of an extended space charge layer in the subsurface region. The resulting electrostatic potential causes band bending and prevents more charges from the bulk to reach the surface, increasing the energy cost per defect. On the other hand, charged defects are stabilized due to electrostatic attraction to the space charge. As a result, the surface defect formation energy strongly depends on defect coverage. In case of p-doped MgO (100), the free energy of formation of an isolated (\textit{i.e.}, at very small coverage) doubly charged surface F-center ($F_{s}^{2+}$) becomes negative at $T > 600$ K and oxygen pressure $p = 1$ atm. However, at higher defect coverage, band bending increases the formation energy by up to 1 eV, limiting the equilibrium coverage and stabilizing the surface. Nevertheless, the equilibrium $F_{s}^{2+}$ coverage can be as high as ~0.5 at\% at realistic ($T$, $p$) and doping conditions ($\sim10^{18}$ cm$^{-3}$). The $F_{s}^{+}$ and $F_{s}^{0}$ coverage is found to be negligible at realistic ($T$, $p$) and any doping (n- or p-type).

Electrically Detected Magnetic Resonance – basic concepts and applications

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Magnetic resonance techniques attract considerable attention in many research fields. Advantages compared to other techniques are among others, high sensitivity and selectivity. In general, the technique can be used to investigate local static and dynamic interactions, or in other words the microscopic surroundings of the spin. Among MR techniques Electrically Detected Magnetic Resonance (EDMR) is a powerful tool for materials and electronic device characterization. In this talk, we shall present a short review on the use of EDMR in different semiconductors: a-Si(Ge):H [1], Si/SiGe heterostructures [2] and Alq$_3$ based OLEDs [3]. We will also present a brief introduction to the fundamental concepts of the technique.

Elementary processes at nanostructured (photo)catalysts

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The need for renewable energies is of growing demand worldwide. One of the most promising approaches circumventing problems with the fluctuations of the renewable energy sources is the chemical storage of solar energy. However, in order to be able to tailor make the best photocatalysts for achieving high efficiencies of photoinduced processes it is crucial to gain a principle understanding of the underlying elementary processes. Some of the key features are long life times of electronically excited states and the concomitant dissipation into the desired molecular motions prior to bond breaking and bond making. A promising approach is to reduce the photoactive material to nanometer dimensions to enhance cross sections of photochemical reactions [1,2]. Real time femtosecond measurements using time resolved second harmonic generation at metal-semiconductor interfaces will be presented. They exhibit the intriguing influence of interfacial trapping of hot electrons on electron phonon coupling processes. Fundamental investigations using femto- and nanosecond laser pulses combined with quantum state resolved detection methods give insight into the energy partitioning processes in photo desorption and photo reaction. Results on laser induced desorption of CO and NO adsorbed on Pt and Pd-nanoaggregates on an oxidic support will be compared with each other. Phenomena such as energy pooling processes in adsorbates at nanoparticulate surfaces on ultrafast time scales, adsorbate induced nanoparticle reshaping in the course of photochemical reactions, spill over in photochemistry or the role of the particle perimeters will be presented. As an example of a photo reaction results on the photodissociation of methane will be shown. New perspectives for future designs of more efficient photochemical materials will be outlined.

The water gas-shift reaction (WGSR), which deals with the conversion of CO with steam producing CO$_2$ and H$_2$, is one of the main reactions to purify the H$_2$ produced from steam reforming reactions (methane, ethanol), a critical step for applications in fuel cells. The WGSR, despite being a widely used reaction at industrial scale, with well-established catalysts based on iron oxides (high temperature shift catalyst) or Cu/ZnO (low temperature shift catalyst), has attracted considerable attention in the last years with special interest on noble metals. In this work, the interaction between Pt and support and its impact on the catalytic activity for the WGSR was investigated. Catalysts with low content of platinum (<1 %), to improve the metallic dispersion, were prepared using alumina and cerio-alumina supports. The metal-support interaction was studied by *in situ* X ray absorption spectroscopy and Fourier transform infrared spectroscopy (FTIR) during the reduction process and reaction. The results showed electronic and structural changes on platinum due to the interaction with the support and as a consequence differences in the catalytic activity.
H₂ reduction reaction of CuₙNi₁₋ₙ/CeO₂ (x = 0, 0.5, 1) nanoparticles

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Ceria (CeO₂) is an advanced material used for catalytic applications mainly because oxygen vacancies at the surface can be rapidly formed and eliminated which gives to ceria the property of high capacity for oxygen storage [1]. Compared to different supports of metallic nanoparticles, ceria enhances the performance of catalysts in a variety of reactions such as the water gas-shift and the preferential oxidation of CO [1]. The reduction reaction is a key process employed in catalytic applications and it is very important to elucidate the atomic phenomena (core-shell structure formation, changes on the oxidation state, SMSI effect) existing in the nanoparticles in order to project the final desired properties of the catalysts. We have investigated in situ and ex situ the electronic and structural properties of Cu-Ni nanoparticles supported on CeO₂ and subjected to H₂ reduction. The metallic nanoparticles (~ 5 nm diameter) were synthesized by using the ionic liquid BMIBF₄ [2]. Thereafter, the nanoparticles were supported on CeO₂ and heated up to 500 °C in a H₂ atmosphere. The system was investigated by means of XPS (X-Ray Photoelectron Spectroscopy) and in situ XAS (X-Ray Absorption Spectroscopy) and DXAS (Dispersive XAS) techniques. All XAS measurements were performed in the transmission mode at the Ce L₃ edge, Ni K edge and Cu K edge. The XPS and DXAS results show that Cu and Ni atoms were initially oxidized. Structural information was obtained by XAS technique and DXAS measurements reveal details about the kinetic of the H₂ reduction as a function of the reduction temperature and time. The reduction of the nanoparticle starts at ~285 °C for Cu/CeO₂, ~160 °C for Ni/CeO₂, ~190 °C (Cu) and ~435 °C (Ni) for Cu₀.₅Ni₀.₅/CeO₂ nanoparticles. After the beginning of the reduction it takes ~10 min for Cu/CeO₂, ~14 min for Ni/CeO₂, ~12 min (Cu) and ~14 min (Ni) for Cu₀.₅Ni₀.₅/CeO₂ to reduce completely the nanoparticles supported. The atomic arrangement at the surface of the nanoparticles is discussed based on the XPS results.

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Au adsorption on oxygen defective CeO$_2$(111) studied by density functional theory

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Recent experiments employing low-temperature scanning tunnelling microscopy and spectroscopy to study the adsorption of individual Au atoms on slightly reduced CeO$_2$(111) films found two types of Au species on the surface. The first one appears as isolated protrusion, while the second type always forms pairs of predominantly 8 Å distance. The present work tries to elucidate the nature of formation of the Au pairs by virtue of DFT+U and hybrid DFT. Our results indicate that three charge states of gold, namely Au$^+$, Au$^0$, [1-3] and most importantly Au$^-$, are stabilized at the ceria surface. Particularly, the presence of Ce$^{3+}$ ions at the reduced surface enables (partial) electron transfer into Au-6s states leading to the formation of Au$^{(5-)}$ ions. In order to disentangle the reasons behind the “pairing” of Au atoms, the formation of O divacancies was studied as well.

Our results indicate a strong interaction between Au-6s and Ce-4f states, whose relative stabilities determine the oxidation states (Au$^0$, Au$^-$ versus Ce$^{4+}$/Ce$^{3+}$) of the involved species. As previously reported in the literature [3] energy differences obtained using DFT are very small and depend critically on equilibrium structure and details of the functional and method used.

Semiconductor materials with a wide bandgap (\( > 2.5 \text{ eV} \)) such as SiC, GaN, ZnO, or diamond have in common that the Fermi level of typical catalytic metals (Pt, Pd, Au, etc.) is energetically situated within the bandgap of these semiconductors. This opens up the possibility to influence or even control the catalytic activity of metal nanoparticles on the surface of such semiconductors via optically induced charge transfer between the semiconductor substrate and the catalytic particles. As a model system, we have investigated Pt nanoparticles with a size of several nm on the surfaces of n- or p-type doped GaN.

GaN is one of the few wide-gap semiconductors which can be doped both n-type and p-type by addition of substitutional dopants such as Si or Mg. The photochemical reactivity of the GaN surface depends strongly on the type of doping: upon illumination with high energy photons above the bandgap of GaN, photogenerated electrons accumulate as minority carriers at the surface of p-type GaN, whereas excess holes appear at the surface of n-type GaN. These photogenerated minority carriers can be transferred onto metallic nanoparticles on the semiconductor surface, if the Fermi level of the metals lies within the bandgap of the semiconductor support.

The combination of GaN substrates and Pt nanoparticles exactly fulfills these requirements, as evident from a strongly different photochemistry on n- and p-type GaN:Pt heterostructures. High pressure photoelectron spectroscopy performed at the BESSYII synchrotron in Berlin will be presented to demonstrate this fact. In addition, we have shown in collaboration with the Chair of Technical Chemistry II at TU München (Prof. Johannes A. Lercher and Sonja Wyrzgol) that the same GaN:Pt heterostructures exhibit catalytic activities in a model ethene hydrogenation reaction which can be changed by almost one order of magnitude for n-type versus p-type GaN.
Raman Spectroscopy Analysis of Graphene-Related Systems

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In this work the use of Raman spectroscopy, combined with other microscopy techniques, will be discussed, as applied to surface science problems in graphene-related structures. Nanomanipulation of single-walled carbon nanotubes deposited on a crystalline quartz substrate [1], the properties of twisted bi-layer graphene produced by folding a single layer [2], and the structural aspects of charcoal-like structures present in anthropogenic Amazonian soils [3] will be explored.

This work has been supported by CNPq, CAPES, FAPEMIG and Inmetro.

Revealing the optical properties of intrinsic defects in crystalline ZnO films

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Over the last hundred years, zinc oxide has been widely applied as white pigment, antiseptic substance, as transparent oxide for solar cells and gas sensing. Although, enormous progress on the use of ZnO has been made over the years [1], some key fundamental questions are still not well understood regarding the role of its intrinsic defects on the electric and optical properties. Previous studies have suggested that defects are responsible for the widely observed n-type conductivity of the material, although it was accepted only recently that lattice-hydrogen serves as the hidden donor. At present, insights into the nature of native ZnO defects comes mostly from theoretical studies [2], while experimental results are not always conclusive and sometimes in conflict to each other [3]. In this study, we have prepared well-defined ZnO films on Au(111) substrate as a model-system and investigated the luminescence response locally by scanning tunneling microscopy and cathodoluminescence spectroscopy. In order to relate the observed emission peaks to intrinsic defects, we have varied the ZnO growth conditions, e.g. the temperature and \( \text{O}_2 \) pressure, and reduced the films with atomic hydrogen and laser irradiation. In well-prepared films, band recombination gives rise to the dominant peak at 373 nm, while three additional peaks at higher wavelength indicate the presence of defects in the oxide lattice. To identify the nature of these emission centers, the abundance of typical ZnO defects has been varied by purpose. Film growth at reducing conditions produces a prominent band at 730 nm, suggesting a correlation to O-vacancies in the lattice. Incorporation of atomic oxygen, on the other hand, leads to an increase of the 595 nm emission peak. Varying the availability of Zn during film growth finally modulates the intensity of the 535 nm defect line. The results of our luminescence data are summarized in an energy diagram of the ZnO defect levels and compared to recent DFT calculations. Our study [4] offers conclusive evidence on the nature of the underlying lattice defects, providing a correlation between structural, electronic and optical properties of ZnO.

Bimetallic catalysts have attracted considerable interest in recent times because of their improved catalytic and electrocatalytic properties in various important reactions. Key for the mechanistic understanding is detailed information on the structure and local composition of the surface, which is hardly accessible for nanoparticle surfaces. This is different for planar bimetallic surfaces, where high resolution scanning tunneling microscopy (STM) imaging with chemical contrast has been demonstrated to resolve the different metal species in a surface and thus give direct access to the quantity [1;2] and, after appropriate statistical evaluation, to the lateral distribution of the respective surface species [3;4].

Trends in the chemistry and catalytic behavior of bimetallic surfaces will be derived, based on systematic studies on a variety of different systems. The importance of close interaction with theory will be highlighted. The potential of this approach, which aims at the description of the overall catalytic behavior on the basis of the reactivity of individual nanostructures, will be discussed.

References
Superparamagnetic Response of Fe-coated W Tips in Spin-polarized Scanning Tunneling Microscopy

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Spin-polarized scanning tunneling microscopy/spectroscopy (sp-STM/S) has been successfully applied to characterize spin-ordering, spin-dependent electron confinement [1], and magnetization reversal of individual nanostructures [2]. However, in spite of its crucial function in SP-STM, quantitative insights regarding the magnetization state of the tip are scarce [3].

Tips used in SP-STM can be classified in three categories with respect to their response to an external magnetic field: 1) the tip magnetization orientation is fixed and unaffected by the external magnetic field, 2) the tip magnetization orientation is bistable and switches by the external magnetic field, and 3) the tip magnetization direction follows the external magnetic field [3]. Here we focus on the case 3), where we exploit the temperature dependence of SP-STS measurements in magnetic fields to characterize the magnetization state of the tip quantitatively.

We performed SP-STM on biatomic-layer-high Co nanostructures grown on Cu(111) in magnetic fields oriented normal to the sample surface, with a Fe-coated W tip. Increasing the temperature from 10 to 30 K, we observe a reduced slope of the differential conductance around zero field. A quantitative analysis of the field- and temperature-dependent differential conductance data in the framework of superparamagnetism as described by a Langevin function gives an excellent description of the experimental results. The analysis suggests that a Fe nano-apex at the W tip, which is composed of 220–300 Fe atoms, determines the magnetic response of the tip.

Nitrogen and Boron doping of Graphene

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The application of graphene in future devices will depend on the possibility to tune its band structure. One desirable way to achieve this is substitutional doping, as this leads to a considerably higher stability than e.g. charge transfer doping by adsorbates. Here we will discuss the formation of graphene on Ni(111) and different ways to prepare nitrogen- and boron-doped graphene, i.e., via classical CVD approach and in the case of nitrogen doping also via ion implantation. The systems are analyzed with x-ray photoelectron spectroscopy (XPS) and angle resolved photoemission (ARPES). The experimental findings are supported by ab-initio density functional calculations. [1-4] At first the preparation of graphene on a Ni(111) surface is discussed. We find two energetically equivalent structures that coexist on the surface. The structures show a strongly differing core level shift in their XP spectra. In the case of nitrogen doping we find two chemically different nitrogen species on the surface, namely pyridinic and substitutional nitrogen (see Figure 1), whose concentration and relative abundance can be altered by the experimental conditions. The ARPES measurements show a broadening of the bands and p-doping. In order to decouple the nitrogen-doped graphene from the nickel surface we used gold intercalation, leading to the electronic structure of quasi free standing graphene, while preserving the nitrogen doping. The DFT analysis shows excellent agreement; furthermore, it indicates the possibility to obtain n-doping for substitutionally doped graphene. The introduction of boron in the graphene network leads to solely one chemical species and a strong p-doping. ARPES shows similar effects as for nitrogen, with a broadening of the bands and a retained band structure. From the DFT calculations we find a strong preference of boron-doped graphene for the top-fcc geometry, while in the case of nitrogen doping no preferred site was found. Additionally, we find a buckling of the graphene layer due to the reduced adsorption distance of boron as compared to carbon.

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Influence of magnetic annealing and interdiffusion on the exchange bias of CoFe/IrMn layered nanostructures

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Magnetic annealing is broadly used to set exchange bias (EB). The EB field depends on the magnetic field and the temperature at which the F/AF exchange interaction is set. Atomic interdiffusion is also expected to have strong influence on EB. For systems containing IrMn, different results have been reported regarding the effect of setting EB between 200 and 400 °C. We study the effect of atomic interdiffusion on the exchange bias of polycrystalline IrMn/(57Fe+CoFe) multilayers due to the magnetic annealing between 225 and 500 °C. The samples have been prepared by magnetron sputtering, and 57Fe probe layers (10 Å thick) were grown at the F/AF interface, and 1 nm and 2 nm above it, inside the 40 Å thick CoFe layer. Depth-resolved 57Fe conversion electron Mössbauer spectroscopy (CEMS) and X-ray photoelectron spectroscopy (XPS) were used to quantify atomic interdiffusion, and vibrating sample magnetometry was used to monitor the variation of exchange bias and magnetisation.

We found that interface sharpness is only affected above ~350 °C. Three different stages for the setting of exchange bias can be inferred from our results. At temperatures up to 350 °C, no interdiffusion is observed and the F/AF exchange coupling establishes partial spin alignment of interfacial and bulk AF spins. At intermediate setting temperatures (350-450 °C) interfacial spin order is dominant over chemical intermixing effects, and both exchange field and coercivity increase up to 450 °C. Above 450 °C, severe chemical intermixing reduces significantly (~ 50%) the F/AF coupling [1].

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From pure metal supported oxide films to two-dimensional zeolite films

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In general the properties of thin oxide films different from bulk materials converge towards properties similar to the bulk material already for a surprisingly small number of atomic layers. Such oxide thin films are used to model supports in heterogeneous catalysis and carry nanoparticles as active components, both as metal particles and transition metal oxide particles. However, oxide films of only very few layers thickness may be designed as catalytic materials in their own right.

We have prepared a variety of thin films, including those of importance as supports in heterogeneous catalysis, i.e. alumina, silica, magnesia, ceria, vanadia, chromia, and niobia etc. Those materials are characterized at the atomic level including infrared spectroscopy and other relevant techniques such as scanning tunnelling microscopy, photoelectron spectroscopy, and electron spin resonance.

In our group silica thin film systems have been investigated during the last decade and more. The goal was to use such films as model supports. Monolayer and Bilayer silica films have been successfully prepared. In fact, the bilayer SiO$_2$ film could be imaged in both, crystalline and amorphous phase. The phase transmission is being studied.

Moreover, it has been possible to incorporate aluminium into the film leading to the formation of two-dimensional alumosilicates, i.e. zeolites with “infinite cavities”. The incorporation of aluminium into the bilayer film follows Löwenstein’s rule and we demonstrate the formation of bridging OH groups with high acidity. Experimental evidence using STM, FTIR, and XPS are given. This study paves the way for studies in surface science of zeolite surfaces.

Abstracts of poster contributions
We have performed electrical resistance measurements on films of Bi and hybrid films of Co/Bi consisting of Co nanoclusters with a mean size of ~ 4.5 nm covered by Bi. The films were produced by deposition of Bi on top of a layer of well-defined Co clusters onto sapphire substrates kept at low temperatures.

As-deposited Co-clusters/Bi films reveal a superconducting-like transition close to Tc of amorphous Bi, however, with variable range hopping behavior below Tc, i.e., with a diverging resistance for \( T \to 0 \). Upon annealing at low temperature, a superconducting state with zero resistance for \( T \to 0 \) is found. Finally, annealing at higher temperatures leads to non-superconducting crystalline Bi showing weak-localization behavior typical for a disordered semimetal (or metal).

Annealing some of these films results in a power law behavior as \( \sigma(T) = \sigma_0 T^\alpha \) with \( \alpha = 2/3 \), indicating that they are close to a quantum critical point separating superconducting and insulating phases. A phase diagram including all experimental observations is proposed.

Evaluation of skin depth properties of thin films in microwave absorption process

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Radar absorbing materials (RAM) are frequently used to minimize the effects of compatibility and interference electromagnetic in several electronic devices, being widely used in civilian and military industry. Traditionally, RAM materials are developed and used by the industry are compounds based on carbon black, polymers additives with ferrites and, presently, metallic thin films [1].

The attenuation process of these materials is associated with the generation of induced currents – identified as induction of Eddy currents - discovered by the French physicist Leon Foucault in 1851 [3]. The Eddy currents attenuate the electric and magnetic fields by causing ohmic losses, which imposes electromagnetic energy dissipation [2]. The depth at which these currents penetrate in the surface of a conductor film layer is called skin depth. This layer, when evaluated as absorber surface, has its property as a function of frequency, conductivity and permeability of the material. The process of radiation attenuation occurs when the coating is thinner than the material skin depth – once the electromagnetic wave incident on a given surface can penetrate in. By means of this phenomenon is that the microwave absorptions occur [3].

The present work discusses the influence of conductivity of metallic thin films in order to quantify the associations between skin depth properties and absorptions parameters. Inducing the variation of surface resistivity it is possible to verify, through the present work, that it is possible to manipulate the skin depth parameter aiming the optimization of energy transformation process from electromagnetic energy into heat energy.

Emission of correlated positron-electron pairs from surfaces

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Electron pair emission is a valuable tool, in particular for surfaces, to study the electron-electron correlation, which is mediated by the Pauli principle and Coulomb interaction. It manifests itself in a zone of reduced intensity in electron pair emission, related to the exchange-correlation hole. One way to study the Coulomb interaction alone is to explore correlated positron-electron pair emission upon primary positron impact. The existence of this process has been proven experimentally [1]. A theoretical treatment [2] predicts momentum distributions, which exhibit a central region of high intensity due to positron-electron correlation. These facts encouraged us to initiate further coincidence studies. We developed a dedicated laboratory positron source employing Na22 which provides a flux of 4x104 e+/s for kinetic energies of 30-100 eV. We employ a symmetric geometry in which the incoming positrons hit the target along the surface normal. The emitted particles are measured in coincidence via a pair of energy dispersive spectrometers. In analogy to the (e,2e) process we term the positron-electron pair emission as a (p, ep) process. From previous (e,2e) studies it was discovered that NiO/Ag(100) display an order of magnitude higher coincidence count rate compared to metals [3]. NiO is a material of particular interest, because the physical properties are decisively influenced by the electron correlation. Therefore, (p, ep) investigations at primary positron energies between 42 – 62 eV were performed on a NiO/Ag(100) film and Ag(100) crystal. We found up to a factor of two higher (p, ep)-emission probability for NiO/Ag(100) than for Ag(100).

Ru nanostructures grown on Pt single crystal surfaces are interesting model systems for studying functional properties of the Pt-Ru system, which is widely used for fuel cells applications\(^1\). Systematic studies using UHV techniques have been extensively reported in the literature for low Miller index Pt single-crystal surfaces, mostly for Ru-modified Pt(111)\(^2,3\). However, this is not the case for Ru-modified high Miller index Pt surfaces. These model systems are interesting because of the high density of steps, which brings them closer to nanoparticle systems.

In this research, Ru was grown by vapor deposition on Pt(332) in UHV conditions, at room temperature. The surfaces were studied using UHV-STM and XPS. For low coverage, Ru deposits preferentially on the step edges forming 1D chain structures (step decorating) and some 2D structures (monolayers). When Ru coverage is increased, STM shows that the formation of 3D structures is favored (bilayer growth). The Ru nanostructures grow following the terrace lines with a narrow distribution of size and shape.

Additionally, the effect of annealing the surfaces at 350 °C was studied. In all cases surface alloying occurs.


Hydroxylation of a metal supported sheet-like silica films

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Water and silica are the most abundant compounds on our planet and their interactions are vitally important in many fields including catalysis, material science, geochemistry, etc. It is generally accepted that the performance of silica in catalysis, where silica may be involved either as a support for catalyst particles or as a reactive surface, is primarily determined by surface hydroxyl species. Although a vast amount of studies has focused on high-surface-area silicas such as powders, dried gels etc. there are only few studies on a well-defined, planar silica surfaces.

In this study, adsorption of water on a metal-supported well-ordered silica thin film grown on Ru(0001) was studied by infrared reflection absorption spectroscopy (IRAS) and temperature programmed desorption (TPD)[1]. As expected, the silica surface is essentially hydrophobic. Hydroxo species, primarily in the form of isolated silanols (Si-OH), were observed only upon water adsorption at low temperatures and subsequent heating above 200 K. Most of these hydroxyl groups are thermally stable up to ~ 800 K and desorb via recombination as water above 950 K. Isotopic experiments showed that surface hydroxyls are formed exclusively from the adsorbed water molecules, and they do not undergo considerable scrambling with the lattice oxygen atoms upon heating. Steps on a silica sheet and/or “holes” in these ultrathin films are proposed as active sites for hydroxylation.

The acidity of silanol species were studied with adsorption of weak and strong bases, such as CO and NH3 respectively. It is found that CO does not interact with silanols. In the case of NH3, an H-D reaction was observed between surface OD species and NH3. The same reaction was also observed for OD(OH) and H2O(D2O), respectively.

The Pt(111)/O₂ solid-gas interface: A reactive MD approach

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As one of the central model systems in surface science and electrochemistry, the Pt(111)/O₂ interface has been the subject of numerous experimental and theoretical investigations, scrutinizing the adsorption, desorption, dissociation, and diffusion of oxygen on Pt(111) (see for example Refs. [1,2]). By thus characterizing and quantifying the mobility, stability and reactivity of oxygen in this system, these studies have begun to offer structural and mechanistic insights into technologically important catalytic processes, such as the electrochemical oxygen reduction reaction and the oxidation of CO and hydrocarbons.

However, what has thus far emerged is a collection of disjointed and occasionally contradictory explanations for the experimental results rather then a universally accepted, complete picture of oxygen platinum surface chemistry. In particular, this has barred the way to a fundamental understanding of oxygen's influence on the catalyst's morphology and activity. Many of the atomistic details necessary for arriving at such a fundamental understanding are often obtained using ab-initio based methods, and in particular, density functional theory (DFT). However, strong limitations in the size and complexity of systems, which DFT methods are capable of treating, has contributed to the situation insofar as there are important aspects of the experimental systems, which theory has thus far been unable to describe.

To address these deficiencies, we have developed a reactive interaction potential (force field) within the ReaxFF framework [3], whose parameters were obtained by optimization against an extensive set of DFT-obtained energies and geometries for a variety of structures involving platinum and oxygen, including adlayer structures, surface and bulk oxides and oxygen adsorbates at various surface sites and defects. Equipped with this ReaxFF force field description we investigated elementary phenomena at the Pt(111)/O₂ interface, including oxygen adsorption, dissociation, diffusion and finally the stability of different oxygen adlayers. Because ReaxFF provides a means of drastically reducing the computational expense associated with DFT calculations, we were not only able to reproduce DFT-results (and thus validate our ReaxFF force field description), but we were also able to explore structural features and reactive events that are well beyond the capabilities of standard DFT methods.

Superparamagnetic Response of Fe-coated W Tips in Spin-polarized Scanning Tunneling Microscopy

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Spin-polarized scanning tunneling microscopy/spectroscopy (sp-STM/S) has been successfully applied to characterize spin-ordering, spin-dependent electron confinement [1], and magnetization reversal of individual nanostructures [2]. However, in spite of its crucial function in SP-STM, quantitative insights regarding the magnetization state of the tip are scarce [3].

Tips used in SP-STM can be classified in three categories with respect to their response to an external magnetic field: 1) the tip magnetization orientation is fixed and unaffected by the external magnetic field, 2) the tip magnetization orientation is bistable and switches by the external magnetic field, and 3) the tip magnetization direction follows the external magnetic field [3]. Here we focus on the case 3), where we exploit the temperature dependence of SP-STS measurements in magnetic fields to characterize the magnetization state of the tip quantitatively.

We performed SP-STM on biatomic-layer-high Co nanostructures grown on Cu(111) in magnetic fields oriented normal to the sample surface, with a Fe-coated W tip. Increasing the temperature from 10 to 30 K, we observe a reduced slope of the differential conductance around zero field. A quantitative analysis of the field- and temperature-dependent differential conductance data in the framework of superparamagnetism as described by a Langevin function gives an excellent description of the experimental results. The analysis suggests that a Fe nano-apex at the W tip, which is composed of 220–300 Fe atoms, determines the magnetic response of the tip.

Growth and characterization of doped graphene obtained by CVD

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In recent years, graphene has attracted major attention from the physics and device research communities due to its atomic thickness, excellent electric properties and to its various applications in electronic devices proving to be as one of the most promising candidates for future nanoelectronics. Several methodologies have been developed for the growth of graphene and the chemical vapor deposition (CVD) technique has allowed to obtain large area of high quality uniform graphene film [1]. Substitutional doping has been demonstrated an effective method to modify the electronic properties of graphene. In this work Boron, nitrogen and phosphorus-doped graphene were synthesized by the CVD method on copper foils substrate using liquid source as precursors (Triisopropyl Borate for boron-doped and acetonitrile for nitrogen-doped) and Triphenylphosphine P(C6H5)3 as precursor for phosphorus doped samples. Graphene samples from methane were used as reference samples. was used as liquid precursor [2]. Twenty-five micrometer thick, Cu foils were immersed in deionized water, acetone and isopropanol for 10 minutes in each solvent. The Cu foils were then loaded into a quartz tube and exposed to a 2 sccm of H2 at 70 mtorr environment while the temperature was raised to the growth temperature, optimally 1000°C. This temperature was held for 20 min inside the quartz tube to remove any generated oxide layer on the Cu. The Cu films were exposed to the boron vapor for approximately 5 minutes at pressures ranging from 25 to 400 mtorr. The flow of vapor was maintained while the system was rapidly cooled to room temperature at rates around 300°C/min.

Raman spectroscopy was used for structural characterization. The properties of graphene as a function of defects present in the different samples, was investigated by measuring the intensity ratio \(I_D/I_G\) and \(I_{2D}/I_G\) of the D, G and 2D bands in the Raman spectrum obtained from each sample. X-ray photoelectron spectroscopy was used to investigate the chemical ambient of boron atoms. Optical and scanning electron microscopes were also used during the characterization process.

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Adsorption of carbendazim herbicide on Ag surface nanoparticles
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The Raman scattering is a technique widely used to obtain information about the structure of molecules, however, its low cross section hampers the analysis of molecules in highly dilute solutions. This problem can be solved with the use of metallic colloids (nanoparticles) that allow the study in low density system owing an amplification of the Raman signal in several orders of magnitude. This phenomenon is so-called surface-enhanced Raman scattering (SERS)[1]. Nevertheless, the molecule must have an affinity for the metal to adsorb on the surface of the nanoparticle[2]. Carbendazim is a fungicide broadly applied in agriculture and the increase of its use draws attention concerning the risks caused by this fungicide. Here, we study an adsorption of the fungicide, carbendazim, on surface nanoparticles by SERS under different experimental conditions, such as nanoparticle synthesis, colloid pH, excitation wavelength and fungicide concentration with the aim to detect carbendazim at low concentrations. The experiments were carried out with three kinds of nanoparticles: Ag and Au reduced by citrate and Ag reduced by hidroxilamine: AgCT, AuCT and AgH, respectively, activated with KNO3 at several pH. Prior to SERS experiments, the influence of carbendazim on the plasmon of nanoparticles was studied by UV-Vis absorption spectroscopy. Carbendazim shows two pKas (4.6 and 10.6) and the adsorption on nanoparticle surface is closely related to the pH of colloids. Carbendazim in AuCT colloids did not show SERS signal, which indicates that carbendazim molecules probably do not adsorb onto the Au nanoparticle surface. SERS spectra of carbendazim in AgCT and AgH colloids depend on pH. The best conditions were achieved between pH at 5 and 10 in AgH colloid with excitation wavelength at 532 nm (Figure 1). Then, under these conditions, several spectra of carbendazim in different concentrations were obtained. The adsorption of this fungicide on the Ag surface followed a Langmuir model, with the coefficient of adsorption of 6.06 ±0.55 x 10^5 L/mol and the limit of detection around 1.0 x 10^-7 mol/L. This value is lower than what is found in the literature (5.0 x 10^-5 mol/L) [3] to detect carbendazim in low concentrations using SERS. To complement this study, we propose theoretical calculations of Raman spectra of carbendazim with and without Ag surface to help understanding the mechanisms responsible for the interaction between carbendazim and Ag.

Figure 1: Raman and SERS spectra of carbendazim collected at pH 6 with excitation wavelength at 532 nm (left). Schematic representation of carbendazim adsorption on silver surface (right).

Growth and transformations of iron oxide thin films: a spectro-microscopic characterization

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Iron oxide, widely used as a catalyst and as a support for catalytically active systems, has been intensively studied with various techniques [1]. However, controversies in the literature regarding the surface termination and structural inhomogeneities hinder the direct linking of surface electronic and structural properties to chemical properties. Therefore, our aim is a comprehensive and consistent characterization of the Fe$_3$O$_4$ and Fe$_2$O$_3$ film growth on Pt(111) and Ag(111) substrates by using the SMART instrument [2], operating at BESSY-2, the soft x-ray light source of the Helmholtz Center in Berlin. This energy-filtered LEEM/PEEM instrument is specially designed to obtain chemical and structural information with high lateral resolution in-situ and in real time. It is the first instrument achieving 2.6 nm in LEEM and 18 nm in energy filtered XPEEM, which is possible only by simultaneous correction of spherical and chromatic aberrations.

The combined LEEM/LEED and XPEEM study shows that the oxide thin film reveals defects depending on different preparation conditions, such as coexistence of different stoichiometric phases (Fe$_3$O$_4$, Fe$_2$O$_3$ and FeO), rotational domains and domains of different surface terminations [3]. We found that the substrate influences the quality of the supported oxide surface and its thermodynamics; e.g. the phase diagram of co-existing Fe$_3$O$_4$ and Fe$_2$O$_3$ phases can differentiate significantly from that calculated for bulk materials. We systematically characterized the conditions to reversibly transform α-Fe$_2$O$_3$ to Fe$_3$O$_4$ thin films on Pt(111) and on Ag(111). A comprehensive characterization of oxidation and reduction of mixed-phase films, the various defects in the film, as well as the substrate role in such reactions, will be discussed.

Photoelectron diffraction investigation of the Au/Cr₂O₃/Pd(111) model catalyst

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Surface Science has been widely applied to study the electronic and structural properties of catalysts, but their morphological and structural complexity is a barrier to obtain a detailed knowledge of their microscopic properties, and the consequent development of new and more efficient catalysts [1]. Another difficulty concerns the difference between the high pressure and temperature conditions in which the catalysts are applied in the industry, in contrast with the UHV requirements of the Surface Science techniques. One solution is the simplification of the real material, prepared as a model catalyst, with the advantage of being compatible with the UHV-based techniques. The model catalysts allow the introduction of controlled structural features on a surface in a controlled manner, simplifying the real catalyst [2]. This work presents an investigation of the surface atomic structure of the Au/Cr₂O₃/Pd (111) system. This model catalyst was produced by in situ MBE deposition and characterized by LEED (Low Energy Electron Diffraction), XPS (X-Ray Photoelectron Diffraction), ARXPS (Angle-resolved XPS) and Photoelectron Diffraction (PED) [3]. The composition of the Cr₂O₃ films and Au were determined by XPS. The degree of crystallographic ordering of the films were examined by LEED. The atom specific structure of the sample was studied by PED, using the computer simulations obtained by the MSCD (Multiple Scattering Calculation of Diffraction) program. As a result, we determined that 2ML of Au was deposited, and that a structural relaxation occurred in the three outmost atomic layers of the Au/Cr₂O₃ system. Evidences on the formation of Au islands on the Cr₂O₃ surface will also be presented and discussed.

Iron Nano-Clusters in Ytterbium Films: A $^{57}$Fe Mössbauer Spectroscopic Study

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We have performed Mössbauer and magnetization studies on iron clusters that are formed in ytterbium films prepared by vapor co-deposition onto kapton substrates kept at room temperature. The film thicknesses were chosen in a range between 2.5 and 2.8 µm. XRD of the films reveals a mixture of fcc- and hcp-like ytterbium. Iron concentrations were between 0.3 and 5 at%.

All samples reveal hyperfine spectra attributed to only two types of iron clusters with well-defined hyperfine parameters. In addition there is found a small contribution from monomeric iron. From spectra taken under various applied external magnetic fields at 30 K we are able to show that the clusters in a (5 at% Fe) Yb film are ferromagnetic with average magnetic moments of about 70 µB.

Spectra between 10 and 30K reveal dynamic line broadenings due to spin freezing. This is also supported by susceptibility data that are typical for spin-freezing of only weakly interacting clusters at temperatures below ca. 20 K. This proves that the iron clusters have sizes on the order of nm. Spectra taken at 4.2 K reveal a complex distribution of magnetic hyperfine fields which is related to inhomogeneous static dipolar fields.

Spectra of films with lower iron concentrations reveal reduced spin freezing temperatures indicating weaker inter-cluster interactions. Sizes of clusters apparently do not change significantly with varying iron concentration.

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Dehydrogenation of dodecahydro-N-Ethylcarbazol on Pt(111)

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The dehydrogenation of the liquid organic hydrogen carrier dodecahydro-N-ethylcarbazole (H₁₂-NEC) on Pt(111) was studied by high-resolution X-ray photoelectron spectroscopy (HR-XPS) in order to elucidate its dehydrogenation reaction to N-Ethylcarbazol (NEC). The pair H₁₂-NEC/NEC is a potential candidate for chemical hydrogen storage in mobile applications: The material is a high boiling organic molecule that can be reversibly hydrogenated and dehydrogenated in catalytic processes.

H₁₂-NEC was adsorbed under ultra high vacuum (UHV) conditions by physical vapor deposition, and subsequently the reaction was monitored during heating. Although the molecules are quite complex, we were able to identify the reaction steps after detailed analysis of the C1s and N1s core levels. During adsorption at low temperatures the development of monolayer and multilayer peaks was observed. Interestingly, the N1s peak assigned to the multilayer is found at lower binding energy than the monolayer peak. When heating the sample continuously, the multilayer desorbs up to temperatures of about 285 K while the signature of the monolayer increases due to decreased damping. Subsequently, the dehydrogenation of the H₁₂-NEC to NEC follows successively in the range of 280 to 500 K. Above 430 K, the dealkylation reaction of the NEC to carbazole is observed. Upon further heating to 1000 K decomposition to adsorbed carbon takes place.

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Structural characterization of highly ordered graphene on Nickel (111) via Photoelectron Diffraction (XPD)

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Graphene, a zero density of state metal at Fermi level, is a material of great scientific and technological interest currently. This is due to their exceptional physical properties such as surface protection against oxidation. It has high hardness, since it is 200 times stronger than steel. Added to that, graphene has high thermal and electrical conductivity due to conduction electrons that behave as massless Dirac fermions presenting ballistic transport properties, which makes this material a strong candidate for circuit fabrication. However, graphene has "gap" zero near the Fermi level, which does not allow the control of electrical conductivity in electronics devices. Theoretical and experimental works suggest the possibility of opening gaps in graphene by introducing periodic modulations in their crystal lattice. One way to induce gaps in graphene is epitaxially growing it on different substrates (Ni, Ir, Pt, Ru and Co for example). The investigation of the structural properties of graphene on Ni substrates is one of the research lines of the surface physics group at UFMG. In this work we grow graphene on Nickel (111) via decomposition of propylene in ultra-high vacuum environment. Our XPS results show that this procedure results in one atomic layer of graphene on the surface, resulting in the system graphene / Ni (111). The structural quality of the sample was confirmed via LEED pattern. In this case the pattern is of type p(1x1). We studied the structure of graphene / Ni (111) via photoelectron diffraction (PED) in angular mode using x-ray source (1486eV), measuring the diffraction patterns of emission lines C1s and Ni2p as well as C1s peak using Synchrotron light source (hv=450 eV). Our results indicate that Carbon assumes a top_fcc structure, producing a reliability factor (Ra) of 0.15 for the Nickel emitter and 0.14 for the Carbon emitter. Our diffraction patterns of the Carbon emitter indicate that our growth has produced a surface with a very high crystallographic order. The interatomic distance of Carbon Nickel is 2.11 Å and the distance between the two first Nickel atom layers is 2.03 Å. These results agree with previous LEED calculation made by us group.

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Self-assembled monolayers (SAMs) of thiols on gold are an important system that allows an understanding of the interaction between organic molecules and metallic surfaces and have a wide range of applications [1]. However, the possibility of introducing functional groups into organosulfur molecules has opened new challenges to describe the influence of these groups in the formation of the self-assembled monolayer and in the functionalities of the system [2].

We have studied the adsorption of thioacetic acid (TAAH) on Au(111) from solution deposition. The close proximity of the SH groups to CO groups makes this molecule very attractive for exploring the effect of the functional group on the stability of the S–C and S–Au bonds. Although thioacetic acid was supposed to decompose slowly in water by hydrolysis supplying hydrogen sulfide, this behavior is not expected in nonpolar solvents such as toluene or hexane. Therefore, we have used these solvents for TAAH selfassembly on the Au(111) surface. The characterization of the adsorbates has been done by electrochemical techniques, X-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy (STM). We have found that even in nonpolar solvents thioacetic acid decomposes to S. The results have been discussed on the basis that the adsorbed species suffer a cleavage on the Au surface, leaving the S attached to it. The dissociation is a spontaneous process that reaches the final state very fast once it is energetically favorable, as can be interpreted from DFT calculations. The thioacetic acid adsorption reveals the strong effect that produces a functional group and the key role of the S–H bond cleavage in the self-assembly process.

Transition metal nanostructures have been extensively studied for several applications in different areas of research. Single crystalline surfaces of high Miller index offer the possibility to model materials of technological interest and study the correlations between electronic and geometrical factors and the role of defects [1].

In this presentation we will show the results obtained in the study by STM and XPS of two vicinal surfaces of Au modified by Pt [2]. The Au surfaces studied are Au(332) and Au(788), both vicinal to the (111) plane. Although the (788) face is well known to undergo a reconstruction that generates two different sites for nucleation of a new phase (fcc and hcp), the (332) face do not suffer such a reconstruction, turning this two systems suitable for studying the effect of the surface crystallography using a foreign metal that strongly interacts with the substrate.

STM measurements obtained for Pt-modified Au(332) and Au(788) surfaces suggest that a different mechanism of formation of the new phase on the surface takes place. For instance, in the case of the Pt/Au(332) surface, there is a brake up of the periodic monoatomic steps, probably due to Pt atom incorporation. On the other hand, in the case of Pt/Au(788) the formation of nanoislands solely on the fcc sites are observed leaving the hcp sites free from Pt.

XPS results for both Pt/Au(hkl) surfaces reveal the formation of an Au-Pt alloy at room temperature, especially at low θPt, and visible at all Pt coverage explored. The alloy formation was detected from Pt4f photoemission line shifting to lower BE, a fact that was already observed by Hörnström et al.[3] for bulk Pt-Au alloys.

Additional STM and XPS results regarding the study of the influence of thermal annealing on the morphological and electronic properties of Pt/Au(hkl) surfaces will be presented for various Pt coverage.

Properties of surfaces can be modified by addition of a self-assembled monolayer (SAM). If this layer contains molecular switches, the surface properties become variable by external stimuli like irradiation with light. Densely packed SAMs of azobenzene molecules on flat surfaces generally do not switch, i.e., undergo a trans-cis isomerization, due to steric hindrance and excitonic coupling, even when they are decoupled from the substrate.[1] We aimed at overcoming both of these constraints by creating from solution mixed SAMs in which we either tuned the individual optical absorption characteristics of the components by functional end-groups or increased the free volume around the chromophores. In all cases, mixing at the surface strongly depends on the interactions between components and the choice of solvent during the 24 hours of immersion. We have investigated two-component mixtures of different photochromic molecules based on ω-(4-(phenyldiazenyl)phenoxy)alkyl-α-thiols among each other and with a C12 alkane thiol as lateral spacer. The chromophores are decoupled from the Gold (111) substrate by hexyl or undecyl linker chains and modified in the para-position of the phenyldiazenyl moiety. We employed four derivatives, with a trifluoro methyl, a cyano, and two with a hydrogen substituent, denoted as TF-Az6, CN-Az6, H-Az6, and H-Az11, respectively.[2]

We succeeded in creating mixed SAMs with freely adjustable component ratios, which we investigated by UV/vis differential reflectance and X-ray photoelectron and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. The optical absorption bands of the chromophores slightly broaden and strongly shift depending on the component ratios. Reducing the packing density of the azobenzene units changes their orientation with respect to the surface normal and allows varying the excitonic coupling between the chromophores from single molecules to aggregates. A relatively small dilution with C12 spacers already enables efficient switching of H-Az11 molecules in a SAM, comparable to that in solution.

SYNTHESIS AND CHARACTERIZATION OF BaZnO₂ NANOCRYSTALS

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The study of zinc oxide has recently been extended due to the wide application that this material can produce and may be used in nanostructured materials, surface electrodes with a significant increase in the interface surface [1] and piezoelectronics materials [2]. In recent years a wide variety of zinc compounds have been used as blue light emitting diodes and diode lasers. In particular, ZnO has some remarkable properties of large clamping force and extreme stability of excitement, offering the possibility of forming practical lasers with low thresholds, even at high temperatures [3].

As the BaZnO₂ can be used in materials piezoelectronics, this study aimed at the synthesis of BaZnO₂ from acetates, Ba²⁺ and Zn²⁺ for the use of matrices luminescent applying the technique of thermoluminescence, thermal decomposition shows that the compound can be obtained at stable levels at temperature 600°C (Figure 1) dynamic air and N₂ atmosphere, heating to high temperatures ensures the purity of the material, the XRD showed the compound phases and comparing between their respective oxides.

Fig. 1. Thermal decomposition of BaZn(O₂C₂H₃) · 2.5 H₂O.

Fig. 2. The crystal structure of BaZnO₂.

Fig. 3. X-ray powder diffraction patterns of BaZnO₂ and [BaO, ZnO (bottom)].

References.
Development of surface-anchored metal organic frameworks with increased water stability for biological application

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Metal organic frameworks are a class of highly porous materials, which consist of two different components, metal or metal-oxo nodes and organic linkers. Due to their large surface area, tunable pore size and physiochemical properties combined with their high crystallinity, these hybrid materials are ideally suited for numerous applications, ranging from gas separation and catalysis to drug release. [1]

The deposition of highly ordered thin films of these materials on functionalized gold substrates (SURMOFs) is a key prerequisite for a number of applications in different fields, including sensorics and electrochemistry. The development of a step-by-step liquid-phase epitaxy (LPE) has made it possible to grow nearly perfectly oriented MOF thin films on appropriately functionalized solid substrates. [2]

Here we present results of studies aiming at an enhancement of water stability and biocompatibility of SURMOFs, (i) by varying the type of SBU or linker used for the SURMOF synthesis as well as (ii) by protecting preformed SURMOFs using polymer coatings. The enhanced water stability of MOF thin films would widen the scope of their potential applications, especially in the biological area. [3]

Different MOF families like MIL (Materials of Institut Lavoisier) and UiO (University of Oslo) show in general a good stability in water and biological media. To deposit these materials as oriented thin films on gold substrates we choose two members of these families - MIL-88(Fe) and UiO-66(Zr). To lower the reaction energy and enable the low temperature LPE process, we follow the SBU approach: in a first step we synthesis isolated, carboxylic iron or zirconium SBUs and introduce them in a second step to the LPE-process.

Electron quantization is a fundamental phenomenon that accompanies the transition from bulk metals to nanoclusters. The associated opening of a gap at the Fermi level crucially affects various properties of the nanostructure, e.g. its electrical and optical behavior and its performance in catalytic reactions [1]. By using low-temperature STM and STS, we have investigated the electronic structure of differently shaped 2D Au islands grown on MgO/Ag(001) thin films, concentrating on the size regime of the metal-insulator transition that occurs between 50-200 atoms in gold clusters. The observed symmetries and energy positions of quantum well states were rationalized by simple analytical models as well as by a density-functional-tight-binding approach that accounts also for structural disorder in the islands. Based on a statistically relevant number of single-cluster experiments, we derived general conclusions on the size of the HOMO-LUMO gap as a function of atom count and symmetry of the metal nanostructures.

Nanoscale photoelectron mapping and spectroscopy with an atomic force microscope

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The tip of an atomic force microscope is used as a local probe for photoelectrons excited by laser illumination. The tip-sample distance is precisely controlled by the van der Waals force and the pure photoemission current is measured without tunneling current contribution. The nanoscale photoelectron mapping with high current contrast is obtained on a cesium covered Au(111) surface. By sweeping the laser photon energy, the local photoelectron spectra are measured on Cs islands and terraces. The results reveal distinct electronic states and photoemission thresholds for different Cs coverage, providing the photoemission current contrast mechanism. The contrast in photoelectron mapping can be further tuned by the incident laser polarization exploiting the symmetry selection rules in the optical excitation.
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