

Atomic structure of nanosystems from first-principles simulations and microscopy experiments

Physics Boat 2013

4th – 6th June 2013

Helsinki, Finland – Stockholm, Sweden

Organizers

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Programme

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| 11:00 | <i>Registration</i> | | <i>chair: Banhart</i> | 9:00 | <i>chair: Kirkland</i> |
| 11:30 | <i>Lunch</i> | 14:00 | Egerton | 9:40 | Krivanek |
| 12:30 | <i>Opening</i> | 14:40 | Pantelides | 10:20 | Dedkov |
| | <i>chair: Busse</i> | 15:20 | Zhao | 10:40 | Resta |
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| 14:00 | Jonsson | | <i>chair: Coraux</i> | 11:20 | Coraux |
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| 15:00 | Sweetman | 18:40 | Kantorovich | | |
| 15:40 | Nony | 19:00 | Tonner | | |
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- 11:30 - 12:30 *Lunch*
- 12:30 - 12:40 *Opening*
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- 12:40 - 13:20 **Palmer**
Atomic structure and dynamics of supported, size-selected metal nanoclusters (and prospects for super-abundant production)
- 13:20 - 14:00 **Frederiksen**
Quantum transport from first principles
- 14:00 - 14:20 Jonsson
Structure and structural changes in gold clusters containing 55 to 3000 atoms
- 14:20 - 15:00 *Coffee at posters*
chair: Palmer
- 15:00 - 15:40 **Sweetman**
Understanding molecular interactions using NC-AFM
- 15:40 - 16:20 **Nony**
The non-contact atomic force / Kelvin probe force microscope simulator: a tool to address atomistic processes influencing imaging
- 16:20 - 16:40 Watkins
Simple models for efficient simulation of AFM
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chair: Egerton
- 17:50 - 18:30 **Banhart**
Electrical transport in atomic carbon chains measured by in-situ electron microscopy
- 18:30 - 19:10 **Kirkland**
Aberration Corrected Imaging of Defects in Graphene
- 19:10 - 19:30 Bollmann
The role of the quantum size effect on the growth of metallic nanostructures
- 19:30 - 19:50 Hung
First-principles low-loss EELS of HfO_2
- 20:00 - 22:00 *Dinner*

Atomic structure and dynamics of supported, size-selected metal nanoclusters (and prospects for super-abundant production)

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The controlled deposition of size-selected nanoclusters (nanoparticles), assembled from atoms in the gas phase, is a novel (and economically efficient) route to the fabrication of surface features of size <10 nm [1]. However theoretical treatments of the atomic structure of clusters far outstrip direct experimental measurements. In this talk I will focus on the creation and imaging of stable, monodispersed, monometallic and bimetallic [2] cluster arrays which represent new model systems for precision catalysis [3] and can also be used to trap and orientate individual protein molecules [4]. The atomic structure of the deposited clusters is revealed [5] by aberration-corrected scanning transmission electron microscopy (STEM) in the high-angle annular dark field (HAADF) regime with a spatial resolution of 0.1 nm; measuring the intensity of the incoherent scattering from individual atomic columns enables us to count atoms [6] and thus obtain 3D information rather than just 2D projections. Results include mass spectrometry of passivated Au clusters [7], atomic imaging of Au adatom dynamics on the surface of Au₉₂₃ magic-number nanoclusters [8], the purposeful transformation of the same Au₉₂₃ clusters under the electron beam to obtain more stable structures [9] and first atomic imaging results for small Au clusters, notably Au₅₅ and Au₂₀ [10,11]. We hope that these new data will help to enhance theoretical treatments of both structure and dynamics, e.g., via the refinement of semi-empirical potentials. One issue of particular interest which seems to arise from our work on Au₉₂₃ clusters is the distinction - for a given initial, non-equilibrium atomic configuration - between the lowest energy (ground) state and the most accessible state in manipulation experiments. Finally I will also propose a new kind of cluster beam source with the potential to allow super-abundant generation of such size-selected nanoclusters; proof of principle experiments will be reported.

- [1] R.E. Palmer et al., *Nature Materials* 2, 443 (2003).
- [2] F. Yin et al., *J. Am. Chem. Soc.* 133, 10325 (2011).
- [3] F. Yin et al., *J. Chem. Phys.* 134, 141101 (2011).
- [4] R.E. Palmer, *Trends in Biotechnology* 25, 48 (2007).
- [5] Z.Y. Li et al., *Nature* 451, 46 (2008).
- [6] N.P. Young et al., *Phys. Rev. Lett.* 101, 246103 (2008).
- [7] Z.W. Wang, *J. Am. Chem. Soc.* 132, 2854 (2010).
- [8] Z.W. Wang, R.E. Palmer, *Nano Lett.* 12, 91 (2012).

- [9] Z.W. Wang, R.E. Palmer, *Phys. Rev. Lett.* **108**, 245502 (2012).
- [10] Z.W. Wang, R.E. Palmer, *Nanoscale* **4**, 4947 (2012).
- [11] Z.W. Wang, R.E. Palmer, *Nano Lett.* **12**, 5510 (2012).

Quantum transport from first principles

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Electron transport in atomic-scale devices is an important research area where both fundamental physics and technological opportunities are simultaneously addressed. From the theoretical point of view one of the great challenges is to develop general methods for quantitative simulations of real devices taking into account the atomistic details. One widespread approach is based on ground-state density-functional theory (DFT) for the electronic structure in combination with nonequilibrium Green's functions (NEGF) for the transport.

In this talk I will describe recent developments based on the DFT+NEGF approach and discuss capabilities and limitations to various quantum transport problems. Some recent results obtained with the DFT+NEGF code TranSIESTA [1] will be used to demonstrate how calculated low-bias conductances of single-C60 junctions compare with experimental findings and yield insight into the transport mechanisms [2].

NEGF theory also provides a framework for describing electron-vibration interactions in quantum transport, such as the signatures of vibrational excitation revealed in inelastic electron tunneling spectroscopy (IETS). I will describe our efforts to extend the DFT+NEGF methods to include inelastic scattering and local heating effects in the code Inelastica [3]. The methods allow us to address questions such as: (i) What are the fingerprints of specific molecules in IETS? (ii) How are IETS signals modified by tip functionalization [4]? (iii) How does vibrational excitations manifest themselves in shot noise [5]?

[1] M. Brandbyge, J. L. Mozos, P. Ordejon, J. Taylor, K. Stokbro, *PRB* **65**, 165401 (2002).

[2] G. Schull, T. Frederiksen, A. Arnau, D. Sanchez-Portal, R. Berndt, *Nature Nanotechnology* **6**, 23 (2011).

[3] T. Frederiksen, M. Paulsson, M. Brandbyge, A-P. Jauho, *PRB* **75**, 205413 (2007).

[4] A. Garcia-Lekue, D. Sanchez-Portal, A. Arnau, T. Frederiksen, *PRB* **83**, 155417 (2011).

[5] R. Avriller, T. Frederiksen, *PRB* **86**, 155411 (2012).

Structure and structural changes in gold clusters containing 55 to 3000 atoms

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We have carried out global optimization and long time scale simulations of gold clusters of magic size containing 55 to 5083 atoms. An algorithm which brings the clusters from one local minimum to another via first order saddle points is used to explore the energy surface and optimize the atomic ordering [1]. The local atomic structure was analyzed using common neighbor analysis [2]. The same minimum, supposedly the global minimum, was obtained starting from a wide variety of initial structures for clusters with up to 561 atoms. EMT and Gupta potentials were used for the most computationally intense simulations but the results for clusters with up to 561 atoms were also tested and refined with DFT using the PBE functional approximation. The 55 and 147 atom clusters were found to have distorted icosahedral structure. The transition from cuboctahedral to icosahedral ordering of the 147 atom cluster was found to occur through a low saddle point of only 0.7 eV and involve nucleation at one of the corner sites. An unexpected distortion of the icosahedral structure was observed for the 561 and 923 atom clusters. As the clusters grown, face centered cubic local order becomes more and more abundant until at 5083 atoms the optimal structure becomes that of the face centered cubic crystal. For clusters with 309 atoms, a detailed comparison could be made with aberration-corrected scanning transmission electron microscopy measurements [3] and excellent agreement was found between the measured and calculated structures.

[1] A. Pedersen, J-C. Berthet and H. Jonsson, *Lecture Notes in Computer Science* 7134, 34 (2012).

[2] D. Faken and H. Jonsson, *Computational Materials Science* 2, 279 (1994).

[3] Z. Y. Li, N. P. Young, M. Di Vece, S. Palomba, R. E. Palmer, A. L. Bleloch, B. C. Curley, R. L. Johnston, J. Jiang and J. Yuan, *Nature* 451, 46 (2008).

Understanding molecular interactions using NC-AFM

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Both NC-AFM and STM have been used to great success in understanding the role of molecule-molecule interactions on surfaces, and recently impressive results have been obtained showing sub-molecular resolution during the imaging of single molecules by the controlled functionalisation of a scanning probe tip with inert molecular and atomic species [1-3]. Measurement of intermolecular interactions has also been shown by using 'inverse' imaging, that is, functionalising the tip with the molecule of interest and 'inverse' imaging the adsorbed molecule with both well characterised surface features and other adsorbed molecules [4-5]. Using these techniques allows for the exciting possibility of directly probing intermolecular interactions in three dimensions with sub-molecular resolution. Such experiments might offer a fascinating insight into molecular interactions, but a key issue in interpreting data produced in such 'tip-functionalised' experiments remains that the orientation of the tip adsorbed molecule is (in general) unknown. In this talk I will offer an overview of molecule-on-molecule interactions measured using NC-AFM at cryogenic temperatures, and suggest possible routes by which the tip molecule orientation might be determined.

[1] L Gross et al, *Science* **325**, 1110 (2009).

[2] L Gross et al, *Science* **337**, 1326 (2012).

[3] G Kichin et al, *PRB* **87**, 081408 (2013).

[4] G Schull et al, *Nat. Nano* **6**, 23 (2010).

[5] C Chiutu et al, *PRL* **108**, 268302 (2012).

The non-contact atomic force / Kelvin probe force microscope simulator: a tool to address atomistic processes influencing imaging

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The non-contact atomic force / Kelvin probe force microscope (nc-AFM/KPFM) simulator is a realistic numerical implementation of the electronics of a nc-AFM setup including KPFM operational modes [1,2]. The simulator has been demonstrated to be able to reproduce the dynamical performances of the instrument upon the operating conditions and the used probe (cantilever or tuning fork) [3]. The code may either receive a pre-computed ab initio interaction force field, or computes it at run time by means of analytical expressions or semi-empirical potentials. Thus, the simulator is able to perform virtual experiments such as images at constant Δf or constant height, or spectroscopic measurements: Δf vs. z or bias voltage. In the near past, the simulator has been used to unravel the origin of the atomic-scale contrast in KPFM images on a bulk KBr(001) single crystal [2]. Thus, the influence of the polarizability of both, the foremost tip atom and surface atoms has been pointed out. Recently, following the results from the IBM Zurich group [5,6], the code has been upgraded and targeted at the calculation of images of molecules on surfaces and molecular systems on surfaces with stiff sensors such as tuning forks [3,4]. In this talk, the numerical scheme of the simulator will be presented along with a set of results illustrating the potential of such a tool to address the atomistic processes influencing imaging and spectroscopic measurements in nc-AFM and KPFM.

[1] L.Nony et al., *Phys.Rev.B* **74**, 235439 (2006).

[2] L.Nony et al., *Phys.Rev.Lett.* **103**, 036802 (2009).

[3] F.Castanie et al., *Beilstein J.Nanotechnol.* **3**, 301 (2012).

[4] F.Castanie et al., *submitted to J.Phys.Chem.C* xxx, xxx (2013).

[5] L.Gross et al., *Science* **337**, 1326 (2012).

[6] F.Mohn et al., *Nature Nanotechnology* **7**, 227 (2012).

Simple models for efficient simulation of AFM

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Even with recent advances in computational power the simulation of AFM imaging remains challenging. The problem is that it has been found that in almost all cases the atomically sharp tip must be included explicitly in the simulation at each lateral and vertical position above the surface: this can easily lead to 10,000s of simulations needed to be carried out to construct and image of a complex surface, molecule or defect. Our recent work suggests two classes of problem when this difficulty can be alleviated, and images constructed from a single simulation leading to 3-4 orders of magnitude speed-up in image simulation: (i) Ionic materials, such as NaCl or NiO, when imaged using a carefully prepared metallic tip at large tip-surface separations. (ii) AFM in liquid when a sharp tip with a closely bound water molecule or hydroxyl group is primarily responsible for imaging. In the first case we find we can obtain quantitative agreement with experiment by considering only the electrostatic contributions from the tip and the surface [1]. In the second class of problems we show that an argument based on statistical mechanical properties of the adsorbed liquid above a surface can be used to construct approximate images of the surface.[2]

[1] G. Teobaldi, K. Lammle, T. Trevelyan, M. Watkins, A. Schwarz, R. Wiesendanger and A. L. Shluger, *Phys. Rev. Lett* **106**, 216102 (2011).

[2] M. Watkins and B. Reischl, *J. Phys Chem* **submitted**, - (2013).

Electrical transport in atomic carbon chains measured by in-situ electron microscopy

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It is known since a few years that one-dimensional carbon exists, represented by chains of carbon atoms. These may be bonded by either alternating single/triple carbon-carbon bonds (polyynes) or by double bonds throughout the chain (cumulene). By using a combination of STM and TEM in an in-situ electron microscopy study, carbon atom chains have not only been made but also characterized electrically [1]. The chains were obtained by unraveling carbon atoms from graphene ribbons while an electrical current flowed through the ribbon and, successively, through the chain. The electrical conductivity of the chains was found to be much lower than predicted for ideal chains. First-principles calculations show that strain in the chains determines the conductivity in a decisive way. Indeed, carbon chains are always under varying non-zero strain that transforms their atomic structure from cumulene to polyynes, thus inducing a tunable band gap. The modified electronic structure and the characteristics of the contact to the graphitic periphery explain the conductivity of the locally constrained carbon chains. These are the first electrical measurements on atomic carbon chains and show a perspective toward their synthesis and application as the smallest possible interconnects or even as one-dimensional semiconducting devices.

[1] O. Cretu, A. R. Botello-Mendez, J.-C. Charlier, I. Janowska, C. Pham-Huu, F. Banhart, *arXiv* **0**, 1302.5207 (2013).

Aberration Corrected Imaging of Defects in Graphene

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To usefully deploy Graphene and related materials in electronic applications [1-3] it is essential to understand the behavior of point defects which have been the subject of extensive research over decades for silicon devices. High resolution Transmission Electron Microscopy is the ideal characterization tool for studying the formation and evolution of defects in Graphene in real space. Moreover, recent instrumental advances make it possible to image these defects at primary energies below those that cause significant specimen damage whilst retaining sufficient spatial resolution to resolve the local atomic configuration in the Graphene lattice around the defect site. In this paper we will discuss the controlled formation of several defect types in Graphene, including mono- and di-vacancies and will demonstrate that the evolution of these into more complex extended defects can be controlled by electron beam irradiation. In the case of the simplest vacancy type (the mono vacancy) two configurations have been observed and we have quantitatively measured the strain in the lattice surrounding these. Density functional theory (DFT) calculations have been used to evaluate the energetics of the two configurations and to indicate pathways by which this defect can evolve. We will also report dynamic studies of small defect structures in Graphene, which enable reaction pathways between different structural forms to be evaluated. Finally we will show how quantitative measurement of local bond lengths in various defect structures and dislocations when compared with DFT calculations provides an insight into the local charge distribution at defect sites.

[1] K. S. Novoselov, et al. , *Nature* **490**, 192 (2012).

[2] F. Schwierz, *Nature Nanotech* **5**, 487 (2010).

[3] L. Britnell et al. , *Science* **335**, 947 (2012).

The role of the quantum size effect on the growth of metallic nanostructures

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In the 1990s a novel growth mode was found, which resembles Stranski-Krastanov growth, but is qualitatively different from the classical growth modes in that quantum size effects (QSEs) seem to dominate, leading to non-trivial smooth film growth described as electronic or quantum growth. In this novel growth mode, the growth of thin Pb(111) films has attracted particular interest, since its Fermi wavelength is nearly commensurate to the bilayer atomic spacing and QSE driven growth sometimes persists even over 30 layer thick islands [1]. Another candidate we propose is Bi, a material that is 'hovering' between being a metal and a semiconductor, making electronic effects more pronounced than strain effects. This property makes thin Bi films prime candidates for allotropism and a candidate for electronic growth.

QSEs are usually found on surfaces with a bandgap in the surface projected bulk bands, making a direct coupling between the electrons of the film and the substrate bulk impossible. Examples are semi-conductors such as Si(111) and Ge(111), as well as metals such as Cu(111) and Ag(111), but the substrate of our choice, Ni(111), just misses such a bandgap. We will demonstrate a route, where the intrinsic modification of the electronic properties of the Ni(111) surface by the mere presence of a Bi- or Pb-film may just suffice, to generate a situation with a surface projected bandgap.

We present (I/V-) Low Energy Electron Microscopy (LEEM) and selective area (I/V-) Low Energy Electron Diffraction (μ LEED) measurements in combination with modeling and Tensor LEED calculations, illustrating indeed the QSE driven growth for Pb on Ni(111) in comparison to the key examples of QSEs [2,3]. We demonstrate the importance of the QSE on the growth of thin films by showing the influence in thin Bi films, where the QSE determines the thin film structure, density and interlayer distance, in order to embrace the standing Fermi waves with a wavelength far smaller than in the bulk material [4]. We expect the structures found in the thin bismuth films to be far better conductors than ordinary bismuth, and expect other physical and chemical properties of the newly discovered crystal structures to differ from those in the bulk bismuth as well.

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- [2] T. R. J. Bollmann, R. van Gastel, H. J. W. Zandvliet, and B. Poelsema, *Phys. Rev. Lett.* **107**, 136103 (2011).
- [3] T. R. J. Bollmann, R. van Gastel, H. J. W. Zandvliet, and B. Poelsema, *New J. Phys.* **13**, 103025 (2011).
- [4] T. R. J. Bollmann, R. van Gastel, H. J. W. Zandvliet, and B. Poelsema, *Phys. Rev. Lett.* **107**, 176102 (2011).

First-principles low-loss EELS of HfO₂

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HfO₂ is a high- κ dielectric material with applications in microelectronics. Its structure has been studied at nanoscale resolution using transmission electron microscopy (TEM) in conjunction with electron energy loss spectroscopy (EELS). We describe how theoretical spectroscopy can be used to validate, interpret, and complement experimental measurements. We simulate the ground state electronic structure of crystalline HfO₂ with Kohn-Sham density functional theory (DFT) and a planewave pseudopotential implementation; the valence (or low-loss) EEL spectra of HfO₂ are computed using time-dependent DFT. Results from the random phase approximation are found to be in good agreement with experimental measurements. The spectra of the monoclinic, tetragonal, and cubic polymorphs of HfO₂ are characterized, and we demonstrate how the presence and relative energy of the f-band affect the spectra. We also model the dispersion of plasmons with increasing momentum transfer, and Fourier transform the spectra to visualize the electron density response to external perturbations.

Wednesday 05.06.2013

- chair: Banhart*
- 14:00 - 14:40 **Egerton**
Recent advances in TEM-EELS
- 14:40 - 15:20 **Pantelides**
Probing complex systems with a combination of density functional theory and scanning transmission electron microscopy
- 15:20 - 15:40 **Zhao**
Free-standing single-atom iron layers suspended in graphene perforations
- 15:40 - 16:00 **Seitsonen**
Hexagonal boron nitride on transition metal surfaces: A perspective from density functional theory
- 16:00 - 17:20 *Coffee at posters*
chair: Coraux
- 17:20 - 18:00 **Liljeroth**
Molecular self-assembly on graphene on SiO₂ and h-BN substrates
- 18:00 - 18:40 **Stich**
Intricate Mechanism of Lateral and Vertical Manipulation of Super-Cu Atoms on the Cu₂O Surface: Experiment and Theory
- 18:40 - 19:00 **Kantorovich**
Self-assembly of p-Terphenyl-m-Dicarbonitrile on the Ag(111) surface: Simulations of assisted isomerisation reaction mechanism
- 19:00 - 19:20 **Tonner**
Density-functional study of alkyne adsorption on Si(001) and comparison to STM results
- 20:00 - 22:00 *Dinner*

Recent advances in TEM-EELS

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The commercial development of electron-lens aberration correctors has improved the spatial resolution of the transmission electron microscope (TEM) to below 0.1 nm, while electron-beam monochromators have improved the energy resolution of transmission electron energy-loss spectroscopy (EELS) to below 0.1 eV. In many cases, the spatial resolution of TEM-EELS is therefore determined by basic principles: radiation damage and the delocalization of inelastic scattering, while the energy resolution of core-loss spectroscopy is limited by initial- or final-state broadening.

Probing complex systems with a combination of density functional theory and scanning transmission electron microscopy

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The talk will describe recent developments in linking density functional theory (DFT) calculations for electron excitations in a solid with diffraction theory for the focused electron beam of a scanning transmission electron microscope to simulate measured probe-position-dependent electron-energy-loss spectra (EELS) and extract information about the local bonding and electronic properties.[1] It will also describe several examples of using a combination of DFT, Z-contrast imaging, and EELS to demonstrate the role of oxygen vacancies in several transition-metal oxide systems. Primary collaborator: S.J. Pennycook Work supported in part by the Department of Energy Basic Energy Sciences Directorate.

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Free-standing single-atom iron layers suspended in graphene perforations

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Atomic mono-layers which are truly two dimensional (2D) exhibit a variety of novel properties due to electron confinement and loss of coordination in the thickness direction. Examples include graphene, monolayer hexagonal-BN, WS₂ and MoS₂ [1] Metallic mono-layers, in particular, magnetic mono-layers (e.g. Fe & Mn) are also attractive, however, thus far they have only been demonstrated whilst supported on a substrate [2,3]. The magnetic properties of atomically thin Fe are of great interest as they have an unusual enhancement of the magnetic moment as compared to bulk Fe as well as a large perpendicular magnetic anisotropy. For these reasons Fe mono-layers are considered promising candidates for next generation recording media with both high density and high read-write rates [4]. The graphene samples used in our experiments are grown by CVD over Ni/Mo substrates and then transferred on to lacey carbon transmission electron microscopy (TEM) grids. An FeCl₃ etching solution was used in the transfer process [5]. The transfer process tends to leave behind residual Fe atoms and clusters on the graphene surface. These atoms and clusters can move on the surface relatively freely and move to perforations in the graphene membrane forming novel structures in the process. By using Cs aberration corrected TEM, image simulations and first principles calculations, we conclusively show the structure of single-atom free-standing iron crystal layers for the first time. Because there are no underlying substrate interactions, all the advantages of 2D structures are preserved. Different kinds of mono-layer Fe-graphene interface atomic arrangements are explicitly investigated and compared with the ab-initio calculations. These atomic interface arrangements are shown to have crucial effects on the stability and strain/stress distributions of 2D Fe crystals. The dynamics of suspended mono-layer Fe under electron beam irradiation are also investigated in-situ showing both their formation as well as their bending. The structure we present is of great importance for various reasons. Firstly, this is the first direct observation of suspended mono-layer Fe crystals. Secondly, since the magnetic properties are very sensitive to the lattice type and lattice constant, these studies now provide invaluable experimental data for more accurate theoretical investigations. Moreover, we show that perforated graphene can be used as an in-plane support tool for other two dimensional structures which are usually unstable at the macroscopic scale.

This makes perforated graphene a promising candidate for high density packaging of 2D structures which could be attractive for magnetic recording, photonic and electronic applications.

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Hexagonal boron nitride on transition metal surfaces: A perspective from density functional theory

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Single layer of hexagonal boron nitride (h-BN) can form both commensurate and incommensurate structures when adsorbed on surfaces of transition and noble metals. The latter form Moire patterns that lead to different vertical corrugation, sometimes up to about 1 Å. These have periodicities of several nanometres and can act as templates for adsorbed atoms and molecules (<http://www.nanomesh.ch/>).

In this contribution we shall review our recent calculations [1] using density functional theory (DFT) to support and explain recent experiments on the h-BN structures on Ni(111), Cu(111), Ru(0001) and Rh(111). We make connections to methods which provide information of the geometrical (LEED, STM, SXRD) and electronic (STM, STS, ARPES) structure of these systems.

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Molecular self-assembly on graphene on SiO₂ and h-BN substrates

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After almost a full decade of experimental work on graphene, a controllable way to manipulate its electronic properties is lacking. The ability to control the graphene band structure, including the possibility of opening a band gap, would be crucial in paving the way for graphene-based electronics. One of the suggested ways of controlling the electronic properties of graphene is to establish a periodic potential modulation on it, which could be achieved by self-assembly of ordered molecular lattices. The use of molecular lattices for this purpose would allow the interaction strength and the period of the potential modulation to be tuned through the choice of the molecules.

We have studied the self-assembly of cobalt phthalocyanines (CoPc) on graphene grown by chemical vapor deposition (CVD) transferred onto silicon dioxide (SiO₂) and hexagonal boron nitride (h-BN) substrates. Our scanning tunneling microscopy (STM) experiments show that on both substrates, CoPc forms a square lattice. However, on graphene on SiO₂, the domain size is limited by the surface corrugation, whereas on h-BN, the domain size is limited only by the step edges of the underlying h-BN. In addition to the increased domain size, the molecular ordering within one domain is better on G/h-BN than on G/SiO₂. Additionally, scanning tunneling spectroscopy (STS) shows that the energies of the molecular orbitals shift from one molecule to another. This implies that CoPc molecules are doped by the substrate, and that the level of doping varies from molecule to molecule. This variation is larger on graphene on SiO₂, which is likely to be due to the larger charge fluctuations compared to G/h-BN. The peaks in the tunneling spectra have a lorentzian lineshape and their width yields the tunneling coupling of the molecular orbitals with the graphene substrate. These results suggest that graphene on h-BN is an ideal substrate for the study of molecular self-assembly towards engineered potential landscapes on graphene.

Intricate Mechanism of Lateral and Vertical Manipulation of Super-Cu Atoms on the Cu:O Surface: Experiment and Theory

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We present a joint experimental and theoretical study of lateral and vertical manipulations of super-Cu atoms on the oxygen-terminated $p(2\times 1)$ Cu(110) surface with Non-Contact Atomic Force Microscopy (NC-AFM). The surface consists of rows of alternating Cu and O atoms on the bare Cu(110) surface. Cu adatoms occupy positions between two adjacent Cu-O rows opposite two O atoms in each of them. Using NC-AFM we find that using an O terminated tip [1] vertical manipulation events, consisting of both removal and deposition of Cu atoms, are frequently seen. Interestingly, no change of contrast is observed. At the same time, lateral manipulation events were observed only at the edges of $c(6\times 2)$ islands, no lateral manipulation was found to be possible on the $p(2\times 1)$ terraces.

In order to understand these observations, we attempted a comprehensive theoretical study of both lateral and vertical manipulations of the super-Cu atoms on the $p(2\times 1)$ Cu(110):O surface with the O-terminated NC-AFM tip. Using DFT calculations in conjunction with nudged elastic band method for calculating transition barriers, as well as kinetic Monte Carlo (KMC) simulations, we propose detailed mechanisms of both lateral and vertical manipulations, which fully explain experimental observations. The mechanism consists of several stages: two stochastic (thermal with an energy barrier) and one conservative (dragging), which happens in between. KMC simulations confirm the viability of this mechanism and give statistics information.

We find that lateral manipulation can only be rationalized if the tip comes much closer to the surface, which explains why these particular events were not frequently observed.

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Self-assembly of p-Terphenyl-m-Dicarbonitrile on the Ag(111) surface: Simulations of assisted isomerisation reaction mechanism

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Transformation of molecules during the growth of their assemblies on crystal surfaces is the most intriguing feature in molecular self-assembly. This effect may be either undesirable (e.g. degradation of the growing network) or desirable as the only way to formation of new stable structures. One such case, which has been recently studied experimentally using Scanning Tunnelling Microscopy (STM), is the adsorption at room temperature (RT) of p-Terphenyl-m-Dicarbonitrile molecules on the Ag(111) surface [1]. The molecule has Cis and Trans isomers, but on the surface Trans isomers appear as chiral (L and D). Initially there were approximately 50% of Cis and 25% of each Trans isomers on the surface; however, when STM images were taken, almost no Cis isomers were found. The authors explained the effect by Cis-to-Trans isomerization, which must have happened during the growth of the nanostructures. In this study we attempted to understand this phenomenon using a tool kit of various types of theoretical modeling. Using ab initio density functional theory (DFT) calculations, we found that the molecules adopt geometries in which their N atoms make direct bonding with Ag atoms underneath, i.e. the molecules prefer standing on the surface with two legs making two strong covalent bonds. Using Nudged Elastic Band (NEB) calculations, we then established their diffusion mechanism. We find that the molecules walk, i.e. they perform a rocking motion whereby at each time only a single leg changes its position pivoting around the other leg, with the barriers of the order of several tens of meV. These results confirm an experimental observation that the molecules are quite mobile on the surface at RT. In order to explain formation of molecular chains, extensive calculations were performed in the gas phase and with molecules on the surface. We argue that the chains are formed by Trans homochiral molecules making double hydrogen (H) bonding with each other. However, NEB calculations for the Cis-to-Trans and back isomerization reactions on the surface for a single molecule do not show any preference towards any of the isomers. Instead, we find that Cis-to-Trans isomerization can be preferred (as opposed to the back reaction) if it is assisted by a neighboring Trans molecule in which case the free energy of the system is lowered by approximately 0.3 eV due ability of them forming two H bonds with each other. This observation is sufficient in our view to explain

the observed disappearance of the Cis isomers during the growth. Corresponding Kinetic Monte Carlo simulations of the assembly based on molecules being able to walk, bond to each other and change their isomerization, are currently in progress.

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Density-functional study of alkyne adsorption on Si(001) and comparison to STM results

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The organic functionalization of semiconductor surfaces is an important task in order to improve upon existing devices (e.g. molecular electronics) in the long-term. To this end, an accurate experimental and theoretical description of promising organic molecules on these surfaces is necessary.[1] In this computational study, we used dispersion-corrected density-functional theory (PBE-D3)[2,3] in order to shed light on the adsorption of acetylene and cyclooctyne on the Si(001)c(4x2) surface. While the adsorption of simple unsaturated molecules like ethylene[4] and acetylene has been thoroughly explored in the past, the smallest cyclic molecule with a carbon-carbon triple-bond — cyclooctyne — and its interactions with this highly relevant surface was not known prior. Starting from a high-resolution STM study of this system by our collaborators in Marburg[5], we explored the adsorption behavior of cyclooctyne from the low to the high coverage regime. The focus of these computational investigations was the explanation of the observed features in the STM pictures.[5] To this end, we conducted STM simulation of the adsorption modes found in the Tersoff-Hamann approximation[6] and were able to shed light on the observed features and could test the experimental hypotheses of possible adsorption modes. We could conclusively explain the adsorption mode of cyclooctyne in agreement with the experimental observations.

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Thursday 07.06.2013

- 9:00 - 9:40 *chair: Kirkland*
Krivanek
Advances in monochromators and aberration correctors
- 9:40 - 10:20 **Dedkov**
Electronic structure and imaging contrast of graphene moire on metals: combined STM/AFM/Kelvin-probe and DFT studies
- 10:20 - 10:40 **Resta**
Silicene: first Combined non-Contact Atomic Force Microscopy and Scanning Tunneling Microscopy Observations
- 10:40 - 11:20 *Coffee at posters*
chair: Dedkov
- 11:20 - 12:00 **Coraux**
Intercalation between graphene and a metal
- 12:00 - 12:40 **Busse**
Ion beam induced defects in graphene studied by STM, MDS, and DFT
- 12:40 - 14:00 *Closing and Lunch*

Advances in monochromators and aberration correctors

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Electron-optical instrumentation and its applications have advanced rapidly in the last few years. In this paper, the Nion contribution to the general progress is reviewed. The scanning transmission electron microscope (STEM) which we recently introduced combines a bright, stable and mono-energetic cold field emission electron gun (CFEG) with an ultra-stable probe-forming column corrected to 5th order and a high-stability sample stage operating in an ultra-high vacuum [1,2]. It has allowed experiments to be carried out that seemed unthinkable only a few years ago. Examples include the determination of the position and type of every atom in a monolayer material [3], detecting single atoms by X-ray spectroscopy [4], and even exploring the atomic environment of single atoms, based on their near-edge EELS fine structures [5,6]. More recently still, we have developed a High Energy Resolution Monochromated EELS-STEM (HERMES) system that uses several new design principles [7,8]. The monochromation is carried out at the ground potential (i.e., at the full primary energy) rather than inside the electron gun, with an all-magnetic monochromator (MC) consisting of a main energy-dispersing prism, spectrum-magnifying quadrupoles, auxiliary prisms that bend the beam into an alpha-type trajectory, an energy-selecting slit equipped with intensity sensing, and aberration-correcting sextupoles and octupoles. The MC uses dispersing-undispersing optics such that the energy dispersion of the beam is precisely cancelled at its exit. The MC's main prism winding is connected in series with the prism of an all-magnetic EEL spectrometer, which means that the energy spectra formed at the slit and at the EELS detector track each other, and small instabilities in the prism supply current do not change the position of the spectrum on the final detector. The high tension (HT) of the microscope is stabilized by sensing the electron current falling on the two halves of the MC's slit in a feedback scheme that adjusts the HT such that the energy-dispersed beam remains precisely centered on the slit opening. HERMES has been able to reach 12 meV full-width at half-maximum (FWHM) of the EELS zero loss peak (ZLP) in a short-exposure spectrum at a primary energy of 60 keV, and 20 meV FWHM in spectra acquired for several seconds. For inner shell loss spectra, it routinely reaches a resolution of about 40 meV and has resolved a rich variety of near-edge fine structures, for instance in Si L_{2,3} spectra of an SiO₂ layer in a MOSFET and in elemental silicon. Further

improvements in energy resolution, to 10 meV and beyond, should become possible once the detector part of the column and the EELS are brought up to the ultra-stable design standards used in the probe-forming part of the column, and we are now working in this direction. When the energy-selecting slit is opened to admit an electron beam about 100 meV wide at 60 keV primary energy, the spatial resolution of the system is improved compared to running with the MC turned off (and the beam going straight through it), or the MC on and the energy-selecting slit withdrawn from the beam [8]. This is because at primary energies <100 keV, the size of the unmonochromated probe in the Nion STEM is mainly limited by chromatic aberration (C_c), and decreasing the beam energy spread reduces C_c 's influence. Bypassing the chromatic resolution barrier shifts the attention back to geometric aberrations. We are presently working on incorporating extra sextupoles in the Nion C3/C5 quadrupole-octupole probe corrector [9] for more flexible control of parasitic aberrations. The sextupoles work together with other multipoles of the corrector and produce a rich set of combination aberrations, which allows all the important parasitic aberrations up to fifth order to be adjusted via a small subset of controls that addresses each aberration in turn. This should allow HERMES to form aberration-corrected electron probes with semi-angles of up to about 50 mrad, and to reach probe sizes of about 0.8 Å at 60 keV and about 1.2 Å at 30 keV.

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Electronic structure and imaging contrast of graphene moire on metals: combined STM/AFM/Kelvin-probe and DFT studies

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Graphene layer on metal surfaces have been attracting the attention of scientists since several decades, starting from middle of the 60s, when catalytic properties of the close-packed surfaces of transition metals were in the focus of the surface science research [1,2]. The recent demonstration of the fascinating electronic properties of the free-standing graphene renewed the interest in the graphene/metal systems, which are considered as the main and the most perspective way for the large-scale preparation of high-quality graphene layers with controllable properties. For this purpose single-crystalline as well as polycrystalline substrates of $3d - 5d$ metals can be used. One of the particularly exciting questions concerning the graphene/metal interface is the origin of the bonding mechanism in such systems [2-4]. This graphene-metal puzzle is valid for both cases: graphene adsorption on metallic surfaces as well as for the opposite situation of the metal deposition on the free-standing or substrate-supported graphene. In the last case the close-packed surfaces of $4d$ and $5d$ metals are often used as substrates. A graphene layer prepared on such surfaces, i. e. Ru(0001), Rh(111), Ir(111), or Pt(111), forms so-called moire structures due to the relatively large lattice mismatch between graphene and metal substrates. As a consequence of the lattice mismatch the interaction strength between graphene and the metallic substrate is spatially modulated leading to the spatially periodic electronic structure. Such lateral graphene superlattices are known to exhibit selective adsorption for organic molecules or metal clusters. Especially, the adsorption of different metals - Ir, Ru, Au, or Pt - on graphene/Ir(111) has been intensively studied showing a preferential nucleation around the so-called FCC or HCP high-symmetry positions within the moire unit cell [5], which was explained via local sp^2 to sp^3 rehybridization of carbon atoms with the bond formation between graphene and the cluster. However, a fully consistent description of the local electronic structure of graphene/Ir(111), the observed imaging contrast in scanning probe experiments and the bonding mechanism of molecules or clusters on it is still lacking, motivating the present research. Here we present the systematic studies of a graphene layer on different lattice mismatched surfaces [Ru(0001), Rh(111), and Ir(111)] with the focus on the graphene/Ir(111) system [6]. This research was performed via a combination of the density functional theory (DFT) calculations, low-energy electron

diffraction, angle-resolved photoelectron spectroscopy (ARPES), and scanning tunneling and atomic force microscopy (STM and AFM) as well as Kelvin-probe techniques. The microscopy experiments were performed in constant current / constant frequency shift (CC/CFS) and constant height (CH) modes (combination of SPECS SPM Aarhus 150 and KolibriSensor). ARPES data clearly demonstrate a free-standing-like character of the electronic states of graphene in this system. Our further results obtained via combination of DFT calculations and scanning probe microscopy imaging allow to discriminate the topographic and electronic contributions in these measurements and to explain the observed contrast features. We found that in STM imaging the electronic contribution is prevailing compared to the topographic one and the inversion of the contrast can be assigned to the particular features in the electronic structure of graphene on Ir(111). Contrast changes observed in constant height AFM measurements are analyzed on the basis of the energy, force, and frequency shift curves, obtained in DFT calculations, reflecting the interaction of the W-tip with the surface and are attributed to the difference in the height and the different interaction strength for high-symmetry sites within the moire unit cell of graphene on Ir(111). The presented findings are of general importance for the understanding of the properties of the lattice-mismatched graphene/metal systems especially with regard to possible applications as templates for molecules or clusters.

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Silicene: first Combined non-Contact Atomic Force Microscopy and Scanning Tunnelling Microscopy Observations

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Silicene is a honeycomb arrangement of silicon atoms forming a new synthetic atom-thin two dimensional honeycomb silicon allotrope. This new silicon structure, which does not exist in nature, has recently generated a very strong interests [1] since it was first grown by silicon deposition on Ag(111) substrates [2]. Silicene first layer synthesis appears now as well recognized by the research community. Recently the research effort has been on the growth of silicene multilayers. Here, we report observations of the two major silicene structures, single layer and double-layer, epitaxially grown on silver (111) surfaces. For the first time they are observed by combining non-contact Atomic Force Microscopy and Scanning Tunneling Microscopy. Comparison of consecutively acquired AFM and STM images reveals the dominant role of geometry over electronic effects, typically, in the appearance of the archetype single silicene layer, which is 3×3 reconstructed (4×4 supercell in terms of Ag(111)). We further establish that the following $\sqrt{3} \times \sqrt{3} R(30)$ silicene reconstruction ($4/\sqrt{3} \times \sqrt{3} R(30)$ with reference to Ag(111)) is observed upon further silicon deposition, stems from the second layer grown, thus suggesting the existence of bi-layer silicene. We also extend the interpretation of the Ag(111) $\sqrt{7} \times \sqrt{13} R(13.9)$ reconstruction [3], recognizing the four domains arising from the rotational epitaxy of first layer $\sqrt{7} \times \sqrt{7} R(19.1)$ honeycomb domains in coincidence with the silver superstructure, therefore suggesting that also this arrangement might effectively belong to silicene.

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Intercalation between graphene and a metal

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The exploration of the unique properties of graphene, an atomically-thin sheet of sp^2 -hybridized carbon, has fostered remarkable efforts since 2004. Recently the possibility to insert graphene into heterostructures, by successive exfoliations of various lamellar materials (e.g. graphite, MoS_2 , BN) has opened new perspectives, of which mostly those concerning electronic transport have been considered thus far. Surface science allowed to broaden this scope, from the point of view of both the experimental probes and the preparation of graphene-based heterostructures. Intercalation of various species between graphene and a metallic substrate, a method which has been known since the 1980's [1], encounters renewed interest in this respect. It was for instance shown accordingly that the weak spin-orbit constant of pristine graphene could be considerably enhanced by the immediate proximity of a gold atomic layer [2], or that graphene could recover the electronic properties of free-standing graphene when decoupled from its substrate by an intercalated atomically-thin oxygen layer [3]. Though intercalation is now routinely used in a number of research groups, the mechanisms by which it occurs remain essentially speculated.

Using a combination of microscopy (with electrons and scanning probes) and spectroscopy (X-ray photoemission, Raman, tunneling) techniques we have investigated the intercalation of various species under various conditions between graphene and Ir(111), a prototypical system for high quality [4] quasi free-standing graphene [5]. In this presentation I will present the in situ study of the ultra-high vacuum intercalation of Co ultra-thin films, and of how the magnetic properties of Co are deeply influenced by the interface with graphene [6,7]. I will then address the intercalation of oxygen under atmospheric conditions, and will describe the local formation of an intercalated ultra-thin oxide that it involves as well as the resulting changes in the electronic properties of graphene, which becomes fully decoupled from its substrate [8]. On these two examples I will illustrate the role of defects in graphene (vacancies, edges, wrinkles) in the intercalation process.

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Ion beam induced defects in graphene studied by STM, MDS, and DFT

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Graphene grown epitaxially on metal surfaces can be used as a model system to study fundamental properties of this new material using surface science methods. Here, the system of graphene on Ir(111) is of special importance as the interaction between the carbon atoms and the substrate is weak [1], leaving the electronic structure largely identical to the one of free graphene [2]. Furthermore, the carbon sheet can be grown as an extended layer of high structural quality [3].

In this model system, we study defects induced by ion irradiation using STM. The experiments are corroborated by MDS and DFT calculations. Under grazing incidence, ions are channeled between graphene and its substrate, giving rise to chains of vacancy clusters. The presence of the metallic substrate induces a funnel-shape to these clusters as the broken C-C bonds saturate by binding to the metal. By tuning the balance between defect creation, annihilation, and migration, we were able to create a periodic pattern of holes in the graphene (nanomesh) [4].

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Density functional simulations of phase-change materials: Insights on crystallization

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Phase change materials (PCM) function in commercial rewriteable optical disks (DVDs, Blu-ray Disc) and nonvolatile computer memory (PC-RAM) because the amorphous-crystalline transition is rapid, reversible, and accompanied by changes in the optical and electrical properties. The amorphous structures of PCMs are difficult to determine, and the nature of the ultra-fast crystallization mechanism remains the subject of much study and speculation. We have performed two large scale density functional simulations (several hundred atoms over hundreds of picoseconds) of crystallization in the prototype "nucleation dominated" phase change material $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST-225) and can provide details of the changes in order as crystallization proceeds.

Our first DF/MD simulations [1] were on a 460-atom sample at 500, 600, and 700 K for up to 600 picoseconds, where crystallization was promoted by fixing the structure of a crystalline "seed" (58 atoms, 10% vacancies). The second simulations were also on a 460-atom sample at 600 K, but with no constraints on the geometry. The density was adjusted during the simulation to allow for the difference between the amorphous and crystalline forms. Crystallization occurs in stages and was complete within 0.3–1.1 ns, depending on the simulation parameters (constraints, temperature). The structural changes were monitored by calculating the pair distribution functions, appropriate order parameters, the number of "wrong bonds" (bond pairs that do not occur in the ordered form), the variation in the cavities, and the electronic density of states. The simulations reveal the course of the crystallization process at the atomistic level, and the important stages include pre-structuring, nucleation, percolation, and final (rapid) collapse to the crystalline state. Interestingly, the behavior of the individual elements (Ge, Sb, Te) is temperature-dependent.

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Unexpected strong interaction at a single-layer graphene/ α -Al₂O₃(0001) interface

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We have studied the vertical atomic structure of a single-layer graphene/ α -Al₂O₃(0001) interface by the density-functional theory. The vertical distance between the top of sapphire surface (0001) and the graphene sheet is predicted to be about 0.26 nm which is exactly equaled to the experimental value. We consider that the small distance is caused by the strong interaction at the interface. An electronic structure calculation supports the existence of the strong interaction that originates from the electrostatic interaction between graphene π -system and unsaturated electrons of surface oxygen layer rather than van der Waals interaction.

On stability of silicon nanoclusters passivated by hydrogen atoms

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Silicon nanoclusters are very promising objects in constructing of nanoelectronic devices. Particularly for their compatibility with existing silicon semiconductor technology. Our aim is to determine the cluster ensemble's phase composition. We developed the algorithm based on linear programming methods which allows to compute reaction energies and phase composition using given clusters energies, concentration of passivating H_2 molecules. The most important results are the following: 1) The reaction energy as a function of passivation degree has irregular behavior; 2) There are H_2 concentrations favorable for homogenic ensemble of stable clusters (Si_{10} , $Si_{10}H_{14}$, $Si_{10}H_{16}$, $Si_{10}H_{22}$). Other H_2 concentrations lead to the binary mixture compositions. 3) The structures with minimal dangling bonds number are the most stable.

In-situ growth of cellular two-dimensional silica layers on metal substrates

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Silicon dioxide films have attracted much interest due to their potential use in many technological applications, e.g., as insulating barriers in devices, as a gate oxide in field effect transistors, for applications in catalysis, or for protecting metal surfaces. Recently, the preparation and the atomic structure of a new quasi-two-dimensional phase of silica have been reported. Corner-sharing SiO₄ tetrahedra form a mono- or bilayer structure on substrates. The phase shows either a disordered (vitreous) network or a honeycomb lattice on metal surfaces with hexagonal symmetry. This novel phase of silica has a well-defined thickness and might be superior to amorphous silicon dioxide films in nanotechnology. All studies of the synthesis of the 2D silica layer have hitherto been carried out ex-situ and could not reveal details about the growth mechanism. Here a new route is reported towards the synthesis of 2D silica in a solid-state growth process that was carried out in-situ in a transmission electron microscope [1]. The experiments allow us to obtain detailed information on the nucleation, growth, and the epitaxial relationship with the crystalline symmetry of the metal surface. The cellular structure was grown on different metals substrates (Fe, Co, Ru) at temperatures around 500°C in the heating specimen stage of an electron microscope. The growth was monitored at high image resolution and by electron energy-loss spectroscopy. Whereas the cells form a hexagonally ordered network on the (0001)-surfaces of hexagonally close-packed Co and Ru layers, growth on other metal surfaces shows a disordered arrangement of the cells and the appearance of defective structures. The defects resemble in a striking way the known non-hexagonal rings in graphene (pentagons, heptagons etc.).

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Rupture and folding of exfoliated graphene and the role of the interfacial layer

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We demonstrate three different methods to modify single layer graphene (SLG) sheets mechanically exfoliated under ambient conditions on 6H-SiC(0001) namely, (i) swift heavy ion (SHI) irradiation, (ii) rupture by a force microscope tip and (iii) severe heating where we anticipate the interfacial layer (IFL) to play a major role [1]. SHI irradiation results in rupture of the SLG sheets, creating foldings and bilayer graphene (BLG) [2]. Applying the other modification methods enlarges foldings with rupture along zigzag and armchair edges. Peeling at a folding under an angle can create twisted BLG, with a similar height as Bernal stacked BLG. Twisted BLG, however, exhibits a significant contrast in the local contact potential [1].

The role of the IFL is investigated in more detail by annealing few layer graphene (FLG) on CaF₂(111). Reducing the IFL by annealing to temperatures up to 600K, yields ordered arrays of pits and mounds similar to (inverse) droplet phases found for Langmuir films. Annealing to temperatures over 700K results in the rupture of FLG areas, where for SLG protrusions of several nm in height are found. The stress due to boiling in the IFL is anticipated to drive this rupture.

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Ab-initio calculations of the photoelastic constants of the large band gap II-VI type semiconductors

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Abstract: Residual defects after growth of semiconductors crystals is a hot issue to be solved for manufacturing new efficient electronic or optic devices. These defects can be conveniently observed using birefringence optical microscopy for extended defects that will create a local strain field which in turn can cause a nominally isotropic optical material to become anisotropic and induce birefringence. In order to perform a quantitative analysis, the knowledge of the photoelastic constants (P_{ij}) of the material that measure the strength of the change of the refractive index under application of strains or stresses is necessary. As an experimental determination of the whole set of constants is not always possible, a theoretical evaluation can be of valuable interest. In this work, we propose ab-initio calculations by the WIEN2k program of the optical properties of the zinc blende II-VI type semiconductors with a self-consistent scheme by solving the Kohn-Sham equations using a full potential linearized augmented plane waves (FPLAPW) method in the framework of the density functional theory (DFT) along with the generalized gradient approximation (GGA). A combination of specific compressive and tensile strains is applied to the two atoms unit cell and the tensor containing each specific combination of the P_{ij} constants is extracted.

Ab initio molecular dynamics study of liquid water on NaCl(100) surface

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By employing ab initio molecular dynamics (AIMD) [1], we have simulated the liquid water–solid surface interaction of 256 water water on a (4x4) NaCl(100) unitcell. In this system, our AIMD results show that these water molecules occupy approximately in four layers. The liquid water density distribution has a maximum peak of 1.40 g/cm³ in the first layer 2.8 Å above the NaCl surface, which agrees with the previous AIMD results [2, 3]. The water density decreases to 1.10 g/cm³ in the fourth layer. The first layer water is about 1 ML on NaCl(100) surface, in which the oxygen atoms mainly occupy Na sites statistically. The liquid water structure appears when water is further away from the NaCl(100) surface by about 7.0 Å from oxygen–oxygen radial distribution function.

To understand the dissolving process of NaCl into liquid water, we have calculated the dissolve barriers of Cl⁻ and Na⁺ ions from flat, vacancies, stepped and the corner of the island on the NaCl(100) surfaces using constraint method.

The barrier heights for producing Cl⁻ or Na⁺ ions on flat NaCl(100) surface are 0.78 eV and 0.75 eV, respectively. The dissolve barriers for Cl⁻ and Na⁺ ions on stepped surface are 0.19 eV and 0.13 eV respectively. The barriers for producing Cl⁻ or Na⁺ ions from the corners of island on NaCl(100) surface are 0.12 eV and 0.11 eV, respectively. These results indicate that NaCl crystal dissolves starting from the corners of an island or a step surface. Thus, the departure of a Na⁺ ion has slightly lower barriers than dissolving Cl⁻ ion at the initial stage. However when more Na⁺ ions are dissolved, the Na⁺ and Cl⁻ ions have approximately the same barrier as tested on the stepped surface.

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Hydrogen adsorption in carbon nanotubes bundles mediated by various gas environments at the gamma-irradiation.

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Results of experimental studies Co-60 gamma-irradiation influence on the hydrogen adsorption in bundles of carbon nanotubes are presented. In contrast to other studies, we have conducted the radiation treatment of carbon nanotubes in the different gases before the hydrogen saturation. Investigated nanotube bundles have metallic conductivity [1] and Raman spectroscopy measurements shows two peaks for the breathing modes that correspond to vibration of individual nanotubes with diameter (1.02-1.05) nm and (1.68-1.73) nm [2]. Irradiation of carbon nanotubes was performed at room temperature in hermetic cell filled with hydrogen, deuterium, oxygen or nitrogen at atmospheric pressure. For the comparison, the irradiation of nanotubes was carried out in a vacuum, too. The exposure dose of gamma-irradiation was (1.5-1.7) 10^7 rad. The hydrogen sorption - desorption of irradiated nanotubes was investigated in the wide temperature interval 10K-1270K. Obtained results were compared to sorption properties of nonirradiated nanotubes. We have observed an essential influence of preliminary irradiation of nanotubes in gases on physical and chemical absorption of hydrogen. In the low temperature range 10-100K the highest increase of physically absorbed hydrogen in nanotubes was observed after irradiation in deuterium. The ratio of the total amount of physically absorbed hydrogen after irradiation in deuterium in comparison with non-irradiated nanotubes reached 3.6 times. We found no change in the hydrogen adsorption capacity after irradiation in vacuum with the same dose. Before high temperature measurements of chemically adsorbed hydrogen the irradiated nanotubes were kept in vacuum at room temperature during 48 hours in order to remove the residual gases. Then, the saturation with hydrogen was carried out at atmosphere pressure and room temperature for 48 hours. After that the hydrogen has been pumped away and nanotubes were heated from room temperature to 1270K in steps of one hundred degrees. In such series of measurements the hydrogen desorption started after the heating to 800K and have continued up to 1270K. In carbon nanotubes irradiated in a hydrogen atmosphere, the total amount of chemically adsorbed hydrogen which we have collected after the heating in the temperature interval 300-1270K, was reached 3.85% of hydrogen molecules per carbon atom. This value is more than ten times higher than for

the non-irradiated carbon nanotubes [3]. The results obtained are discussed in a view of our recently developed model the gas environment contribution on defects introduction rate into carbon nanotube at the gamma irradiation [4] and calculations of friction force for high energy atoms in nanotubes [5].

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Gold-embedded zigzag graphene nanoribbons as spin gapless semiconductors

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Recently, the new concept of spin gapless semiconductor (SGS) [1] has been proposed by Xiaolin Wang, who analyzed the electronic properties of doped PbPdO₂ systems using first-principles calculations. The SGS materials have unique band structures. The top of the valence band of a spin channel and the bottom of the conduction band of at least one spin channel touch at the Fermi level. The SGS materials have more interesting features than the conventional semiconductors [2, 3]. For example, no energy is required to excite electrons from the valence band to the conduction band, while the density of states at the Fermi level is zero, and both electrons and holes can be 100% spin polarized at the Fermi level, which is the most desirable property of semiconductors in spintronics.

Using density-functional theory calculations, we studied the electronic and magnetic properties of zigzag graphene nanoribbons (ZGNRs) with gold (Au) atoms embedded into different sites of the ZGNRs [4]. Strong site dependence was found, and the system had the ferromagnetic or antiferromagnetic ground state depending on the Au atom position. The SGS behavior was observed when the Au atom was embedded into the center and edge sites of the ZGNRs. The simulations showed that the electronic structure of the ribbon strongly depends on ZGNR width, but the SGS behavior is always present when the Au atom is embedded into the center and edge sites. The SGS properties were also found to be dependent on impurity atom concentration, so that they can be tuned by either selecting the proper positions of Au atoms or changing their concentration. Our results suggest a flexible way of designing SGSs, which could be used in various spintronic, electronic, and optoelectronic applications.

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Defect mediated manipulation of nanoclusters on an insulator

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Metallic nanoclusters adsorbed on insulating surfaces and thin films are promising candidates as next generation catalysts in many industrial processes. Non-contact Atomic Force Microscopy (nc-AFM) has recently begun to be applied to these systems, potentially providing atomic resolution of the surface and the adsorbed nanoclusters. Furthermore, atomic control on the size of deposited nanoclusters and nc-AFM's ability to manipulate the clusters on the surface means one can examine the properties of clusters of specific sizes at chosen sites on the surface.

We study Au cluster manipulation on NaCl (001), a prototype system, by both experiments and simulations [1]. Two types of clusters are found experimentally: isotropically and anisotropically moving ones, the latter only moving in $\langle 110 \rangle$ surface directions. Density functional calculations show that the anisotropy in preferred paths of clusters depends on the type of vacancy they attach to. The anisotropic movement can be explained as a result of the clusters attaching to a row of Cl ions in the presence of Na vacancies. Since the clusters can slide along rows of Cl ions on the surface, they prefer to move in the $[110]$ direction. In contrast, clusters attached to Cl vacancies are expected to move in all directions. The results demonstrate how the behavior of metallic clusters on insulators during manipulation can be dominated by the interaction between the clusters and the defects found on the surface.

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STM study of argon ion sputtering of epitaxial graphene on Ir(111)

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The electronic structure of pristine graphene has been studied extensively in recent years, both experimentally and computationally. Graphene in reality is however never completely defect free. Even individual defects begin to play a significant role when graphene devices are decreased in size. Individual defects in graphene have been shown by *ab initio* calculations to change many of graphenes properties locally, giving rise to magnetism, for instance. Experiments on defects are however lacking behind the computational effort.

We have studied defects induced by argon ion bombardment in epitaxial graphene on iridium by scanning tunneling microscopy (STM) and electron spectroscopies. In addition to simple point defects we also observe trapped atoms in the graphene iridium interface. We compare the yield of various types of defects as a function of the kinetic energy of the ions and compare the experimental results to molecular dynamics simulations.

Spin split of the zigzag end state in finite armchair graphene nanoribbons in the presence of doping and defects

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Theoretically, an antiferromagnetic zigzag edge state has been predicted in infinite zigzag nanoribbons, associated with antiferromagnetic order between the ribbon edges and the opening of a band gap [1]. The interpretation of experiments regarding these spin-split states [2,3] might not be straightforward. Recently, finite armchair graphene nanoribbons have been synthesized on Au(111), and in scanning tunneling spectroscopy (STS) measurements, a double peak structure in the state close to zero bias localized at the zigzag-terminated end has been observed [4]. By creating a defect at one end of the ribbon using a voltage pulse from the scanning tunneling microscope tip, thus connecting the ribbon to the substrate, the intensity of the split peak was found to decrease. Instead of a spin-split zigzag end state, the peak structure was attributed to phonon-assisted tunneling, the decrease in peak intensity reflecting a shorter lifetime of the electrons in the substrate-connected ribbon.

Here, we provide density-functional theory calculations to further support this interpretation. We consider the effect of different edge hydrogen terminations for the finite ribbons, as well as the effect of doping and structural defects on the end-localized states, and their corresponding energy gaps. We show that, in general, introducing a defect at one end has little effect on the electronic states at the other, intact end. Moreover, even minor doping, for instance due to the gold substrate, destroys the spin-split of the end state. We also provide simulated STS maps suitable for identification of the different edge hydrogen terminations.

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Encapsulated Inorganic Nanowires within Single-Walled Carbon Nanotubes: On-Tube Potential Modulation Effects and Self-Repair Dynamics

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The large variety of hybrid carbon nanotube systems synthesized to date (e.g., by encapsulation, wrapping, or stacking) has provided a body of interactions with which to modify the host nanotubes to produce new functionalities and control their behavior. Each, however, has limitations: hybridization can strongly degrade desirable nanotube properties; noncovalent interactions with molecular systems are generally weak; and interlayer interactions in layered nanotubes are strongly dependent upon the precise stacking sequence. Here we show that the electrostatic/polarization interaction provides a generic route to designing unprecedented, sizable and highly modulated (1 eV range), noncovalent on-tube potentials via encapsulation of inorganic partially ionic phases where charge anisotropy is maximized. Such potentials lead to significant redistribution of the wave function around the nanotube, with implications for conceptually new single-nanotube electronic devices and molecular assembly.

On the other hand, realizing robust nanoscale systems requires them to have the ability to self-repair. Therefore, understanding what can drive self-repair is critical for a good design. We show that single-walled carbon nanotubes (SWCNTs) filled with inorganic nanowires do indeed sustain reconfiguring dynamic phenomena that involve both the nanotube and the filling, and allow them to self-repair. We studied competing dynamic phenomena of ejection, motion and repair and uncovered regimes and interactions that favor repair, highlighting a pathway towards a more general mechanism for nanowire repair. These results demonstrate remarkable capabilities nanostructures can possess to self-repair and reconfigure when subjected to extreme confining environments.

These phenomena are investigated with *ab-initio* and molecular dynamics simulations combined with high resolution transmission electron microscopy, and in the first case, also with scanning tunnelling microscopy and spectroscopy.

Defects in two-dimensional transition metal dichalcogenides: From vacancies to substitutional random alloys

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Transition metal dichalcogenides (TMDs) are a class of layered materials, similar to graphite and BN, with promising future in nanoelectronic and photonic applications. Due to recent advances in successful production of two-dimensional monolayers they have started to attract considerable attention. In order to take full advantage of the promise of these materials, a good control over the defect production is required. In particular, defects could be produced intentionally during chemical vapor deposition growth or by ion irradiation, whereas unintentional production may be expected during transmission electron microscope (TEM) imaging.

In this work, we first investigate vacancy formation under electron irradiation in TMD materials. Displacement thresholds are evaluated from molecular dynamics calculations and compared to the experiments in the case of S vacancy formation in MoS₂ [1]. Isolated vacancies are stable, but with increasing exposure and vacancy concentration, they are found to agglomerate to form lines. With the help of first-principles calculations, we determine their atomic structure and also discuss possible formation mechanisms.

Filling of the vacancies is observed in TEM images. Thus, we examine chalcogenide substitution processes within these materials. Substitution by other atomic species is found to be energetically favorable, thereby suggesting a way for doping of these materials [1]. Finally, as extended substitution by isoelectronic ions leads to alloying, we study the stability and electronic structure of alloys consisting of MoS₂, MoSe₂, and MoTe₂ [2].

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Theoretical study of changes of the work function of graphene nanostructures. The way to high electronic emission from pure carbon medium.

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It is well known that Graphene is currently considered as a base for the whole future nanoelectronics. For example, for the field electron emission (FEE) an individual single-layer graphene has been applied [1, 2]. The work function value decrease is highly desirable for successful graphene application in the FEE area. The electrons emit mainly from the graphene edges [3]. Here the impact of the edges and presence of dopants to the work function (WF) of graphene nanoribbons (GNR) and nanoflakes was studied by ab initio approach. The strong dependence of the WF upon the GNR structure and on the presence of the donor type impurities was observed. Basing on that impact of the nanostructure edges to the emission properties, the small graphene flakes were investigated as a possible source for the electron emission. It was found the weak dependence of the low WF values of the graphene flakes on their size and shape which allows to suggest that the pure carbon medium with high and uniform emission properties can be fabricated by today technology. This work is currently in press in the Applied Physics Letters and was supported by the Russian Foundation for Basic Research (project no. 11-02-01453/12). The authors are grateful to the Joint Supercomputer Center of the Russian Academy of Sciences and "Lomonosov" research computing center for the possibilities of using a cluster computer for the quantum-chemical calculations. P.B.S. also acknowledges the Russian Foundation for Basic Research (project no. 12-02-31261) and the Russian Ministry of Education and Science (Contract No. 14.B37.21.1645). D.G.K. also acknowledges the support from the Russian Ministry of Education and Science (No. 948 from 21 of November 2012).

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Identification and study of the most stable clusters $Si_{10}H_{2m}$ ($m = 0 \dots 11$)

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The most stable structures of silicon clusters $Si_{10}H_{2m}$ ($m = 0 \dots 11$) passivated by hydrogen have been identified using an evolutionary algorithm and the characteristics of their electronic spectrum have been studied. It was found that the arrangement of atoms in the clusters studied, except $Si_{10}H_{16}$, significantly differs from that of crystalline silicon. The performed analysis has shown that the most energetically favorable structures are those in which all the valence electrons form interatomic bonds and there are no electrons corresponding to broken bonds. For the clusters considered this means that each silicon atom has four nearest-neighbor atoms.

To study the optical and other electronic properties of clusters the knowledge of the one-electron spectrum is important. Performed calculations of the electronic structure of stable clusters using density functional theory showed that as a number of hydrogen atoms grows, the gap in the electronic spectrum at first decreases slightly and then increases. The behavior of the gap, in general, correlates with the change in the degree of stability of the clusters.

Electron transfer at the semiconductor-dye interface in dye-sensitised solar cells

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Solar cells are among the most promising ways of producing renewable energy. They are semiconductor-based devices which convert solar energy to electricity. However, their cost and efficiency is still below that of fossil fuels. The efficiency of solar cells is controlled by the rates of charge transfer processes in the cell. In this work, we study the rates of charge transfer processes in dye-sensitised solar cells (DSSCs). DSSCs are composed of semiconductor nanoparticles with adsorbed dye molecules in electrolyte solution. We focus on the processes taking place at the semiconductor-dye interface: electron injection from semiconductor to dye and electron recombination from semiconductor to dye cation.

Our computational approach combines density-functional theory (DFT) description of the dye-semiconductor (TiO_2) interface with non-adiabatic electron transfer theory for the calculation of charge transfer rates. [1] We investigate the influence of the dye-semiconductor interface on electron injection by varying the dyes' structures [1], chemistry of the dyes' anchoring to TiO_2 [2], and TiO_2 crystallographic surface orientation [3].

We also model electron recombination (the undesirable electron transfer from semiconductor to dye cation, resulting in efficiency loss), taking into account the presence of the electrolyte, and rank dyes according to their recombination rates [4]. Based on our model for injection and recombination, we propose a new design for DSSC dyes, where injection is fast and recombination forbidden by symmetry [5], thus leading to efficient solar cells.

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Control of the morphology and the organization of colloidal nanoparticles by template assisted method

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Metallic nanostructures with various morphologies have been a subject of intensive research in recent years because it provides an effective strategy for tuning the electronic, magnetic, optical, and catalytic properties. Especially, the controllable preparation of metal nanostructures with different shapes is of great interest because it allows one to fine-tune the properties with a greater versatility in many cases. Among these structures, silver nanoparticles (NPs) have received high attention due to their potential applications in areas such as biomedicine, optical filters, and nanoelectronics. In this work, we report our investigation on both, the control of the morphology and the organization of silver NPs on a steel substrate using a template-assisted process. Their electrochemical activities were then studied vs their 3D self-assembly. First, the phase separation of a poly(styrene-block-4vinylpyridine) (PS-P4VP) block copolymer thin film was used to create highly organized nanopores onto the substrate. Then, gold nanocolloids or evaporated gold clusters were confined into the nanoholes leading to the facile fabrication of hexagonally arranged gold NPs onto the substrate. Finally, silver nanocrystals were grown by a soft chemical method over these templated surfaces. The resulting hybrid nanocomposite has been then characterized by Atomic Force Microscopy (AFM), Energy-dispersive X-ray spectroscopy and X-Ray Spectroscopy (XPS). The electrochemical response of these patterned metallic substrates was investigated by Scanning Electrochemical Microscopy. The effectiveness of these nanostructured electrodes were compared to those of raw ones. It was found that by organizing these silver nanocrystals into specific pattern the electrochemical sensitivity can be further enhanced by several times and this enhancement was highly dependent on the separation distance of the lattice patterns.

Dynamic charge transfer potential for modeling oxide interfaces

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In order to develop future economical, efficient and reliable microelectronic devices, it's of great importance to model and understand novel semiconductor/oxide interfaces. High-k dielectrics like HfO₂ are promising new materials in this direction. In this work the charge-optimized many-body potential (COMB), an empirical potential that is being parameterized for Si/SiO₂ [1,2] and Hf/HfO₂ systems [3], has been used. It allows for the adjustment of atomic charges in response to changing atomic environment, so it's particularly well suited for the interfaces at the heart of next generation devices.

The COMB potential has been implemented within Pysic, an ASE calculator in an object-based Python environment that allows charges to dynamically evolve during the simulation. The implemented potential has been tested simulating Si₃O_y (y = 1:6) clusters, using COMB10 parameters [2]. We will present the methodology of the potential implementation in Pysic and provide preliminary test results regarding the same. Once the potential works for Si₃O_y clusters, the COMB potential will be implemented for Hf/HfO₂ systems as well, and tested for HfO_n (n=2:6) clusters. The final objective is to simulate new kind of semiconductor/oxide interfaces, like Si/SiO₂/HfO₂, that can be used in next-generation CMOS devices.

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Field emission resonances on hexagonal boron nitride on Ir(111)

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Monolayers and thin layers of the wide-gap insulator hexagonal boron nitride (h-BN) have attracted growing interest from the research community in recent years. This is due to its electronic properties and geometric structure; h-BN offers a wide range of potential applications as either an atomically smooth insulating substrate or, when grown on a suitable support, as a well-defined nanopatterned surface to be used as a nano template.

Owing to its insulating character, it allows for efficient electronic decoupling of nanostructures from conducting or semiconducting substrates, while its crystalline structure assures an atomically flat surface. This has been demonstrated previously for graphene (G) on h-BN on silicon oxide. Here, the electron mobilities measured in G approach those measured in suspended graphene [1].

Growing single layers of h-BN on suitable metal surfaces can lead to the formation of moire superstructures with periodicities of a few nanometers. This effect is caused by a lattice mismatch between the h-BN layer and the underlying substrate. Sometimes termed 'nanomesh' [2], these kind of superstructures offer a route to pattern nanostructures grown in a bottom-up fashion on top of the h-BN. As the moire pattern induces local changes of the sample work function [3], it might allow to periodically modify the electronic properties of those nanostructures. Mapping these local variations in the work function and understanding their origin as a consequence of the interaction between the h-BN layer and the metal substrate is a crucial task in order to make use of h-BN as a nano template.

We grow single layers of h-BN on the surface of an Iridium (111) single crystal by thermal cracking of the precursor molecule borazine [4]. Using low temperature scanning tunneling microscopy (LT-STM) we probe the atomic structure of the h-BN/Ir(111) sample. Apart from the atomic scale contrast, we verify the formation of a moire superstructure with a periodicity of about 3 nanometers. Probing the differential conductance by scanning tunneling spectroscopy (STS), field emission resonances (FER) forming within the tunneling junction are measured with high spatial resolution on top of the h-BN moire. The energy of these FERs is well known to depend on the local work function of the sample [5]. Thus, the spatial variation of the h-BN/Ir(111) work function within the moire unit cell can be extracted by analyzing the FER spectra.

Finally, the experimental results are combined with state-of-the-art density functional theory calculations. As a result, we are able to track back the variations in the work function to modifications in the atomic interactions between the h-BN layer and the Ir(111) surface, as the B-N-hexagons occupy different adsorption sites within the moire unit cell.

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Theoretical aspects of unzipping of WS₂ nanotubes

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The results of the theoretical analysis of experimental data of unzipping of multilayered WS₂ nanotubes by consequent intercalation of lithium atoms and organic molecules are presented. The extension of the tube was described in the framework of elastic shell theory with parameters evaluated from the ab initio calculations. In assumption that the driving force of attraction organic molecule is its interaction with the intercalated Li ions, the ab initio calculation of connection of organic molecule with Li⁺ was carried out. In addition, non-chemical interaction of dipole of organic molecule with array of negative point charges represented Li⁺ was taken into account. The comparison between energy gain from the interaction and elastic strain energy allows to evaluate the value of tube layers deformation after the organic molecules implantation. The ab initio molecular dynamics simulation confirmed the estimations and shows that stretched nanotube unzip into the WS₂ nanoribbon.

Modelling the MOVPE Growth of GaP on Si(001) by DFT: from Gas Phase Decompositions to thin Layer Structures

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Decomposition mechanism classes of triethylgallane and tert-butyl phosphine, which are used as precursors for the MOVPE coating of Si-integrated III/V-semiconductor materials[1,2], were examined with quantum chemical methods. MP2 and dispersion-corrected GGA[3] were used to calculate thermodynamic and kinetic properties at realistic reactor conditions. Our results provide chemical understanding of class-specific elementary reactions and thermodynamically motivated decomposition networks show pathways to resulting species like atomic Ga and P, respectively. However, due to large thermal barriers, the most likely candidates for adsorption were identified as the two original precursors next to GaH₃ (gallane) and GaH. This study provides fund understanding of pure gas phase decompositions and its methods will consistently be applied to related surface processes in periodic models[4] in the future. This is heterogeneous decompositions, surface diffusion and layer growth resulting in interface structures as known from HR-TEM imaging[5]. Multiscale modeling approaches[6] like kinetic MC or AIMD will complement this project.

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Butterfly defect in bilayer graphene: creation in HRTEM for low radiation energies

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We observe by HRTEM that one type of divacancy, which we refer to as the butterfly defect, is formed in bilayer graphene for radiation energies for which in monolayer graphene no vacancies are formed, thus raising the question of the defect formation mechanism. By using first principles calculations based on DFT, we analyze two possible causes related with the presence of a second layer that could explain the observed phenomenon: the increase of the defect stability or a catalytic effect during its creation. For the former, the obtained formation energies of the defect in monolayer and bilayer systems show that the change on its stability is negligible. For the latter, we simulate by *ab initio* Molecular Dynamics the kinetic process of the creation of a vacancy by the expulsion of an atom and creation of a Frenkel pair. In both cases, we do not observe the formation of the vacancy below the monolayer expulsion threshold energy. Finally, we conclude that the mechanism of the creation of the butterfly defect for bilayer graphene is not simple and we suggest a more complex pathway where we obtain a divacancy defect within the energetically permitted region.

Freestanding vs supported graphene - Simulated ion irradiation

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Defects in nanomaterials can have drastic effects on the properties of these materials. This allows, in principle, controlled modification of these materials for example with ion irradiation. While nanomaterials can have a different response to irradiation than their bulk counterparts, existing theories only occasionally apply in their case. Therefore, to answer the question of what are the specific defect production mechanisms in graphene under ion irradiation, we have studied ion irradiation of graphene using molecular dynamics simulations [1,2,3]. We show that the defect types in freestanding graphene depend strongly on the energy of the specific ion, defects occurring at distinct energy ranges that differ from one defect to the next. Our results also indicate, that with growing amount of defects, the membrane is stable, even with defect concentrations up to 35% of the atoms missing. Besides freestanding graphene, we have recently extended our studies for graphene on a Pt(111) surface to analyze the effect of the substrate to the defect production mechanisms in graphene under ion irradiation.

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