

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

Physics Boat 2012

15th – 17th May 2012
Helsinki, Finland – Stockholm, Sweden

Organizers

Prof. Adam Foster

Department of Physics, Tampere University of Technology
Department of Applied Physics, Aalto University

Dr. Teemu Hynninen

Department of Physics, Tampere University of Technology
Department of Applied Physics, Aalto University

Dr. Arkady Krasheninnikov

Department of Applied Physics, Aalto University
Department of Physics, University of Helsinki

Prof. Risto Nieminen

Department of Applied Physics, Aalto University

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Psi-k Network

Aalto University

Tampere University of Technology



Programme

Tuesday		Wednesday		Thursday	
11:00	<i>Registration</i>	14:00	Hofer	9:00	Chuvilin
11:30	<i>Lunch</i>	14:40	Esch	9:40	Martinez
12:30	<i>Opening</i>	15:20	Spijker	10:00	Bittencourt
12:40	Schwarz	15:40	<i>Coffee at posters</i>	10:20	Kolmer
13:20	Wehling	16:20	Yakobson	10:40	Weiner
14:00	Ivas	17:00	Golberg	11:00	<i>Coffee at posters</i>
14:20	<i>Coffee at posters</i>	17:40	Susi	11:30	Giessibl
15:00	Michely	18:00	<i>Break</i>	12:10	Stirling
15:40	Jelinek	18:20	Lauritsen	12:30	Prauzner-Behcicki
16:20	Liljeroth	19:00	Federici Canova	12:50	Slobodskyy
16:40	<i>Discussions</i>	19:20	Komsa	13:10	<i>Lunch</i>
18:00	Pennycook	19:40	Koskinen		
18:40	Kotakoski	20:00	<i>Dinner</i>		
19:20	Swart				
19:40	Jarvis				
20:00	<i>Dinner</i>				

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Tuesday 15.05.2012

- 11:00 - 11:30 *Registration*
- 11:30 - 12:30 *Lunch*
- 12:30 - 12:40 *Opening*
- 12:40 - 13:20 **Schwarz**
Magnetic Exchange Force Microscopy and Spectroscopy
- 13:20 - 14:00 **Wehling**
Transition metal adatoms on surfaces: Effects of local Coulomb interactions
- 14:00 - 14:20 Ivas
Self-Assembly and Two-Dimensional Spontaneous Resolution of Cyano-Functionalized [7]Helicenes on Cu(111)
- 14:20 - 15:00 *Coffee at posters*
- 15:00 - 15:40 **Michely**
Towards graphene hybrid materials
- 15:40 - 16:20 **Jelinek**
Scanning Probe Microscopy: theory meets experiment
- 16:20 - 16:40 Liljeroth
Quantitative nc-AFM imaging of the atomic scale contrast in epitaxial graphene on Ir(111)
- 16:40 - 18:00 *Discussions*
- 18:00 - 18:40 **Pennycook**
Aberration-Corrected STEM and First-Principles Theory: Unraveling the Atomic Origin of Materials Properties
- 18:40 - 19:20 **Kotakoski**
Knock-on Damage in Graphene Under an Electron Beam - Role of Lattice Vibrations and Bond Rotations
- 19:20 - 19:40 Swart
Direct observation of the Linear Combination of Molecular Orbitals model in real space by combined scanning tunneling microscopy and atomic force microscopy
- 19:40 - 20:00 Jarvis
Identifying passivated dynamic force microscopy tips on H:Si(100)
- 20:00 - 22:00 *Dinner*

Magnetic Exchange Force Microscopy and Spectroscopy

A. Schwarz¹

¹Institute of Applied Physics, University of Hamburg

Mapping spin structures with atomic resolution and quantifying the strength of magnetic interactions between atoms is crucial to gain a deeper understanding of magnetic phenomena on the nanoscale. Magnetic exchange force microscopy (MExFM) utilizes an atomically sharp magnetic tip at the free end of a cantilever to detect the short-ranged electron-mediated magnetic exchange interaction between tip apex and surface atoms. This force microscopy based technique can be employed to image spin structures of insulating [1] as well as conducting [2] magnetic samples with atomic resolution. In its spectroscopic mode of operation, i.e., magnetic exchange force spectroscopy (MExFS), the distance dependence of the the magnetic exchange interaction can be measured quantitatively in a very direct and elegant fashion [3]. Results obtained on the antiferromagnetic insulator NiO(001) and the antiferromagnetic Fe monolayer on W(001) will be presented and compared with theoretical calculations.

[1] U. Kaiser, A. Schwarz, and R. Wiesendanger, *Nature* **446**, 522 (2007).

[2] R. Schmidt et al., *Nano. Lett.* **9**, 200 (2009).

[3] R. Schmidt et al., *Phys. Rev. Lett.* **106**, 257202 (2011).

Transition metal adatoms on surfaces: Effects of local Coulomb interactions

T. O. Wehling¹

¹Institut für Theoretische Physik, University of Bremen, Otto-Hahn-Allee 1, 28359 Bremen, Germany

Achieving a realistic theory of nanoscale structures that accounts for the atomistic details of the systems and for strong electron correlations presents a long standing goal in solid state physics. Here, we discuss how the interplay of local Coulomb interactions, hybridization effects and spin-orbit coupling determines the physics of adatoms on surfaces which are the building blocks of ultimately small nanostructures. It will be shown that this interplay is effective at multiple energy scales and that it can determine the adsorption geometries of the adatoms and their stability, their electronic spectra and low energy magnetic properties like the magnetic anisotropy. This will be illustrated with the examples of rare earth and transition metal adatoms on the surfaces of normal metals, graphene and topological insulators.

Self-Assembly and Two-Dimensional Spontaneous Resolution of Cyano-Functionalized [7]Helicenes on Cu(111)

T. Ivas¹ A. Shchyrba¹ M. Stöhr² S. Boz¹ M. Schär³ M. T. Nguyen⁴
D. Passerone⁴ F. Diederich³ T. A. Jung¹

¹University of Basel

²University of Groningen

³ETH Zürich

⁴EMPA, Swiss Federal Laboratories for Material Science and Technology

Supramolecular recognition of the chiral molecules in two dimensions is expected to occur more readily due the symmetry breaking induced by the surface, which enhance the chiral interactions[1,2]. The spontaneous resolution of racemic compounds into separate enantiomeric assemblies serves as an indicator for the enantioselective intermolecular and molecule substrate interactions. For the first time we provide the evidence of spontaneous chiral resolution of a helicene on the Cu (111) surface due the enantioselective intermolecular interactions [3]. Racemic 6,13-dicyano[7]helicene forms fully segregated domains of pure enantiomers (2D conglomerate) on Cu(111). The propensity of the system to optimize intermolecular CN–HC(Ar) hydrogen bonding as well as CN–CN dipolar interactions translates into chiral recognition with preferential assembly of homochiral molecules. In addition to the spontaneous resolution in 2D layers, a discussion of the effect of chirality on the nucleation and formation of helicene chains shall be presented.

[1] R. Fasel, M. Parschau, K.H. Ernst, *Nature* **439**, 449 (2006).

[2] L. Perez-Garcia, D.B. Amabilino, *Chem. Soc. Rev.* **31**, 342 (2002).

[3] M. Stöhr et al. , *Angew.Chem.Int.Ed.Engl.* **50**, 9982 (2011).

Towards graphene hybrid materials

T. Michely¹

¹II. Physikalisches Institut, University of Cologne

Carefully optimizing the growth of graphene on Ir(111) yields a virtually defect free, weakly bound and strained epitaxial monolayer of macroscopic extension. Graphene on Ir(111) can be used as a laboratory to construct new types of graphene based composite materials. Specifically, patterned adsorption of atoms and molecules takes place resulting in cluster superlattices with exciting perspectives for nanomagnetism and -catalysis. Intercalation underneath the graphene allows one to manipulate the properties of graphene itself, e.g. its ability to adsorb atoms and molecules or its magnetism.

Scanning Probe Microscopy: theory meets experiment

P. Jelinek¹

¹Institute of Physics of the AS CR, Prague, Czech Republic

Invention of Scanning Probe Microscopy enabled to image surfaces with atomic resolution. Further development converted SPM from imaging to a tool enabling control and modification at atomic scale. With advent of Atomic Force Microscopy, more often scanning procedure takes place in the near-to-the contact regime (see e.g. [1]). In this regime, the probe proximity strongly modifies the surface structure hindering the precise interpretation of experimental results. Further proliferation of Scanning Probe method is strongly dependent on the better understanding of undergoing processes during scanning processes.

Advanced theoretical analysis based on first principle DFT total energy methods combined with the transport calculations based on Green's function techniques [2] offers such possibility. We will discuss key effects playing an important role during the formation of the atomic contact between tip and sample and the electron transport through the contact. The calculations allow to shed more light on factors playing an important role in atomic contact formation such as (i) a structural relaxation [3]; (ii) a modification of the electronic structure [4]; (iii) a collapse of the tunneling barrier [3]; (iv) the importance of elastic multiple-scattering processes of electrons [5]; and (v) modification of surface dipoles [6].

[1] F.J. Giessibl, *Rev. Mod. Phys.* **75**, 949 (2003).

[2] J.M. Blanco et al, *Phys. Rev. B* **70**, 085405 (2004).

[3] M. Ternes et al, *Phys. Rev. Lett.* **106**, 016802 (2011).

[4] P. Jelinek et al, *Phys. Rev. Lett.* **101**, 176101 (2008).

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[6] S. Sadewasser et al, *Phys. Rev. Lett.* **103**, 266103 (2009).

Quantitative nc-AFM imaging of the atomic scale contrast in epitaxial graphene on Ir(111)

P. Liljeroth¹ M. P. Boneschanscher² Z. Sun² J. van der Lit²
D. Vanmaekelbergh²

¹Department of Applied Physics, Aalto University School of Science, PO Box 15100, FI-00076 Aalto, Finland

²Condensed Matter and Interfaces, Debye Institute for Nanomaterials Science, University of Utrecht, PO Box 80000, 3508 TA Utrecht, the Netherlands

Scanning probe microscopies have been established as the main experimental tools in studying the atomic scale structure of surfaces. In the case of sp²-bonded carbon (graphene, carbon nanotubes and graphite), both scanning tunneling microscopy (STM) and atomic force microscopy (AFM) have been used to obtain atomically resolved images. However, these images show a rich variety in the atomic contrast depending on the imaging parameters and the atomic termination of the tip apex.[1-4] Extensive DFT calculations have been used to explain this wide variety in measured graphene topographies.[1]

We study these effects experimentally on epitaxial graphene grown by chemical vapor deposition on Ir(111). On the atomic scale, STM shows the complete hexagonal pattern of the carbon atoms in graphene. In addition to the atomic scale contrast, there is a moire pattern caused by the mismatch of the graphene lattice with the underlying substrate atomic lattice. On Ir(111), the moire contrast in STM is mostly an electronic effect and can be inverted depending on the bias voltage and tip termination.[5,6]

Our experimental nc-AFM results with a metallic tip show that depending on the tip-sample distance, the carbon atoms appear either as force minima (attractive regime) or force maxima (repulsive regime). Controlled modification of the tip apex by pick-up of a carbon monoxide molecule changes the tip reactivity. This results in a large change in the atomic scale force contrast, with the more reactive, metal-terminated tips yielding the largest contrast.

[1] M. Ondracek et al., *Phys. Rev. Lett.* **106**, 176101 (2011).

[2] S. Hembacher, F.J. Giessibl, J. Mannhart, C.F. Quate, *Proc. Acad. Nat. Sci.* **100**, 12539 (2003).

[3] M. Ashino, A. Schwarz, T. Behnke, and R. Wiesendanger, *Phys. Rev. Lett.* **93**, 136101 (2004).

[4] B.J. Albers et al., *Nature Nano.* **4**, 307 (2009).

[5] C. Busse et al., *Phys. Rev. Lett.* **107**, 036101 (2011).

[6] A.T. N'Diaye et al., *New. J. Phys.* **10**, 043033 (2008).

Aberration-Corrected STEM and First-Principles Theory: Unraveling the Atomic Origin of Materials' Properties

S. J. Pennycook^{1,2,3} M. Varela¹ T. J. Pennycook^{2,1,4} W. Zhou^{2,1} J. C. Idrobo^{1,2}
J. Lee^{1,2} M. P. Oxley^{2,1} Y. M. Kim¹ A. Y. Borisevich¹ M. F. Chisholm¹
S. T. Pantelides^{2,1}

¹Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6071, USA

²Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235, USA

³Materials Science and Engineering Department, University of Tennessee, Knoxville TN 37996, USA

⁴Now at SuperSTEM Facility, Daresbury, UK

The successful correction of lens aberrations has greatly advanced the ability of the scanning transmission electron microscope (STEM) to provide direct, real space imaging at atomic resolution. Several case studies will be presented, showing how microscopy data can be compared to results of density functional calculations to provide microscopic insights into functionality. Yttria-stabilized zirconia (YSZ) in YSZ/strontium titanate (STO) epitaxial heterostructures with nanometer layer thicknesses have been shown to exhibit up to eight orders of magnitude enhancement in ionic conductivity near room temperature [1]. Density functional simulations predict O to be in a disordered form in the strained YSZ, with a greatly reduced migration energy barrier consistent with experiment [2]. Spectroscopic imaging directly confirms the theoretical predictions for a disordered O sublattice in the strained YSZ [3]. Z-contrast images of LiFePO₄ show anomalous intensities at many Li columns, suggesting occupation by Fe. Spectroscopic analysis of such sites confirms the presence of Fe, and shows it to be in an unexpected valence state. Theoretical simulations indicate the origin of the effect and explain the experimental results [4]. Interfaces in complex oxide heterostructures show many surprising properties. Aberration corrected STEM images can now provide (projected) atomic coordinates with precision of a few pm for comparison to density functional calculations. Examples will be shown of BiFeO₃, mapping polarization, lattice parameter and octahedral rotations across interfaces unit cell by unit cell, and implying the presence of interfacial O vacancies [5,6]. Nanocrystals exhibit structures and properties with no relation to the bulk, for example the white-light emission from nano-sized CdSe. Real time imaging combined with quantum molecular dynamics calculations has unraveled the origin of such surprising properties [7]. Finally, the direct imaging and identification of point defect configurations in monolayer BN [8] and graphene [9] will be presented. Such point defects create localized plasmon resonances with sub-nm localization.

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- [1] J. Garcia-Barriocanal et al., *Science* **321**, 676 (2008).
- [2] T. J. Pennycook et al., *Phys. Rev. Lett.* **104**, 115901 (2010).
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- [5] A. Y. Borisevich et al., *Phys. Rev. Lett.* **105**, 087204 (2010).
- [6] J. He et al., *Phys. Rev. Lett.* **105**, 227203 (2010).
- [7] T. J. Pennycook et al., *NanoLetters* **submitted**, submitted (2012).
- [8] O. L. Krivanek et al., *Nature* **464**, 571 (2010).
- [9] W. Zhou et al., *Nat. Nanotech.* **7**, 161 (2012).

Knock-on Damage in Graphene Under an Electron Beam - Role of Lattice Vibrations and Bond Rotations

J. Kotakoski¹ S. Kurasch² F. Eder¹ O. Lehtinen³ V. Skakalova¹
A. V. Krasheninnikov³ U. Kaiser² J. C. Meyer¹

¹University of Vienna, Austria

²University of Ulm, Germany

³University of Helsinki, Finland

Although irradiation damage in graphite has been an important research topic for decades, only recent developments in imaging and computational techniques have allowed its quantitative analysis. In the presented work state-of-the-art transmission electron microscopy is combined with dynamical ab initio simulations to establish a detailed atomic scale understanding of knock-on events in graphene and other nanocarbons under an electron beam.

We study electron-beam driven sputtering of carbon atoms from (C-12) normal and heavy (C-13) graphene to experimentally obtain displacement cross section as a function of electron energy, and notice an excellent agreement with our ab initio simulation results. Surprisingly, it turns out that lattice vibrations play a crucial role in the displacement process, especially at low electron energies.

Moreover, unlike could be naively thought, collisions between energetics electrons and carbon nuclei in graphene do not only lead to displacements of atoms and thus creation of vacancies, but also to bond rotation processes which allow the lattice to effectively reconstruct during the irradiation. The relative prolificity of the two processes can be tuned by changing the acceleration voltage in the microscopy leading to various interesting possibilities.

For example, electron beam can be used to turn graphene into a two-dimensional amorphous membrane, to drive creation and migration of lattice defects, to change the morphology of grain boundary structures, and modify the edge structure of graphene nanoribbons. Atomic scale understanding of irradiation effects also allows to estimate the stability of doped nanocarbon structures during imaging or characterization.

Direct observation of the Linear Combination of Molecular Orbitals model in real space by combined scanning tunneling microscopy and atomic force microscopy

F. Albrecht¹ M. Neu¹ C. Quest¹ I. Swart^{1,2} J. Repp¹

¹Institute of Experimental and Applied Physics, University of Regensburg, Regensburg, Germany

²Debye Institute for Nanomaterials Science, Faculty of Science, Utrecht University, Netherlands

Scanning probe microscopy, most notably scanning tunneling microscopy (STM) and atomic force microscopy (AFM) have been used to study chemical reactions, such as bond formation, and dissociation on the level of single molecules [1–3]. Whereas single-molecule chemistry is not useful for mass-production, it offers the possibility to study model systems in a well-defined environment in a controlled manner. Progress in STM and AFM now allows the electronic and geometric structure of electronically decoupled molecules and their complexes to be investigated with atomic scale spatial resolution, as well as atomic scale manipulation of the species of interest. The combination of these techniques offers the prospect of unraveling chemical reaction mechanisms on surfaces.

Here, we present a combined STM/AFM study of a chemical reaction between individual metal atoms (gold) and organic molecules (phenazine) deposited on an ultrathin insulating film. Metal-ligand complexes were synthesized by means of inelastic excitations. Using atomically resolved AFM images [4], we directly identify between which atoms chemical bonding has occurred. Finally, the electronic structure is studied by scanning tunneling spectroscopy. By exploiting the symmetry of the complex, it will be shown that the electronic structure of the complex can be rationalized from the linear combination of molecular orbitals model. Our results provide a direct experimental observation of this basic quantum chemical principle.

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[4] L. Gross, F. Mohn, N. Moll, P. Liljeroth, and G. Meyer, *Science* **325**, 2009 (1110).

Identifying passivated dynamic force microscopy tips on H:Si(100)

S. Jarvis¹ P. Sharp¹ R. Woolley¹ A. Sweetman¹ L. Kantorovich² P. Moriarty¹

¹School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, U.K.

²Department of Physics, King's College London, The Strand, London, WC2R 2LS, U.K.

The Si(100)[1] surface is a particularly attractive system for the study of single atom/molecule chemistry. When terminated with a passivating layer of hydrogen (Si(100):H), isolated chemically reactive sites can be fabricated by removing a single hydrogen atom allowing interactions to be studied within a unique environment. Particularly interesting information can be obtained via the technique of nc-AFM, which allows the forces and energy of interaction to be measured between molecules and surfaces. Although well studied in STM, thus far only a single nc-AFM image of the Si(100):H surface has been published[2]. We will discuss a nc-AFM study of the Si(100):H surface[3] which elucidates the different force interactions responsible for image contrast. In particular, we observe an inverted imaging contrast thought to originate from atomically repulsive force interactions. Force-distance spectroscopy will also be presented and compared with the results of density functional theory simulations. From these comparisons we provide key insights into the characterisation of the tip-sample system, which may have important consequences for molecular imaging as well as for the fabrication of single chemically reactive sites.

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Wednesday 16.05.2012

- 14:00 - 14:40 **Hofer**
Theory of scanning tunneling microscopy: studying dynamic processes
- 14:40 - 15:20 **Esch**
Dynamics of truly monodisperse clusters under the STM
- 15:20 - 15:40 **Spijker**
Insights from the modeling of AFM measurements at the calcite-water interface
- 15:40 - 16:20 *Coffee at posters*
- 16:20 - 17:00 **Yakobson**
From nanotubes to graphene, graphite, and other elemental layers
- 17:00 - 17:40 **Golberg**
In situ transmission electron microscopy reveals defects vs properties of nanomaterials
- 17:40 - 18:00 **Susi**
Atomic-scale description of electron beam damage in nitrogen-doped graphene and carbon nanotubes
- 18:00 - 18:20 *Break*
- 18:20 - 19:00 **Lauritsen**
Atomically resolved STM imaging of molecular adsorption on MoS₂ nanocatalysts
- 19:00 - 19:20 **Federici Canova**
Atomic scale dynamics of frictional processes
- 19:20 - 19:40 **Komsa**
Defects in electron irradiated transition metal dichalcogenides
- 19:40 - 20:00 **Koskinen**
Twisting Graphene Nanoribbons into Carbon Nanotubes
- 20:00 - 22:00 *Dinner*

Theory of scanning tunneling microscopy: studying dynamic processes

W. A. Hofer¹

¹University of Liverpool

Dynamic processes in scanning tunneling microscopy (STM) are increasingly the focus of cutting edge research due to their importance for energy conversion and reaction processes. It is in principle possible to study these processes by suitable adaptation of STM theory and a step-by-step analysis of the processes themselves. I shall give several examples where such a detailed understanding is indispensable for a comprehensive understanding e.g. in atomic switching and diffusion processes [1,2,3], in molecular growth processes [4], condensation reactions [5], and long range molecular propagation even on reactive surfaces [6]. At the end of my talk I shall demonstrate that careful statistical analysis in combination with high-resolution STM can even lead to surprising new insights into fundamental physics [7].

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[3] Y Wang et al, *JACS* **131**, 3639 (2009).

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Dynamics of truly monodisperse clusters under the STM

F. Esch¹

¹Technische Universität München, Catalysis Research Center, Chair of Physical Chemistry, Lichtenbergstr. 4, 85748 Garching, Germany

The use of clusters promises to revolutionize our ability to design and control the selectivity and efficiency of catalytic processes owing to the unique chemical and physical properties of these structures [1]. Nanostructures and molecular clusters behave quite differently than bulk materials due to quantum size effects that become dominant upon reducing the dimensionality of the material grains. Every atom counts and thus size becomes a third dimension to the periodic table. A deeper understanding of the interplay between morphology and electronic structure as function of the cluster size will guide the development of a new generation of atomically designed nanostructures for catalysis. In order to access the ultimate fundamentals of the non-scalable size regime of supported cluster chemistry, we developed the preparation of truly monodisperse cluster-assembled materials, i.e. with every cluster of same size and adsorption site and thus chemical environment. To this purpose, we deposited size-selected, soft-landed Pd_N clusters ($7 \leq N \leq 31$) on epitaxial graphene films. Moiré moieties formed on graphene films have been shown to be good candidates for the stabilization of clusters [2]. Such well defined samples allow for the first time to fully complement these local with integrating measurements on cluster reactivity and electronic structure and to study isomer effects at the atomic scale. Our STM measurements show that the Pd clusters are well-dispersed on the graphene surface at room temperature, without any preferential aggregation at the step edges, contrary to what occurs upon physical vapour deposition [3]. Pd₂₀ clusters show a 2-3 monolayer high atomic structure, comparable to that of free-standing clusters in the gas phase. Neither cluster fragments nor surface damage is observed, confirming a well-controlled soft-landing on the graphene surface. On graphene, the clusters are exclusively adsorbed on one of the two ring hollow registries of the superstructure, indicating a strong carbon-metal interaction and a softening of the carbon-carbon bonding at this local registry. Different isomers of Pd₂₀ are observed, and isomerization processes can occur during continuous STM scanning. Clusters can be manipulated by the Push mode or can be removed in a controlled way, leaving behind the pristine surface. The STM study reveals that the cluster mobility/stability depends not only on the cluster size, but also on the footprint specific to isomers of different height. An investigation on the thermal stability of larger, Pd₂₀ clusters by annealing clearly indicates different mechanisms in the sintering process:

cluster diffusion dominates at temperatures below 500 K, Ostwald ripening at temperatures above 500 K. Two approaches are currently implemented in order to increase the STM time resolution for the study of these cluster-assembled materials under reactive gas environments [4].

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Insights from the modeling of AFM measurements at the calcite–water interface

P. Spijker¹ K. Voïtchovsky² M. Ricci² F. Stellacci² J. F. Molinari¹

¹Computational Solid Mechanics Laboratory (LSMS), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH 1015, Lausanne, Switzerland

²Supramolecular Nanomaterials and Interfaces Laboratory (SUNMIL), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH 1015, Lausanne, Switzerland

Solid–liquid interfaces play a fundamental role in many biomolecular and electrochemical applications at the nanoscale. Although spectroscopy and diffraction techniques can provide very accurate information about such interfaces, atomic force microscopy (AFM) has the advantage of probing the investigated system locally, thus allowing a deeper understanding of interfaces. Recently, a new enhancement of AFM based on small amplitude modulation atomic force microscopy (AM–AFM), has demonstrated the capability to probe the solid–liquid interface quantitatively at with sub-nanometer precision [1]. We have applied this technique to investigate the calcite–water interface with atomic-level resolution. The importance of this study is emphasized by the fact that calcite plays an important role in geochemical and environmental systems [2].

In order to enhance the insight obtained through the AM–AFM experiments on these calcite–water interfaces, we performed large-scale molecular dynamics (MD) simulations of similar systems, in which the 10–14 surface of calcite is exposed to a water-ion solution (Na⁺, Ca²⁺, Rb⁺, or Cl⁻). Our simulations show a strong ordering of water near the interface. For instance, the computed density profiles perpendicular to the surface are in good agreement with comparable X-ray scattering measurements [3]. Furthermore, it is shown that despite the charged calcite surface ions do not get adsorbed at the interface, but tend to be blocked by the strong ordered water layer.

Using the strength of having insight at processes at the atomic scale when using MD simulations it is revealed how a single step in the calcite surface can break the water structure and allows for strong ion adsorption at or near the surface. Finally, based on the data from the MD simulations, topographic images similar to those obtained from AM–AFM measurements are constructed, demonstrating a good agreement between simulations and experiments.

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From nanotubes to grahEnes, graphAnes, and other elemental layers

B. Yakobson¹

¹ME&MS Dept., Chemistry Dept., Richard E. Smalley Inst., Rice University, Houston, TX

We will describe recent work in theory of (i) growth of nanotubes [1-2] and graphene [3-4], (ii) two dimensional materials of C, BN, B, etc. [5-6], (iii) edge-interfaces and grain boundaries [3,7]. The central role of the first-principles calculations in the assessment and comparison of various atomic configurations, as well as of the "last principles" of phenomenology and experimental observables, will be emphasized and how their balanced use should serve better progress.

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In situ transmission electron microscopy reveals defects vs properties of nanomaterials

D. Golberg¹

¹National Institute for Materials Science (NIMS), Japan

Diverse in situ experiments aimed at understanding of defects/property relationship in nanomaterials will be summarized and presented [1]. The objects of interests are nanotubes and graphene-like structures in C [2-7] and Boron Nitride [8-13] layered systems, and Si [14], and Ag₂S [15] nanowires. Electrical and mechanical tests are performed inside a high resolution transmission electron microscope (at a spatial resolution of 0.17 nm) using dedicated STM-TEM and AFM-TEM holders, and under a full control of atomic structure and nanomaterial chemistry alternations. The effects of various defects on bending and tensile nanomaterial strength, electrical conductance, phase and morphology change processes will be reviewed and the future perspectives of the in situ TEM methods with respect to the material and instrumentation design will finally be emphasized. DG is grateful to numerous colleagues and co-authors of the in-situ TEM project funded by the World Premier International (WPI) Center for Materials Nanoarchitectonics (MANA) tenable at NIMS, Tsukuba, as evidenced by a selected list of related publications over the recent years.

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

T. Susi¹ J. Kotakoski^{2,3} S. Kurasch⁴ H. Jiang¹ V. Skakalova^{2,5}
A. V. Krasheninnikov^{3,6} E. I. Kauppinen¹ U. Kaiser⁴ J. C. Meyer^{2,4}

¹NanoMaterials Group, Department of Applied Physics, Aalto University, Finland

²Department of Physics, University of Vienna, Austria

³Department of Physics, University of Helsinki, Finland

⁴Electron Microscopy Group of Materials Science, University of Ulm, Germany

⁵Max Planck Institute for Solid State Research, Stuttgart, Germany

⁶Department of Applied Physics, Aalto University, Finland

By combining state-of-the-art electron microscopy [1] with ab initio simulations [2], we study the mechanism of electron beam damage in nitrogen-doped graphene and carbon nanotubes. We show that the incorporation of nitrogen heteroatoms results in noticeable knock-on damage in these structures already at an acceleration voltage of 80 kV. Contrary to an earlier estimate predicting their rapid destruction via sputtering of the nitrogen atoms [3], our graphene results show that damage initiates by first displacing carbon atoms neighboring the nitrogen dopant, leading to the conversion of substitutional dopant sites into pyridinic ones. We estimate that acceleration voltages lower than 70 kV are required to avoid such damage. Besides providing an improved understanding of the irradiation stability of these structures, our results show that the possibility of structural changes cannot be neglected in characterization experiments employing high-energy electrons.

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Atomically resolved STM imaging of molecular adsorption on MoS₂ nanocatalysts

J. V. Lauritsen¹

¹Interdisciplinary Nanoscience Center, Aarhus University

The scanning tunneling microscope (STM) has proven to be phenomenally successful in resolving the real-space, atomic-scale structure of the surfaces and supported nanostructures. A distinct advantage of the STM for catalysis studies is the capability to image single, adsorbed molecules while they interact with the catalytically active nanoclusters. This opens the opportunity to experimentally pinpoint and characterize the atomic-scale nature of the catalytically active sites, and in particular address the questions related to size- and morphology-dependent catalytic properties, i.e. the observation that certain cluster sizes or certain defect sites on nanoclusters may be more active. In this contribution I will discuss STM observations of molecular adsorption on MoS₂ nanoclusters synthesized on a gold model substrate, which serve as a surface science model system for the very important group of hydrotreating catalysts used to produce transport fuels with ultra-low sulfur contents. Using the STM we have successfully elucidated the atomic-scale structure of these catalysts and revealed an interesting size-dependent structure and chemistry of MoS₂ [1,2]. The STM studies have been used successfully to shed light on the particular role of sterical hindrance by imaging the sites that preferentially display a chemical bonding to S-containing probe molecules of the dibenzothiophene (DBT) family, which are the major unreactive species in crude oil. We observe a very strong variation in the interaction strength and type depending on the MoS₂ cluster size (1–3nm) and edge structures, which suggest that improvement in catalytic activity and selectivity may be possible by tailoring on the cluster size [1,2].

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Atomic scale dynamics of frictional processes

F. Federici Canova^{1,2} S. Kawai³ T. Glatzel³ A. S. Foster^{1,2} E. Meyer³

¹Tampere University of Technology, Tampere, 33710, Finland

²Aalto University, Aalto, 00076, Finland

³University of Basel, Basel, 4056, Switzerland

Friction is one of the most fundamental processes in nature, and a key design concept in machines and devices. Friction and wear are the main source of failure in every kind of machinery, macro- and microscopic, as well as biological applications. As the scientific effort pushed towards understanding the nanoscale origin of friction, atomic force microscopy became the tool of choice for creating a controllable nanocontact with a surface, where the friction and wear properties and can be studied with such detail. Combining the conventional NC-AFM technique with the torsional resonance (TR) in the so called bimodal AFM, allows simultaneous mapping of normal and lateral forces gradients via frequency shifts Δf ; the energy lost to atomic scale frictional processes is obtained from the TR excitation signal, but its interpretation remains challenging as the underlying non-conservative processes are unknown at the atomic scale. We study the NaCl (001) surface, which is an important benchmark system for theoretical models and easily prepared in the laboratory, using bimodal AFM and computer simulations. Our experiments revealed a weak tip-sample vertical interaction, giving a faint topographic contrast of the surface and no significant dissipation was measured in the flexural channel; the lateral Δf , on the other hand, provided sharper images, showing the typical checkerboard pattern of ionic crystals, although the TR damping image presented double peak features around one surface atomic type. Using a simple mathematical model for the tip-surface interaction, we can deduce that the highest lateral force should be measured not on the atomic sites, but in the gap between them. Under such intense stress, the tip apex is more likely to change shape, causing hysteresis in the oscillation cycle and therefore energy dissipation. We performed classical molecular dynamics (MD) simulations of such oscillations using a realistic model tip [1] treated to inhibit flexural dissipative processes. The simulated scanline shows how the tip feels the strongest force between two surface atoms, and this indeed triggers reversible tip changes, responsible for the observed hysteresis. The calculated dissipation is in good agreement with the experimental measurements.

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Defects in electron irradiated transition metal dichalcogenides

H-P. Komsa¹ J. Kotakoski^{1,2} S. Kurasch³ O. Lehtinen¹ U. Kaiser³
A. V. Krasheninnikov^{1,4}

¹Department of Physics, University of Helsinki, Finland

²Department of Physics, University of Vienna, Austria

³Central Facility for Electron Microscopy, University of Ulm, Germany

⁴Department of Applied Physics, Aalto University, Finland

Transition metal dichalcogenides are a class of layered materials similar to graphite and BN. Due to recent advances in successful production of two-dimensional monolayers they have started to attract considerable attention. The prototypical material MoS₂ has been previously used for hydrodesulfurization and as a dry lubricant, but also shows promise in hydrogen production, solar cells, and photocatalysis. In addition, electronic applications are enabled by the fairly high carrier mobilities. Since the family of transition metal chalcogenides comprises a large set of materials, they offer unique engineering possibilities within the 2D material systems. 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 under electron or ion irradiation, whereas unintentional production may be expected during transmission electron microscope (TEM) imaging.

In this work, we investigate the vacancy formation under electron irradiation for a large set of materials consisting of several transition metal species (Mo, W, Nb, Ta, Ti, V, and Pt) together with S, Se, and Te chalcogenides. Our first-principles calculations of vacancy formation energies complemented with molecular dynamics simulations of the displacement thresholds indicate that vacancies may be produced with electron energies of 80–96 keV, in accordance with TEM experiments. The vacancies are stable, yet highly reactive, and thus substitution of other species to the chalcogen sublattice is energetically favorable for the purposes of both doping and alloying.

Twisting Graphene Nanoribbons into Carbon Nanotubes

O. O. Kit¹ T. Tallinen^{1,2} L. Mahadevan² J. Timonen¹ P. Koskinen¹

¹NanoScience Center, Department of Physics, University of Jyväskylä, 40014 Jyväskylä, FINLAND

²School of Engineering and Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, MA 02138

For the past 20 years carbon nanotubes have been tributed as "rolled up graphene," though no one ever really did the rolling. Here we predict that, indeed, long and narrow graphene ribbons can be rolled into carbon nanotubes by means of twisting.[1] As today carbon nanotubes, along with many other nanomaterials, are made by atom-by-atom growth, the twisted proposal makes up a quite a different nano-fabrication method. The basic idea, however, is simple and easily grasped: just twist the ends of a strap of your backpack and watch the result. Therefore the mechanism, being classical in origin, is robust and valid in macro-, micro-, and nano-scales. Mechanism also enables experimental control, so it can be used to make carbon nanotubes controllably, to make various kinds of novel carbon nanotubules, to encapsulate molecules inside tubes, or to make tubules from ribbons made of other planar nanomaterials.

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Thursday 17.05.2012

- 9:00 - 9:40 **Chuvilin**
Inclusion of radiation damage dynamics in HRTEM image simulations
- 9:40 - 10:00 **Martinez**
Improvement of STM Resolution with H-sensitized Tips
- 10:00 - 10:20 **Bittencourt**
Electronic states of a thin graphite by NEXAFS-TXM: Mapping polarization dependence of the carbon K-edge
- 10:20 - 10:40 **Kolmer**
Electronic properties of dangling-bond nanostructures formed on hydrogen passivated Ge(001) surface by STM tip-induced hydrogen desorption
- 10:40 - 11:00 **Weiner**
Graphene on Rh(111): combined DFT, STM and NC-AFM studies
- 11:00 - 11:30 *Coffee at posters*
- 11:30 - 12:10 **Giessibl**
Revealing the Angular Symmetry of Chemical Bonds by Atomic Force Microscopy
- 12:10 - 12:30 **Stirling**
Inherent coupling of lateral and normal forces in qPlus AFM
- 12:30 - 12:50 **Prauzner-Bechcicki**
Chemically functionalized metal oxide surface: self-assembly of terephthalic acid on rutile TiO₂(110)
- 12:50 - 13:10 **Slobodskyy**
Cutting SSRM on CIGS solar cells
- 13:10 - 14:00 *Lunch*

Inclusion of radiation damage dynamics in HRTEM image simulations

A. Chuvilin^{1,2} E. Bichoutskaia³

¹CIC nanoGUNE Consolider, Av. de Tolosa 76, E-20018, Donostia-San Sebastian, Spain

²IKERBASQUE, Basque Foundation for Science, E-48011, Bilbao, Spain

³School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom

Computer image simulations are routinely used to interpret experimental high-resolution transmission electron microscopy (HRTEM) images. The variety of well established theoretical methods describe the scattering of electrons by atomic potential, which is the main step in conventional image simulation. It is recognized as well, both in "soft matter" electron microscopy [1, 2] and in the field of nanomaterials [3], that fast electrons of imaging beam in turn cause a modification of atomic structure under observation. Implementation of aberration correction in electron microscopy opened a road for direct experimental imaging of atomic dynamics under the influence of electron beam in controllable conditions with sufficient space and time resolution [4-8]. The ability of AC-TEM to observe the dynamics of individual atoms under the controlled influence of the e-beam provide a mean for direct measurements of diffusion coefficients, cross-sections, chemical constants and other characteristics of the dynamic processes that take place at the atomic scale. These advances in experimental AC-TEM techniques require theoretical solutions capable of combined treatment of the dynamic evolution of structures under the e-beam and their subsequent imaging. We propose a computational framework, which combines an event driven molecular dynamics (MD) approach similar to kinetic Monte-Carlo for prediction of the path and the rate of structure evolution under e-beam, MD simulations and DFT for structure refinement, MD for generation of temperature induced conformations ("frozen phonons") and multislice for image simulations. Both simulation parts (atomic dynamics caused by fast electrons and scattering of electrons by atomic potential) are linked via electron energy and electron dose rate. This approach has a potential to incorporate a variety of processes induced in a sample by high-energy electrons such as atom removal by a direct knock-on, atom rearrangements, ionization and consequent chemical reactions. As a proof of principle, in order to demonstrate the feasibility and simplicity of the proposed approach, we select a system in which direct knock-on damage is the principal effect of electron irradiation - a recently observed process of structural transformation of a small graphene flake into a fullerene cage in HRTEM. We show that proposed approach reproduces the path of the flake evolution into

the fullerene cage, the rate of this evolution and the signal-to-noise ratio for given experimental conditions. By varying experimental conditions under simulation (accelerating voltage and dose rate) we conclude that observation of this process at higher beam energies would be hardly possible due to fast evolution rate or low signal-to noise ratio. The proposed approach adds a new dimension to image simulation concept as it includes robustness of a sample as one of the input parameters. Thus, the HRTEM imaging conditions can be evaluated and optimized not only in respect to the instrument, but also in respect to the sample or the process under study.

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Improvement of STM Resolution with H-sensitized Tips

J. I. Martínez¹ E. Abad¹ C. Gonzalez¹ F. Flores¹ J. Ortega¹

¹Dept. Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid

The general motivation for this contribution is the remarkable attention that the improvement of spatial resolution in STM is attaining in diverse fields such as Surface Science, Nanoelectronics and Catalysis [1]. In particular, recent Scanning Tunneling Hydrogen Microscopy (STHM) experiments on PTCDA/Au(111) have shown unprecedented intramolecular and intermolecular spatial resolution [1,2]. The origin of this surprising behavior is not understood; in particular, the way in which H₂ molecules in the STM chamber may affect the STM image is not clear. In our work, we analyze the effect on the STM images of both atomic and molecular hydrogen interacting with tip or sample, using an accurate STHM theoretical simulation technique that includes a detailed description of the electronic structure of both tip and sample. To the best of our knowledge, this is the first theoretical simulation of STHM, which is a very challenging task. Notice that in the widely used Tersoff-Hamman approach to simulate STM images, the STM current is simply proportional to the density of states of the sample at the tip position. Thus, within a Tersoff-Hamman approach it is not possible to take into account the influence on the STM image of an H₂ atmosphere in the STM chamber.

We find that the STHM resolution enhancement is due to atomic H adsorbed on the tip [3]. At first sight, this is a surprising result, since it is considered that H₂ does not dissociate on Au surfaces. However, the situation is different for Au clusters and nanostructures, that are known to be good catalysts. In our work, the dissociation of H₂ molecules on the Au STM tip is further corroborated by state-of-the-art total-energy calculations using a plane-wave DFT code and the PBE0 exchange-correlation functional. Finally, we analyze the physical origin of the improvement of STM resolution; we find that the adsorbed H-atoms induce important changes in the Density of States (DOS) at the Fermi level (E_F) of the tip, increasing its total value, and making it more directional. Also, due to the interaction with the H-decorated tip, E_F is shifted to the middle of the PTCDA LUMO peak, increasing dramatically the DOS of the sample at E_F . The combination of these effects gives rise to the enhanced STHM intramolecular resolution, as well as the increased visibility of the intermolecular bonds, explaining the experimental observations [3].

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Electronic states of a thin graphite by NEXAFS-TXM: Mapping polarization dependence of the carbon K-edge

C. Bittencourt¹ C. Ewels² P. Guttmann³

¹University of Mons, Mons, 7000, Belgium

²CNRS, IMN, Université de Nantes, Nantes, 44300, France

³Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Institute for Soft Matter and Functional Materials, D-12489, Berlin, Germany

The near-edge X-ray absorption fine structure technique (NEXAFS) is ideally suited to study graphene-based materials, because the C K-edge is very sensitive to the bonding environment, providing diagnostic information about the structure, defects and doping. Using the NEXAFS method electrons are excited from the initial K-shell state into σ and π final states, depending on the orientation of the incident photon polarization with respect to the basal plane. The peak positions and lineshapes of the observed NEXAFS resonances represent, to first approximation, a replica of the unoccupied density of states, modified by core-hole interactions. In a graphene-based material the C $1s \rightarrow \pi$ exhibits strong linear dichroism. By using linearly polarized X-rays, we can probe local anisotropy and structural order by varying its relative orientation to a chosen axis of the sample.

Here we combine NEXAFS with transmission X-ray microscopy to study an isolated, free-standing flake [1]. The assignment of the most intense peaks was straightforwardly obtained by comparing the peak positions of the graphene band structure. A pre-peak structure was associated to metal doping due to the presence of metal impurities in the raw material used.

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Electronic properties of dangling-bond nanostructures formed on hydrogen passivated Ge(001) surface by STM tip-induced hydrogen desorption

M. Kolmer¹ S. Godlewski¹ B. Such¹ F. Krok¹ H. Kawai² M. Saeys^{2,3}
C. Joachim^{2,4} M. Szymonski¹

¹Department of Physics of Nanostructures and Nanotechnology, Institute of Physics, Jagiellonian University, Reymonta 4, PL 30-059, Krakow, Poland

²Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602, Singapore

³Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117576, Singapore

⁴Nanosciences Group & MANA Satellite, CEMES-CNRS, 29 rue Jeanne Marvig, F-31055 Toulouse, France

We report on studies concerning preparation of well organized atomic wires and 2D nanopads by scanning tunneling microscope (STM) tip-induced hydrogen desorption from hydrogen passivated Ge(001) surface. The samples are prepared by ion beam bombardment and annealing in UHV conditions, resulting in a mixed $p(2 \times 2)/c(4 \times 2)$ reconstruction with alternating directions of dimer reconstruction rows on neighboring terraces. Such a substrate, upon exposure to the atomic hydrogen source, forms a stable, monohydride $p(2 \times 1)$ phase of Ge(001):H. Dangling-bond nanostructures on the passivated surface are then created by cryogenic temperature STM tip-induced atomically precise dimer-by-dimer hydrogen desorption. We present very efficient protocol allowing for at will fabrication of pre-designed DB structures. Their morphological characterization is performed with atomic resolution by means of LT STM. Furthermore, it is demonstrated that $I(V)$ scanning tunneling spectroscopy (STS) characteristics of the fabricated nanostructures could give direct information about the spatial distribution of the density of states, which can be measured successfully with a lateral resolution reaching an individual dangling-bond. Experimental observations are supported by ab-initio density functional theory (DFT) calculations, STS results are compared with the transmission spectra, $T(E)$, calculated using the Green function method.

Graphene on Rh(111): combined DFT, STM and NC-AFM studies

E. Voloshina¹ Y. Dedkov² S. Torbrügge² A. Thissen² D. Weiner²

¹Physikalische und Theoretische Chemie, Freie Universität Berlin, 14195 Berlin, Germany

²SPECS Surface Nano Analysis GmbH, Voltastrasse 5, 13355 Berlin, Germany

Graphene, a single layer of carbon atoms ordered in a "chicken-wire" lattice [1], is proposed to be used in many technological applications. Among them are gas sensors, THz-transistors, integrated circuits, touch screens, and many others. One of the promising systems on the basis of graphene is its interface with metallic substrates [2]. Here graphene can be used as a protection layer for the underlying substrate, as a spin-filtering material separating two layers of a ferromagnetic material, or, in case of its growth on a lattice mismatched surfaces [for example, Ir(111), Rh(111), or Ru(0001)], as a template for the preparation of ordered arrays of clusters. For graphene on Rh(111) [Fig.1(a-c)] several regions of different arrangements of carbon atoms above a Rh(111) substrate can be found: ATOP [A; carbon atoms are above Rh(S-1) and Rh(S-2) atoms], HCP [H; carbon atoms are above Rh(S) and Rh(S-2) atoms], FCC [F; carbon atoms are above Rh(S) and Rh(S-1) atoms], and BRIDGE [B; Rh(S) atoms bridge the carbon atoms]. These places are marked in Fig.1(a) by circle, down-triangle, square, and stars, respectively. Among them, the BRIDGE positions are expected to be the most energetically favorable for the nucleation of deposited atoms on top of a graphene layer. The nowadays available force spectroscopy and microscopy can shed light on this problem and can be used as a tool, which helps to optimize the preparation of ordered arrays of clusters on a graphene template. In this contribution we present the combined study of the graphene/Rh(111) system via application of the state-of-the-art DFT calculations, STM, and NC-AFM. The calculated imaging contrast for STM between all high-symmetry positions for graphene/Rh(111) is in very good agreement with experimental results and this contrast does not depend on the sign of the bias voltage applied between a tip and the sample. As opposed to the latter observation, the imaging contrast in atomically-resolved AFM measurements depends on the frequency shift of the oscillating tip that can be understood on the basis of measured force-spectroscopy curves. The presented results are compared with the available theoretical data.

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Revealing the Angular Symmetry of Chemical Bonds by Atomic Force Microscopy

J. Welker¹ F. J. Giessibl¹

¹Experimental and Applied Physics, University of Regensburg, Germany

We have measured the angular dependence of chemical bonding forces between a carbon monoxide molecule that is adsorbed to a copper surface and the terminal atom of the metallic tip of a combined scanning tunneling microscope and atomic force microscope. We provide tomographic maps of force and current as a function of distance that revealed the emergence of strongly directional chemical bonds as tip and sample approach. The force maps show pronounced single, dual, or triple minima depending on the orientation of the tip atom, whereas tunneling current maps showed a single minimum for all three tip conditions. We introduce an angular dependent model for the bonding energy that maps the observed experimental data for all observed orientations and distances.

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Inherent coupling of lateral and normal forces in qPlus AFM

J. Stirling¹

¹School of Physics and Astronomy, University of Nottingham

Interpretation of atomic force microscopy (AFM) measurements of nanoscale interactions rely on methods derived from an idealised model of the microscope's sensor. One assumption is that the motion of the tip apex is both normal to the surface and parallel to the motion of the cantilever. Due to the low amplitude and microscopic tips of conventional AFM sensors this approximation is valid. In the case of sensors (such as the qPlus sensor) where the tip length approaches the length of the cantilever, however, this assumption can be shown to be invalid by simple geometry.

By careful consideration of the tip geometry, and the equation of motion of the cantilever we are able to quantify this lateral motion. Furthermore, we derive the effect this has on AFM calibration, imaging, and force measurements. We specifically demonstrate that our conclusions are not at odds with the sub-Ångstrom resolution demonstrated by qPlus sensors, and that force measurements are largely unaffected *unless significant lateral forces are present*.

Chemically functionalized metal oxide surface: self-assembly of terephthalic acid on rutile $\text{TiO}_2(110)$

J. S. Prauzner-Bechcicki¹ S. Godlewski¹ A. Tekiel^{1,2} F. Zasada³ W. Piskorz³
J. Budzioch¹ P. Cyganik¹ Z. Sojka³ M. Szymonski¹

¹Centre for Nanometer-Scale Science and Advanced Materials, NANOSAM, Faculty of Physics, Astronomy and Applied Computer Science, Jagiellonian University, Reymonta 4, 30-059 Krakow, Poland

²Department of Physics, McGill University, 3600 University Street, Montreal QC, H3A 2T8, Canada

³Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland

Many applications of nanotechnology require proper chemical functionalization of surfaces. Stable, flexible and high-quality functionalized surfaces are efficiently manufactured via molecular self-assembly. Such self-assembled monolayers may be used as a direct linker between the monocrystal template and the on-top built structures, for example for on-surface growth of metal organic frameworks (SURMOF). In the presentation, we discuss a self-organization of 1,4-benzenedicarboxylic acid molecules (terephthalic acid, TPA) on a rutile $\text{TiO}_2(110)-(1 \times 1)$ surface, basing on combined experimental and theoretical studies[1-3]. The system in question is analyzed by means of ultra-high vacuum scanning tunneling microscopy (STM), noncontact atomic force microscopy (nc-AFM) and periodic density functional theory (DFT) calculations. On the basis of scanning probe microscopy results the model of TPA adsorption on the rutile $\text{TiO}_2(110)-(1 \times 1)$ is proposed and further corroborated with theoretical modeling. It is concluded that TPA molecules are adsorbed in an upright position forming a well-ordered monolayer. Molecules bind to the surface via carboxylic groups as terephthalic anions in a bi-dentate fashion with the two 5-fold coordinated Ti atoms. The second carboxyl group is exposed to the vacuum interface and allows for dimer formation between the adjacent TPA molecules. To elucidate the reactivity of the functionalized surface, we deposit zinc formate ions on top of the compact TPA monolayer in our simulations. Calculations show that the anchoring properties of the TPA/ TiO_2 system are not perturbed by the dimer formation, auguring well for its prospective application as a promising chemically functionalized surface for on-top growth of metal organic frameworks. Furthermore, STM measurements supported by theoretical modeling show that due to specific tip apex modifications it is possible to image different parts of the electronic structure of the dimer TPA/ TiO_2 layer. In particular, it is possible to obtain enhanced contrast of functional groups on top of the molecular layer. The quality and stability of the monolayer are tested,

including the resistance against air exposure. Finally, for the sake of completeness structural properties of TPA deposited at low coverage are discussed[3; 4].

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Cutting SSRM on CIGS solar cells

A. Slobodskyy¹ S. Haas¹ K. Huska¹ U. Lemmer¹

¹Light Technology Institute (LTI), Karlsruhe Institute of Technology (KIT)

$\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ (CIGS) based thin-film solar cells show highest efficiency among thin-film solar cells over 20%. The main question in the CIGS solar cells efficiency influencing factors is the fact that the polycrystalline cells have bigger efficiency than their mono-crystalline counterparts[1,2,3]. In order to explain this phenomena a local electrical characterization of the solar cells in 3D is needed. This why the question is not clearly answered for nearly a decade. In this talk we will present results of 3D structuring and electrical characterization of thin-film solar cells based on CIGS absorber. The structuring is performed with STM tip. Current measurements between the tip and the sample are performed during the cutting procedure. Despite strong interaction between the tip and the sample the results of cutting are well reproducible. We will show a possibility to control the cutting procedure by subsequently scanning the surface of the solar cells after etch cutting step. We see a strong correlation between the modifications in the topography and the local currents. Moreover, with proper modifications it is possible to perform a detailed electrical characterization of the solar cell 3D electrical properties on nano-scale. First steps toward such characterization will be shown.

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Ion irradiation induced defects in freestanding graphene: an atomistic simulation study

Ab-initio calculation of the photoelastic constants of SiC

K. h. Bouamama¹

¹Laboratoire d'optoélectronique et composant, département de physique, Setif University, Algeria

Calculation of the optical properties, of silicon and SiC in zinc blend structure, were carried out with a self-consistent scheme by solving the Kohn-Sham equation using a FP-LAPW method in the framework of the DFT along with the GGA method by WIEN2k package. A combination of compressive and tensile strain has been applied to two atom unit cells of Si and SiC and the tensors relating to photoelastic constants extracted. Good agreement is found with experimental results for silicon. Predictions are also given for SiC. The presence of a dislocation or extended defect in a crystal causes a local strain field which in turn can cause a nominally isotropic material to become anisotropic and induce birefringence in light passing between cross-polarisers. The photoelastic constants are required to calculate the birefringence image. In the calculations, $RMTK_{max}=7$ is used, which determines the matrix size, where K_{max} is the plane wave cut-off and RMT is the smallest of all atomic sphere radii. We used 28000 k points in whole Brillouin zone. We chose the muffin-tin radii of 1.4, 2.1 Bohr for C and Si, respectively.

Thermal Stability of Organic Langmuir-Blodgett Films by an X-Ray Standing Waves (XSW) and X-Ray Reflectivity

M. Chembeleeva¹ Y. u. D'yakova¹ A. Seregin¹ S. Yakunin^{1,2} T. Bukreeva^{1,2}
E. Tereschenko¹ M. Kovalchuk^{1,2}

¹Shubnikov Institute of Crystallography Russian Academy of Sciences

²National Research Centre

The Langmuir-Blodgett (LB) technique has been shown to be a powerful method for synthesize thin organic films with desired structure, thickness and properties. Such films are useful components in many practical and commercial applications such as sensors, detectors, displays and electronic circuit components and boundary layer lubricants [1]. Therefore it is very important to study structural modifications after heating.

Lead stearate and methacrylic acid copolymer monolayers were deposited onto hydrophobic Si substrate to characterize films' structure after heating by XSW and X-ray reflectivity techniques [2]. XSW method allows to determine the position of an individual atoms by specific features of the angular dependence of the fluorescence radiation. X-ray reflectometry provides an information on the profile of the electron density of organic film on the substrate surface.

For such LB films the electron density distribution was calculated. The starting model of electron density distribution based on pressure isotherms data and molecular modeling results of the monolayer. The model was refined by method of the iterative convergence of X-ray reflectometry theoretical curve to the experimental.

The X-ray reflectivity and the fluorescent yield were measured at various temperatures from 20 to 110 C. More ordered periodic structure of this films was revealed after heating treatment up to 105 C and the degradation was observed above 105 C. Protecting layers behavior was revealed for copolymer.

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Green's function and first-principles simulations of Raman scattering in Si and Ge nanostructures

A. Trejo¹ P. Alfaro² M. Cruz-Irisson¹ C. Wang²

¹Instituto Politécnico Nacional, ESIME-Culhuacan, Av. Santa Ana 100, 04430 D.F., México

²Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, A.P. 70-360, 04510 D.F., México

Semiconductors nanostructures have attracted much attention due to their significant technological implications and theoretical significance. In this work, we model the Raman scattering by confined optical phonons using a local bond-polarization model, in which the displacement-displacement Green's function and the Born potential including central and non-central forces are utilized [1]. This approach has the advantage of being simple and providing a direct relationship between the microscopic structure and the Raman response. The results obtained from this approach are compared with those calculated by using the ab-initio density-functional perturbation theory (DFPT) through General Gradient Approximation. The supercell method is used and ordered pores are produced by removing columns of Si or Ge atoms from their crystalline structures [2], where the central and non-central interatomic restoring force constants are determined. Both approaches predict a remarkable shift of the highest-frequency bulk Raman peak towards lower energies, in comparison with the crystalline case. This shift is discussed within the quantum confinement framework and consistent with the experimental results obtained from PSi samples.

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Calibration of the tip magnetic moment for quantitative MFM experiments

A. M. Cucolo^{1,4,5} A. Scarfato^{1,4,5} F. Bobba^{1,4,5} M. Longobardi^{1,4,5}
F. Giubileo^{1,4,5} M. Iavarone^{2,3} G. Karapetrov³ V. Novosad³ V. Yefremenko³

¹Physics Department, Università degli Studi di Salerno, Via Ponte Don Melillo, I-84084 Fisciano, Italy

²Department of Physics, Temple University, Philadelphia, Pennsylvania 19122, USA

³Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA

⁴CNR-SPIN Laboratory, Via Ponte Don Melillo, I-84084 Fisciano, Italy

⁵Nanomates, Research Centre for Nanomaterials and Nanotechnology, Università degli Studi di Salerno, I-84084 Fisciano, Italy

Quantitative Magnetic Force Microscopy experiments require the knowledge of the tip magnetic structure to recover its magnetic moment. Since determination of the tip micromagnetic configuration is a challenging experimental task, usually the tip is approximated as a point magnetic dipole or as an extended magnetic probe with uniform magnetization and simple shape. Calibration of tip magnetic moment is then performed by using the magnetic microstructure of a sample of well known magnetic configuration, which characteristic size defines and limits the validity of the calibration for the investigation of magnetic configurations of the same length scale. Several magnetic structures have been considered for tip calibration, such as current rings, current wires and well defined striped magnetic domains [1-4]. Among these, a superconducting Vortex carrying quantized magnetic flux, $\Phi_0 = h/2e$, is of particular relevance being the Vortex defined through a single parameter, λ_L , the London magnetic penetration length, with the advantage that the λ_L value can be independently measured by using different experimental techniques. In this report, we show the results of the theoretical fittings of Frequency Modulation-MFM images of superconducting Vortices in Nb thin films obtained by using a flux line model [5] derived from the London equations and assuming a tip point dipole moment. To simplify the calculations, the frequency shift MFM images have been averaged to extract the radial profile of the superconducting Vortex ($df(r)$). In our case, the fitting equation has three independent parameters: the tip magnetic dipole, the Nb London penetration length, and the effective dipole position in the tip volume. To reduce the parameter space, we have performed simultaneous fittings of a set of $df(r)$ curves acquired at different temperatures and scanning heights. Moreover, to correct the effect of the superconductor diamagnetic response causing an offset in the signal image, we artificially induced, by means of the magnetic tip, a Vortex-Antivortex (V/AV) pair on occasional pinning centers and imposed the zero signal level of the background at half height of the

V/AV line profile. We have verified the validity of our method by comparing the obtained values of λ_L with the results of transport measurements.

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Heteroepitaxial monolayers of graphene and hexagonal boron nitride

R. Drost¹ S. K. Hämäläinen¹ P. Liljeroth¹

¹Aalto University Department of applied Physics

Hexagonal boron nitride (h-BN) is a large bandgap insulator structurally similar to graphite. It has recently shown great promise as an insulating support for the fabrication of high quality graphene films with electron mobilities approaching those measured in suspended graphene [1]. In addition to these layered structures, it is possible to grow heteroepitaxial monolayers of graphene and boron nitride, which have been shown to offer a route to engineer the graphene band structure, including the possibility of opening a bandgap [2]. Finally, it has been theoretically predicted that B and N atoms acting as dopants in grain boundary defects in graphene can have profound effects on the electronic properties of graphene [3].

Here, we report the direct growth of heteroepitaxial monolayers of small graphene islands embedded in hexagonal boron nitride by chemical vapour deposition (CVD) on the weakly interacting Ir(111) surface. In a two step process, graphene islands are first grown by temperature controlled growth monolayer coverage is achieved. The resulting films are structurally and chemically characterised by a variety of surface science techniques such as LEED, AES, XPS, and STM with a focus on the geometric and electronic structure of the graphene/h-BN interface.

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Atomistic simulation of morphology and spectral properties calculation of amorphous organic films for OLED application

S. V. Emelyanova^{1,2} V. S. Chashchihin^{1,2} A. V. Odinkov² A. A. Bagaturyants²
M. V. Alfimov²

¹National research nuclear university

²The Photochemistry center of the Russian academy of sciences (PC RAS)

Organic light-emitting diodes (OLEDs) have drawn intense attention during the past decades. 1,3,4-oxadiazole (OXD) and its derivatives are widely studied as materials for organic light emitting diodes. The knowledge of the parameters which control the photophysical and optical properties are crucial for the utilization of these materials in optoelectronic devices. In this work a functional electron transporting amorphous layer consisting of OXD-7 molecules is studied. First, force constants for bonded and non-bonded parameters for the OXD-7 material are derived based on the results of DFT calculations. The appropriate structure of the amorphous layer is obtained by molecular dynamics (MD) and deposition process simulations. To estimate molecular packing in the generated amorphous morphologies radial distribution functions, the density of amorphous films at ambient conditions, and its glass transition temperature are calculated. Next the absorption spectrum is calculated and the modeling of the absorption band shape on a set of configurations of the molecules in a view of the continuum model of solvent is performed.

Surface and defect identification methods in NC-AFM simulation

F. Federici Canova^{1,2} A. S. Foster^{1,2} S. Kawai³ E. Meyer³ M. K. Rasmussen⁴
J. V. Lauritsen⁴

¹Tampere University of Technology, Tampere, 33710, Finland

²Aalto University, Aalto, 00076, Finland

³University of Basel, Basel, 4056, Switzerland

⁴Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Denmark.

As the field of materials science grew larger, research interest was steered towards the nanoscale, since it has been recognized how important processes, for a wide range of fields, originate at such small scale. The advent of scanning probe microscopies (SPM) granted access to atomic scale detailed information, and these techniques are now widely employed. In particular, non-contact atomic force microscopy (nc-AFM), where the oscillation of a cantilever detects the interaction between the tip attached to its end and the sample, quickly became an invaluable tool in nanoscience, as it can achieve true atomic resolution on any surface. This technique allows characterization of surface defects in insulating materials, which is particularly important for catalysis, or even imaging of organic samples in their natural solution environment. Despite the wonders of atomic resolution, often times even the sharpest image of a surface and its defects, is not sufficient to tell how exactly the features observed should be interpreted, mostly because the tip-surface interaction is not trivial, and the atomic scale shape of the tip itself is not known. Furthermore, the machine provides a measurement of the cantilever's frequency shift Δf , which has to be related to the tip-sample interaction with a model. At this point, theoretical calculations become necessary to interpret nc-AFM images. Here we present two example cases where nc-AFM simulation was critical in understanding the experimental imaging mechanisms. Our studies first concentrated both experimentally and theoretically on the MgAl_2O_4 surface [1], where we could obtain in the laboratory nc-AFM images with two different types of contrast, depending on the tip termination. Combining DFT calculations with a virtual-AFM simulation, we were able to reproduce the imaging modes experimentally seen, identify the surface termination and the defects signature. Then we focused out attention on an insulating LiF step edge, where the detail of long range interactions was investigated using both the flexural and torsional oscillations of the cantilever (bimodal nc-AFM). The torsional Δf could image the step with remarkable resolution, and an odd linear dependence on the voltage applied to the sample was measured. Using theoretical calculations we modeled the system starting from macroscopic scale, down to an atomistic representation, and

we found that the changes in the torsional resonance with bias, originates from picometer displacements of the step ions. A virtual-AFM simulation confirmed how such small configuration changes can give rise to a detectable contrast, linearly dependent on the applied bias.

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Armchair Carbon Nanotubes Go Semiconducting: Effect of periodic bi-site perturbation on electronic and transport properties of carbon nanotubes

M. J. Hashemi¹ K. Säaskilahti¹ M. J. Puska¹

¹Department of Applied Physics, Aalto University, B.O.Box 11100, FI-00076 AALTO, Finland

In carbon nanotubes, the most abundant defects, caused for example by irradiation or chemisorption treatments, are small perturbing clusters, i.e., bi-site defects, extending over both A and B sites. The relative positions of these perturbing clusters play a crucial role in determining the electronic properties of carbon nanotubes. Using band structure and electronic transport calculations, we find that in the case of armchair metallic nanotubes a band gap opens up when the clusters fulfill a certain periodicity condition. This phenomenon might be used in future nanoelectronic devices in which certain regions of single metallic nanotubes could be turned to semiconducting ones. Although in this work we study specifically the effect of hydrogen adatom clusters, the phenomenon is general for different types of defects. Moreover, we study the influence of the length and randomness of the defected region on the electron transport through it.

Manipulation of the confined states in graphene quantum dots by adatoms and defects

S. K. Hämäläinen¹ J. van der Lit² Z. Sun² M. Boneschanscher²
D. Vanmaekelbergh² P. Liljeroth¹

¹Department of Applied Physics, Aalto University School of Science, P.O. Box 11100, FIN-00076 Aalto, Finland

²Condensed Matter and Interfaces, Debye Institute for Nanomaterials Science, Utrecht University, P.O. Box 80000, 3508 TA Utrecht, The Netherlands

Defects and adatoms in graphene have attracted great interest in condensed matter physics in recent years. This attention has risen from the possibility of altering the intrinsic properties of graphene by introducing well defined defects or adatoms in the honeycomb lattice. While these systems have been studied in detail theoretically, experiments on atomically well-defined structures are lacking.

Scanning tunneling microscopy and spectroscopy have been shown to be able to map the local density of confined electronic states (LDOS) in small graphene nanostructures grown on Ir(111) [1,2]. We use these quantum confined states as a probe to study the effect of defects and metal adatoms on the electronic structure of graphene. The metal adatoms on graphene can be picked up by the STM tip allowing us to map the LDOS of the nanostructures with and without the adatoms. This gives us direct insight on the effect of individual adatoms on the electronic states of graphene. In addition to studying the spatial structure of the confined states, we can also estimate the change in the electronic dispersion of graphene caused by the individual adatoms by comparing the experimental results with calculations.

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Molecular self-assembly on corrugated and non-corrugated graphene surfaces

P. Järvinen¹ S. K. Hämäläinen¹ M. Morozova¹ P. Liljeroth¹

¹Department of Applied Physics, Aalto University

Graphene continues to attract enormous research attention for future electronics. In order to exploit the full potential of graphene, a controllable way of introducing a band gap should be established [1]. One of the proposed methods involves the generation of periodic potential modulation in graphene. This could be done by the deposition of an ordered lattice of molecules or adatoms. Metal phthalocyanines and related naphthalocyanines can form well-ordered assemblies on epitaxially grown graphene. They interact with graphene mainly through the central metal ions. Thus, the strength and the period of this interaction could be easily tuned via the choice of the central ion, and the shape and the size of the molecule. However, a large gap between advanced theoretical predictions and their realization in real, scalable systems remains. The mere production of large-area, contamination-free graphene devices remains difficult and inherent grain boundaries, defects, and corrugations have to be taken into account. Here, we use scanning probe microscopy to study the self-assembly of metal phthalocyanines on CVD grown graphene transferred onto silica and mica substrates. The ordering of the phthalocyanine molecules depends crucially on the surface roughness of graphene. Using a dry transfer method for transferring graphene onto mica substrates, molecular ordering on an atomically flat surface can be studied. This opens a way to the atomic level the design and engineering of the electronic properties of graphene devices.

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Detailed structure and transformations of grain boundaries in graphene

O. Lehtinen¹ S. Kurash² J. Kotakoski^{1,3} V. Skakalova⁴ J. Smet⁴ C. E. Krill⁵
A. V. Krasheninnikov^{1,6} U. Kaiser²

¹Department of Physics, University of Helsinki, P.O. Box 43, 00014 Helsinki, Finland

²Central Facility for Electron Microscopy, Group of Electron Microscopy of Materials Science, Ulm University, 89081 Ulm, Germany

³Department of Physics, University of Vienna, Boltzmanngasse 5, 1090 Wien, Austria

⁴Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany

⁵Institute of Micro and Nanomaterials, Ulm University, Albert-Einstein-Allee 47, 89081 Ulm, Germany

⁶Department of Applied Physics, Aalto University, P.O. Box 1100, 00076 Aalto, Finland

Graphene has been attracting ever increasing scientific attention due to its unique electrical and mechanical properties. The chemical vapor deposition technique can be nowadays used to grow large crystalline domains in the millimetre-range [1,2]. However, grain boundaries are present also in such samples and, more importantly, graphene samples with much smaller crystallite sizes can be grown. Further on, grain boundaries strongly affect the properties of polycrystalline materials in general and those of graphene specifically. Several works have been dedicated to the structure of graphene grain boundaries, but the detailed structure of grain boundaries observed in, e.g., high-resolution transmission electron microscope (HRTEM) experiments [3] often differs significantly from theoretical predictions [4]. In this work the gap between the experimental and theoretical observations is bridged by means of multiscale atomistic simulations and HRTEM experiments. A theoretical model is presented, which reproduces characteristic features observed in real grain boundaries and predicts low energy transformation routes connecting different low-energy boundary configurations.

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d^0 Ferromagnetic Interface Between Non-Magnetic Perovskites

R. Oja¹ R. M. Nieminen¹

¹COMP/Department of Applied Physics, Aalto University

d^0 magnetism results from spin-polarized p orbitals, whereas conventional magnetic materials have partially filled d or f states. Magnetic effects in hole-doped oxides are a common experimental observation, and holes in oxygen p orbitals have been widely predicted to result in magnetic moments [1]. In perovskite oxides, oxygen p bands are narrow and have a high density of states just below the band gap. Also, oxygen p electrons have a strong exchange coupling. Hence, Stoner's criterion for itinerant ferromagnetism is fulfilled, if the hole density is high enough [2].

Obtaining such high hole densities, moving the Fermi level to the oxygen p band, is easily done by so-called intrinsic doping, by a charge-imbalanced interface between two d^0 perovskites. In our model $\text{KTaO}_3/\text{SrTiO}_3$ interface, SrO and TiO_2 layers are nominally neutral, but $(\text{KO})^-$ and $(\text{TaO}_2)^+$ layers have preferred ionic charges. To retain charge neutrality and compensate for interface dipole, 0.5 holes per p type interface unit cell are localized in the interface oxygen p orbitals. The n type interface, on the other hand, introduces 0.5 electrons per unit cell above the band gap, on the Ti d orbitals. Usually, a 2D electron gas is formed at a charge-imbalanced perovskite interface [3].

We have performed LSDA+U, GGA+U and hybrid calculations of p and n type $\text{KTaO}_3/\text{SrTiO}_3$ interfaces. The hole on oxygen 2p orbitals is partially magnetized even without on-site Coulomb interaction U. Small local Coulomb repulsion U or hybrid exchange stabilize complete spin-polarization and half-metallic, ferromagnetic holes. For the n type interface, on the other hand, the electrons on Ti d orbitals do not magnetize completely, and doped electrons can have a variety of competing magnetic states [4]. The density of states at the top of the O p band is higher than at the bottom of the Ti d band, making p type interfaces between d^0 perovskites candidate materials for combining ferromagnetism and ferroelectricity.

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Ehrenfest molecular dynamics within the projector augmented-wave method: ab initio electronic stopping

A. Ojanperä¹ A. Krasheninnikov^{1,2} M. Puska¹

¹Department of Applied Physics, Aalto University, P.O. Box 11100, FI-00076 Aalto, Finland

²Materials Physics Division, University of Helsinki, P.O. Box 43, FI-00014, Finland

Many phenomena in nature, such as light absorption, ignition of chemical reactions and ion-atom collisions, are related to excited electronic states and their time development. The traditional ab initio molecular dynamics (AIMD) methods cannot be used for simulating such nonadiabatic processes, which involve several coupled electronic states, because they confine electrons to a single adiabatic state. Ehrenfest molecular dynamics (Ehrenfest MD) within time-dependent density functional theory (TDDFT) offers a simple yet effective framework for simulating nonadiabatic processes by coupling the time-dependent Kohn-Sham (TDKS) equations with classical equations of motion via the KS potential energy surface.

We have implemented Ehrenfest MD within the projector augmented-wave (PAW) method [1]. The electronic structure program used for the implementation is GPAW [2,3], which uses real space grids and finite differences. Using our Ehrenfest MD implementation, we study electronic stopping in graphene. Simulating electronic stopping from first principles is difficult due to the nonadiabatic nature of the process. We show that compared to experiments, Ehrenfest MD works well over a wide range of impact energies and projectiles, especially when core electron excitations are not important. In the case of core electron excitations, using non-frozen core waves significantly improves the agreement between simulation and experiment.

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Work function of rough Cu surfaces operated under high external electric field

A. K. Ruzibaev^{1,2} F. Djurabekova^{1,2} M. Hakala^{1,2} E. Holmstrom^{1,2}

¹Helsinki University

²Helsinki Institute of Physics

By means of DFT calculations we analyze presently the redistribution of electron density on 100, 110 and 111 Cu surfaces due to self-adatoms and in existence of a high electric field from 0.1 V/Å up to 1 V/Å (1 to 10 GV/m, respectively). We further investigate local variations of work function around surface rough features, such as step edges and self-adatoms. As a particular distinction of our studies from the case of adsorption of various inorganic molecules and atoms different from the substrate material, we note that we are dealing with intrinsic defects on the surface, that are more sensitively affecting the work function in Ultra High Vacuum (UHV) and in the presence of high electric fields.

Ion irradiation induced defects in freestanding graphene: an atomistic simulation study

E. H. Åhlgren¹ J. Kotakoski^{1,2} A. V. Krasheninnikov^{1,3} O. Lehtinen¹

¹University of Helsinki, Finland

²University of Vienna, Austria

³Aalto University, Finland

We study defect production in graphene under low-energy ion irradiation via atomistic simulations. We show that carbon atoms can be substituted with boron and nitrogen via low energy irradiation with probabilities of 55% for N and 40% for B with the optimum irradiation energy of 50 eV [1]. We have further investigated the effect of pre-existing defects on the irradiation response of graphene, and show that graphene can withstand up to 35% vacancy concentration without showing any signs of critical failure caused by the irradiation. This indicates considerable structural stability of graphene windows for external ion beam experiments. These windows could be used to separate volatile or sensitive targets from vacuum required for operating the ion beam system. We conclude that the limiting factor for usage of graphene windows is not caused by the irradiation but by other factors that cause changes in the permeability of graphene due to introduced vacancies [2] and possible structural instabilities.

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