ECSCD-13

13th European Conference on Surface Crystallography and Dynamics

Donostia-San Sebastián, Spain

June 19-21, 2017



Institutional support and funding



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Preface

The European Conference on Surface Crystallography and Dynamics (ECSCD) is aimed at discussing the recent advances on the characterization of dynamical processes and structure of surfaces, as well as their interplay, at the atomic length scale. The first edition of the conference took place in 1985 in Erlangen (Germany), and it has become a well established meeting point for the surface science community. In its 13th edition, it will tackle two-dimensional materials, single molecules on surfaces, characterization by LEEM and PEEM, oxides, and other representative topics of present-day surface science. Following the ECSCD tradition, networking between experimentalists and theoreticians will be encouraged, bringing together experienced and young researchers working in the field.

The conference aims to cover the following topics:

- Single molecules on surfaces
- Dynamical processes
- Graphene and two-dimensional materials
- Advances in surface characterization
- Nanostructured surfaces
- Quasicrystals
- Oxide surfaces
- Electrochemistry and solid-liquid interfaces

Previous editions of this conference were held in:

- 1985 Erlangen (Germany)
- 1988 Cambridge (United Kingdom)
- 1991 San Miniatio (Italy)
- 1993 Aarhus (Denmark)
- 1995 Banz (Germany)
- 1998 La Grande Motte (France)
- 2001 Leiden (The Netherlands)
- 2004 Segovia (Spain)
- 2007 Vienna (Austria)
- 2010 Reading (United Kingdom)
- 2012 Edinburgh (United Kingdom)
- 2015 Trieste (Italy)

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Conference Locations



Scientific Programme

Keynote talk: 30 min. talk + 10 min. discussion Invited talk: 20 min. + 5 min. discussion Oral contribution: 15 min. + 5 min discussion

| Monday 19 | | | |
|-------------|--------------------------------|-----------|---|
| 9:00-10:00 | Registration | | |
| 10:00-10:10 | Opening remarks | | |
| 10:10-10:50 | Keynote 1 | Repp | Individual Molecules on Surfaces: From Chemical Reactions to Ultra-Short Timescales |
| 10:50-11:15 | Invited 1 | Sykes | Correlated Rotational Switching in 2D Self- assembled Molecular Rotor Arrays |
| 11:15-11:45 | Coffee break | | |
| 11:45-12:10 | Invited 2 | Shimizu | Molecular Adsorption on Anatase TiO ₂ (101) Studied by Submolecular Imaging Technique with Si Cantilever AFM |
| 12:10-12:30 | Oral 1 | Gaberle | Entropy Induced Changes in Molecular Adsorption Behaviour of Organic Molecules at Insulating Surfaces |
| 12:30-12:50 | Oral 2 | Piquero | Precise Engineering of Quantum Dot Array Coupling through Their Barrier Widths |
| 12:50-13:10 | Oral 3 | Jelinek | Multiple Electron Charge States within a Single Molecule |
| 13:10-16:30 | POSTER SESSION During lunch | | |
| 16:30-16:55 | Invited 3 | Lauritsen | Structure and Electronic Properties of Single- Layer MoS ₂ on Au(111) |
| 16:55-17:15 | Oral 4 | Chen | Synthesis and Characterisation of Epitaxial MoS ₂ Nanocrystals |
| 17:15-17:35 | Oral 5 | Zandvliet | Germanene: the Germanium Analogue of Graphene |
| 17:35-17:55 | Oral 6 | Bignardi | Key Role of Rotated Domains in Oxygen Intercalation at Graphene on Ni(111) |

| Tuesday 20 | | | |
|-------------|----------------------|---------------|--|
| 9:00-9:40 | Keynote 2 | Locatelli | Unveiling Complex Graphene Structures Using SPELEEM |
| 9:40-10:05 | Invited 4 | Aballe | Imaging Strain Waves in a PhotoEmission Electron Microscope: Magnetism Goes Surfing |
| 10:05-10:25 | Oral 7 | de la Figuera | Magnetic Domains on Magnetite Islands: from XMCD-PEEM to Micromagnetism |
| 10:25-10:45 | Oral 8 | Horstmann | Ultrafast LEED: Exploring Surface Dynamics with Short Electron Pulses |
| 10:45-11:05 | Oral 9 | Kumpf | Steering the Growth of Multiple Ordered Heteromolecular Phases by Utilizing Intermolecular Repulsion |
| 11:05-11:35 | Coffee break | | |
| 11:35-12:00 | Invited 5 | Lobo-Checa | Curved Crystal Surfaces: A Playground for General Surface Concepts and Dimensionality Transitions |
| 12:00-12:25 | Invited 6 | Gellman | Mapping Enantioselectivity across Surface Structure Space |
| 12:25-12:45 | Oral 10 | Duncan | Benchmarking DFT Calculations for Metal Oxides: Geometric Adsorption Site of Copper and Silver Adatoms on Magnetite |
| 12:45-13:05 | Oral 11 | Schneider | Adsorbate Phases and Structural Evolution Upon Reduction of Quasi One-Dimensional CoO ₂ Chains on Ir(100) |
| 13:05-15:00 | Lunch break | | |
| 15:00-15:25 | Invited 7 | Förster | Quasicrystals and Approximants in Two- Dimensional Perovskite Oxides |
| 15:25-15:50 | Invited 8 | Gallego | Biphase Ordering at Fe Oxides |
| 15:50-16:10 | Oral 12 | Harlow | Nanostructured Aluminum Oxides and Metal Electrodeposition |
| 16:10-16:40 | Coffee break | | |
| 16:40-17:05 | Invited 9 | Moriarty | Can Dynamic Force Microscopy Really "see" Intermolecular Bonds? |
| 17:05-17:25 | Oral 13 | Albrecht | Structure Determination of Individual Non- Planar Molecules by Means of nc-AFM with Functionalized Tips |
| 17:25-17:45 | Oral 14 | Moro | Demonstration of Large Converse Piezoelectric Effect on a Single Molecule |
| 17:45-18:05 | Oral 15 | Pavlicek | On-surface Synthesis and Characterization of Reactive Molecules |
| | Conference dinner | | |

| Wednesday 21 | | | |
|--------------|--------------------|----------------|--|
| 10:00-10:40 | Keynote 3 | Sánchez-Portal | Towards Electronic Devices Using Graphene Nanoribbons |
| 10:40-11:05 | Invited 10 | Africh | In-Situ Atomic-Scale Investigation of CVD- Grown Graphene on Polycrystalline Nickel Substrates |
| 11:05-11:35 | Coffee break | | |
| 11:35-12:00 | Invited 11 | Chuvilin | Accessing Kinetics of Structural Rearrangements in Graphene via Direct Atomic Imaging |
| 12:00-12:20 | Oral 16 | Gastaldo | Topological Line Defects in Graphene Nanoislands |
| 12:20-12:40 | Oral 17 | Balog | Switching the Reactivity of Graphene on Ir(111) by Hydrogen Intercalation |
| 12:40-13:00 | Oral 18 | Menzel | Core Hole Clock Characterization of Intercalated and Compressed Argon under Graphene Monolayers and in Blisters |
| 13:00-15:00 | Lunch break | | |
| 15:00-15:20 | Oral 19 | Zamborlini | Unexpected Multi-Orbital Charge Transfer at Highly Oriented Organic/Metal Interfaces |
| 15:20-15:40 | Oral 20 | Sarasola | On the Origin of Unexpected Core Level Shifts of Tetrapyrrole Molecules on Surfaces |
| 15:40-16:00 | Oral 21 | Soubach | 1D and 2D Extended Materials on Metal Surfaces: Interface Structure with NIXSW |
| 16:00-16:20 | Oral 22 | Woodruff | Understanding Molecular Adsorption Structures: Scanning Tunnelling Microscopy and Density Functional Theory are Not Enough |
| 16:20-16:50 | Coffee break | | |
| 16:50-17:15 | Invited 12 | Magnussen | Surface Dynamics at Electrochemical Interfaces |
| 17:15-17:40 | Invited 13 | Sulpizi | Water Interfaces: Structure and Vibrational Spectroscopy from Ab Initio Simulations |
| 17:40-17:50 | Concluding remarks | | |

Poster session

| Africh | NFFA-Europe: enhancing European competitiveness in nanoscience research and innovation | | |
|-----------------|---|--|--|
| Bana | Transition from Sulfided Molybdenum Clusters to monolayer MoS ₂ on Au(111) | | |
| Blanco-Rey | A Non-Adiabatic Model for Intermode Coupling in Organic Adsorbates: | | |
| | Application to STM-induced Porphycene Tautomerization | | |
| Brede | Mechanisms of the surface-confined Ullmann-reaction on semiconducting | | |
| | TiO ₂ (110) surfaces | | |
| Corso | Graphene nanoribbons growth on kinked Au(16 14 15) | | |
| Gallardo | Magnetic properties of transition metal atoms on a h-BN monolayer | | |
| Gao | Characterization of Pd Nanocrystals on Anatase TiO ₂ (001) Thin Films Grown on | | |
| | SrTiO ₃ (001) Substrates | | |
| Hammer | Structure and Growth of Monatomic TM-Oxide Chains - Copper Against All Others | | |
| Hammer | Structural sensitivity of medium energy intensity data in a LEED analysis | | |
| Ishioka | Coherent optical and acoustic phonons at buried GaP/Si interfaces | | |
| Kißlinger | Structure Determination Considering Surface Dynamics: The O/Rh(100) System | | |
| Kretz | Robustness of topological surface states against magnetic perturbations | | |
| Küchle | Understanding the Geometric Structure of a Superconductor with a Strain | | |
| | Induced High T _c | | |
| Lundgren | The structure of the SnO ₂ (110)-(4x1) reconstruction | | |
| Mandziak | Initial stages of mixed nickel-iron oxides growth on Ru(0001) | | |
| Merino | Electronic Structure Characterization of atomically-precise Chiral Graphene | | |
| | Nanoribbons on gold surfaces | | |
| Niño | Surface spectroscopy and spin filtering of DPEDA chiral molecular film | | |
| Ocal | Decoding crystallographic domains of molecular systems by cantilever torsion | | |
| | imaging | | |
| Ortega | Structure and electronic states of vicinal noble metal surfaces with densely kinked | | |
| | steps | | |
| Oteyza | Non-Covalent Dimerization after Enediyne Cyclization on Au(111) | | |
| Palacios-Rivera | Hierarchical chirality transfer during (S,S) and (R,R) DPEDA growth on Cu(100) | | |
| Pussi | Structure of the SnO ₂ (110)-(4×1) with LEED I(E) | | |
| Schiller | Interplay between metal-organic interface state and donor-acceptor interface | | |
| | mediated charge separation on PTCDA/TiOPc/Ag(111) | | |
| Stolz | Click reaction on the chiral PdGa{111} surfaces | | |
| Wang | Surface Structures of Niobium Oxide 2D Nanostructures and Ultrathin Films | | |
| Zollner | C ₆₀ adsorption on a two-dimensional oxide quasicrystal | | |

Monday June 19

Individual Molecules on Surfaces: From Chemical Reactions to Ultra-Short Timescales

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We investigated different kind of π -conjugated molecules in a combined scanning tunneling (STM) and atomic force microscope (AFM). Whereas both measurement channels show features with sub-molecular resolution, the information they can provide is truly complementary. For example, STM allows the direct imaging of the unperturbed molecular orbitals [1], whereas the AFM channel directly reveals the molecular geometry [2, 3]. Further, we used the AFM-derived technique Kelvin probe force spectroscopy (KPFS) with sub-molecular resolution to image the polarity of individual bonds inside a single molecule [4].

The possibility of tailoring optical waveforms has allowed scientists to steer ultrafast electronic motion directly via the oscillating carrier wave of light - a principle dubbed "lightwave electronics" [5]. Despite tremendous interdisciplinary efforts to combine ultrafast temporal resolution with atomic spatial resolution, the ultrafast dynamics of individual molecular orbitals has remained out of reach.

Terahertz (THz) scanning tunnelling microscopy [6] (THz-STM) has introduced a new paradigm by combining STM with lightwave electronics. In THz-STM, the electric field of a phase-stable single-cycle THz waveform acts as a transient bias voltage across an STM junction. In analogy to the all-electronic pump-probe scheme introduced recently in STM [7] these voltage transients may result in a net current that can be detected by time-integrating electronics.

By means of a low-noise low-temperature lightwave-STM we entered an unprecedented tunnelling regime, where the peak of a terahertz electric-field waveform opens an otherwise forbidden tunnelling channel through a single molecular orbital. In this way, the terahertz peak removes a single electron from an individual pentacene molecule's highest occupied molecular orbital within a time window of ~ 100 fs - faster than an oscillation cycle of the terahertz wave. This quantum process allowed us to capture a microscopic real-space snapshot of the molecular orbital on a sub-cycle time scale. By correlating two successive state-selective tunnelling events, we directly tracked coherent THz vibrations of a single molecule in the time domain [8].



Figure 1: Schematic representation of the lightwave-STM setup, in which the THz-pulse acts as a bias transient.

- [1] J. Repp et al., Phys. Rev. Lett. 94, 026803 (2005).
- [2] L. Gross et al., Science 325, 1110 (2009).
- [3] F. Albrecht et al., JACS 137, 7424 (2015).

Correlated Rotational Switching in 2D Self-assembled Molecular Rotor Arrays

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Molecular devices are capable of performing a number of functions from mechanical motion to simple computation. Their utility is somewhat limited, however, by difficulties associated with coupling them with either each other or with interfaces such as electrodes. Self-assembly of coupled molecular devices provides an option for the construction of larger entities that can more easily integrate with existing technologies. We demonstrate that ordered organometallic arrays can be formed spontaneously by reaction of precursor molecular rotor molecules with a metal surface. Scanning tunneling microscopy enables individual rotors in the arrays to be switched and the resultant switches in neighboring rotors imaged. The structure and dimensions of the ordered molecular rotor arrays dictate the correlated switching properties of the internal sub-molecular rotor units. Our results indicate self-assembly of 2D rotor crystals produce systems with correlated dynamics that would not have been predicted *a priori*.

These are highly emergent properties because individual, isolated molecular rotor units show random rotational behavior, whereas when coupled together in a self-assembled 2D crystal, correlated rotational switching is observed that would not have been predicted from the behavior of the individual units. The systems reported here are operated at low temperature, however, the barriers could be tuned via the design of the molecules themselves. While a lot is known about structure-function relationships in 3D crystals, 2D crystal engineering is still in its infancy. Moving forward, by measuring the properties of 2D crystals and then making subtle changes with organic synthesis, structure-function relationships can be drawn and emergent properties, like in this case correlated rotor switching, understood. This approach provides a new direction for the field of molecular machines, which while having produced a variety of single molecule devices, lacks ways to couple molecular motion between units and perform higher tasks.



Figure 1: Correlated switching in self-assembled molecular rotor crystals.

Molecular adsorption on anatase TiO₂(101) studied by submolecular imaging technique with Si cantilever AFM

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Submolecular imaging using frequency-modulation (FM) atomic force microscopy (AFM) has recently been established as a stunning technique to reveal the chemical structure of unknown molecules, to characterize intra-molecular charge distributions, and to observe chemical transformations. So far, most of these feats were achieved on planar molecules using the so-called qPlus sensor, a specially designed quartz AFM sensor.

Here, we report a novel imaging method using multi-pass routine to achieve submolecular resolution on threedimensional molecules and structures with a silicon (Si) cantilever-based AFM operated with large oscillation amplitudes. At variance with previous implementations, this method allows us to simultaneously image both intra-molecular structures and the atomic arrangement of the substrate [1]. Force volume measurements over C_{60} molecules clarify the validity of our method to achieve submolecular resolution. Using this technique as well as information obtained in our previous study of clean anatase TiO₂(101) surface [2], we have investigated adsorption of pentancene molecules on terraces and steps of anatase TiO₂(101) [3]. Based on comparison with theoretical calculations, we obtain an insight into substrate-molecule interaction and probe tip termination.



Figure 1: (a) Topographic AFM image and (b) multi-pass frequency shift image of pentacene molecules adsorbed on terraces and steps of the anatase $TiO_2(101)$ surface obtained at 77 K. Image size is 20nm×20nm.

[1] C. Moreno *et al.*, Nano Lett. **15**, 2257 (2015).

- [2] O. Stesovych *et al.*, Nat. Commun. **6**, 7265 (2015).
- [3] M. Todorovic et al., in preparation.

Entropy Induced Changes in Molecular Adsorption Behaviour of Organic Molecules at Insulating Surfaces

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The adsorption of functionalised organic molecules on insulating surfaces plays an important role for many applications. However, studies so far have mainly focussed on the enthalpy of adsorption and uncertainties still remain about entropic contributions. Recent theoretical studies on the adsorption of individual flexible and rigid molecules on the KCl (001) surface have shown significant entropy loss during adsorption[1]. In this work we present data on molecular adsorption and diffusion of large organic molecules on terraces and step edges on the insulating KCl (001) surface, specifically focussing on the effects that molecular flexibility has on their dynamic behaviour and what implications that may have on self assembly.

Two functionalised organic molecules, 1,3,5-tri- (4-cyano-4,4biphenyl)-benzene (TCB) and 1,4-bis(cyanophenyl)-2,5-bis(decyloxy)benzene (CDB), were studied on the KCl (001) surface using density functional theory (DFT) and classical molecular dynamics (MD) simulations. MP2 calculations were used to benchmark the performance of Van der Waals corrected DFT-D3 calculations of adsorption energies and geometries and a classical force field was parameterised for each of the molecules using a genetic algorithm.[2] These force fields allowed us to perform long time-scale simulations to study the motion of molecules on the free energy surface.

In order to better understand adsorption of TCB and CDB molecules at non-zero temperatures, potential of mean force calculations were employed. It was found that entropic contributions significantly lower the adsorption free energy, which facilitated desorption. Furthermore, adhesion to step edges was investigated along with the associated change in entropy. While the flexible CDB molecule can readily adapt to step edges, the rigid TCB molecule is unable to and exhibits a significant entropy loss upon step adhesion. We show that the simple rigid rotor model can accurately estimate entropy loss upon step adhesion for TCB but fails for CDB. These results highlight how molecular flexibility directly influences surface dynamics, which can lead to different self-assembly growth modes.

[1] Gaberle J., Gao D. Z., Watkins M. B., and Shluger A. L., *Calculating the entropy loss on adsorption of organic molecules at insulating surfaces*, J. Phys. Chem. C **120**, 3913-3921 (2016).

[2] Gao, D. Z., Federici Canova, F., Watkins, M. B., and Shluger, A. L., *Efficient parametrization of complex molecule-surface force fields*, J. Comp. Chem. **36**, 1187-1195 (2015).

Precise engineering of quantum dot array coupling through their barrier widths

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Quantum dot (QD) arrays on surfaces, generated through molecular self-assembly processes, have so far provided researchers with a vast playground to study the electronic properties of new and exotic 2D materials in ultra-high-vacuum (UHV) conditions. By selecting the proper molecular constituents (tectons) and substrate, long-range ordered, periodic and robust nanoporous networks have been achieved, ranging from hydrogenbonded to metal-organic structures [1]. Not only do they stand out as ideal templates for nanopatterning, but also as adequate candidates for studying fundamental physical phenomena such as confinement through the scattering of two-dimensional electron gases (2DEGs). Indeed, confinement tunability has already been accomplished by varying the pore (i.e. quantum dot) dimensions, geometrical shape and molecule substrate interactions [2,3]. In addition, inter-dot coupling has been shown by photoemission through the generation of new dispersive bands [4] that can be modulated through thermodynamics [5] and the condensation of guest elements (Xe atoms) [6].

To date, the modification of 2DEGs through inter-dot barrier width variations has not been experimentally demonstrated. Herein, sustained upon a combination of local scanning probes (STM/STS/AFM), angle resolved photoemission spectroscopy (ARPES) and extended model calculations, we show that we can precisely engineer the inter-dot barrier width by substitution of a single atom in a haloaromatic compound. As a result, we tune the confinement properties at each nanopore affecting the degree of QD intercoupling both on bulk and thin Ag films alike. These findings pave the way to reach full control over 2DEGs with the prospect of becoming key for future electronic devices.



Figure 1: Inter-dot barrier width engineering: single vs double molecular walls that tune the QD intercoupling properties.

[1] G. Pawin et al., Science 313, 961-962 (2006)

- [2] S. Wang et al., Phys. Rev. B 88, 245430 (2013)
- [3] F. Klappenberger et al., Nano Letters 9, 3509-3514 (2009)
- [4] J. Lobo-Checa et al., Science 325, 300-303 (2009)
- [5] I. Piquero-Zulaica et al., Applied Surface Science 391, 39-43 (2017)
- [6] S. Nowakowska et al., Small 12, 3757-3763 (2016)

Multiple electron charge states within a single molecule

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The field of molecular electronics aims at using a single molecule as building block for electronic devices. Ferrocene-based molecules are extremely appealing as they offer prospects of having a built-in charging functionality. They are known of being stable under redox states and therefore promising as candidates for quantum cellular automata units. Previous works demonstrated charging single metal adatoms [1], molecules or their clusters on insulating films [2] as well as charging of large self-assembled islands of molecules by STM or nc-AFM. [3]

Here we will present experimental evidence of controlling multiple charge states on a single 3,6,3',6'tetraferrocene-9,9'bis-fluorenylidene, deposited on thin insulating NaCl film, by means of nc-AFM. We succeed to control the multiple charge states including their reversible transfer within a single molecule between different redox states. The induced charged states have prominent fingerprints in both the frequency shift and dissipation channels. Moreover, we demonstrate that the charge states can be modified by presence of neighboring charged molecules. The experimental evidence is corroborated with a theoretical model simulating response of a dynamically oscillating AFM probe to temporal changes of force due to the charging effects of molecules on surface.



Figure 1: Frequency shift and dissipation signal images acquired for neutral, one and two-electron charge states of bis-ferrocene deposited on NaCl substrate.

[1] J. Repp et al., Science 305, 493 (2004)

INVITED Structure and electronic properties of single-layer MoS₂ on Au(111)

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Single-layer MoS₂ is one of the most studied of the two-dimensional transition metal dichalcogenides (TMDCs) as it was the first example of how a modified electronic structure reflected by a direct band gap and correspondingly different optical properties may develop when the TMDC becomes a single layer. Single-layer MoS₂ can furthermore give rise to interesting new physics through the possibility of exploiting spin and valley degrees of freedom. We have developed a synthesis method that allows us to selectively form single-layer epitaxial MoS₂ sheets grown with the (0001) basal plane in parallel to Au(111). This has the advantage of a well-defined and well-oriented system that enables us to systematically address the structural and electronic features pertaining to such single MoS₂ layers on a metal support using scanning tunneling microscope (STM) and angle-resolved photoemission spectroscopy (ARPES). Coherent sheets of MoS₂ at varying surface coverage can be formed by sequences of reactive physical vapor deposition of Mo in a H2S atmosphere followed by post annealing in the sulfiding atmosphere. Structurally, the single-layer MoS₂ adopts a large characteristic superstructure due to the lattice mismatch, reflected by a moiré pattern in STM images [1,2]. Our DFT studies furthermore reveal that this modulation is influenced by the preferential bonding of the bottom S in the MoS₂ sheet to on-top positions on the Au(111). The ARPES results [3] show that the Ausupported single-layer MoS₂ retains the important direct band gap at the K point seen in free-standing single-MoS₂, whereas the out-of-plane S bonding to Au leads to some distortions of the band near the $\overline{\Gamma}$ point. By varying the synthesis conditions we can furthermore study isolated MoS₂ islands as well as stacking faults at the interface between MoS₂ patches. This approach in particular allows us to address the edges terminating the MoS₂ sheets, which are found in photoemission and STM studies to be metallic due to the presence of edge states in contrast to the semiconducting basal plane



Figure 1: (a) Atom-resolved STM image showing the atomic lattice and moiré pattern of MoS₂/Au(111) (b) Photoemission results along the Γ-K direction for MoS₂/Au(111).

- [1] S.G. Sørensen, H.G. Füchtbauer, A.K. Tuxen et al., ACS Nano 8, 6788 (2014).
- [2] S.S. Grønborg, S. Ulstrup, M. Bianchi et al., Langmuir **31**, 9700 (2015).
- [3] J.A. Miwa, S. Ulstrup, S.G. Sørensen et al., Phys. Rev. Lett. 114, 046802 (2015).

Synthesis and Characterisation of Epitaxial MoS₂ Nanocrystals

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Two-dimensional (2D) nanocrystals of molybdenum disulphide (MoS₂) are grown on the substrate strontium titanate (SrTiO₃) by chemical vapour deposition (CVD). MoS₂ is an indirect-bandgap material in its bulk form, and exhibits an indirect-to-direct transition when thinned to a monolayer. It also possesses metallic edge states due to the shape finiteness. As a 2D material, MoS₂ is highly sensitive to its substrates, so engineering the substrate is an important step to be able to manipulate it and fully realise its potentials. However, it has only been studied on very few substrates, e.g. Au [1] and Si/SiO₂ [2]. In this project, nanocrystals of MoS₂ are grown on reconstructed SrTiO₃ surfaces.

The new substrate is crystalline and each crystal surface (e.g. (111) and (110)) has a wide range of surface reconstructions [3,4], which were prepared by high-temperature annealing (800-1200°C) in either ultra-high vacuum (UHV) or partial pressures of oxygen. Their near-atomic structures were imaged by scanning tunnelling microscopy (STM). The different surfaces possess different lattice constants and surface energies, which could influence the epitaxy of the nanocrystal growth.

The structural, electronic and optical properties of MoS₂ grown on SrTiO₃ are being characterised by STM, ultra-high vacuum (UHV) scanning electron microscopy (SEM), photoluminescence (PL) and Raman spectroscopy. The good epitaxial relationship between MoS₂ crystals and SrTiO₃ has been noted by SEM and STM (Figure 1), the latter of which also recorded the atomic structure and Moiré patterns of MoS₂. PL and Raman results confirmed the monolayer thickness of the crystals and their good optical properties. They also provided information on the strain and doping levels in the nanocrystals induced by the substrate. It is expected that the new substrate will result in interesting new properties of dichalcogenides and help us explore their new applications in 2D nanodevices.



Figure 1: Figure 1: STM images of MoS₂ nanocrystals (bright triangles) on SrTiO₃(111).

- [1] M. Buscema *et al.*, Nano Res. **7**, 561(2014).
- [2] S. Bhattacharjee *et al.*, IEEE Trans. Electron Devices **63**, 2556(2016).
- [3] B. Russell et al., J. Phys. Chem. C 112, 6538(2008).
- [4] B. Russell et al., Phys. Rev. B 77, 245414(2008).

Germanene: the germanium analogue of graphene

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Recently, a few research groups have reported the growth of germanene, a new member of the graphene family [1]. Germanene is in many aspects very similar to graphene, but in contrast to the planar graphene lattice, the germanene honeycomb lattice is slightly buckled and composed of two vertically displaced sublattices. Frist principles total energy calculations have revealed that free-standing germanene is a twodimensional Dirac fermion system, i.e. the electrons behave as massless relativistic particles that are described by the Dirac equation, i.e. the relativistic variant of the Schrödinger equation. We will give a brief update of the growth and electronic properties of germanene on Pt/Ge(110) nanocrystals [2,3]. Subsequently, we will show that large and continuous single germanene layers can be grown on molybdenum disulfide (MoS_2) [4]. The structural and electronic properties of the germanene layer are studied with scanning tunneling microscopy and spectroscopy. The lattice constant of the germanene layer is 3.8 ± 0.1 Å, i.e. substantially larger than the lattice constant of MoS_2 (3.16 Å), and the interlayer distance between the germanene layer and the MoS_2 substrate is 3.2 ± 0.2 Å, suggesting that we are dealing with a low-buckled germanene layer. The density of states of the germanene layer exhibits a V-shape, which is reminiscent for a two-dimensional Dirac system. The minimum of the density of states is located near the Fermi level.



Figure 1: Scanning tunneling microscopy image (4.5 nm by 4.5 nm) of buckled honeycomb lattice of germanene. Sample bias -0.5 V, tunnel current 0.2 nA.

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- [2] P. Bampoulis et al., J. Phys. Cond. Mat. 26, 442001 (2014).
- [3] L. Zhang et al., Appl. Phys. Lett. 107, 111605 (2015).
- [4] L. Zhang et al., Phys. Rev. Lett. 116, 256804 (2016).

Key Role of Rotated Domains in Oxygen Intercalation at Graphene on Ni(111)

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n this contribution I will provide a description of the oxygen intercalation at the strongly interacting graphene on Ni(111) and of the role of rotated graphene domains in triggering the intercalation. The system was studied by a combination of high-resolution x-ray photoelectron spectroscopy (HR-XPS), photoelectron diffraction (XPD) and angle-resolved photoemission (ARUPS) performed with synchrotron radiation. The HR-XPS measurements provided a full characterization of the interface at each stage of the intercalation, revealing the formation of an oxide layer between graphene and the metal substrate. The ARUPS data showed that the oxide layer efficiently decouples graphene from the substrate, restoring the Dirac cone and providing a slight n-doping. The C1s XPD measurements revealed that the graphene domains not aligned with the Ni substrate are the first to be intercalated with oxygen. At the same time, these domains are also preferential regions under which the oxygen is retained during the deintercalation process.

Tuesday June 20

KEYNOTE

Unveiling complex graphene structures using SPELEEM

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In my talk, I will illustrate the present capabilities of SPELEEM applied to graphene research, reporting examples of structural determination in combination with complementary STM measurements and ab-initio calculations. I will focus in particular on the characterization of complex, laterally inhomogeneous, graphene films grown on Ir(100), describing their rich structural diversity. These films exhibit coexisting physi-sorbed and chemisorbed graphene phases (see Figure 1a), providing a notable exam-ple of a model where the substrate-film interaction can be tuned by temperature, through the formation and rupture of a surprisingly small fraction of chemi-sorption bonds. The effect on the local electronic structure of the film will be discussed [1]. In the second part of the talk, I will address issues concerning the structure of graphene irradiated with low energy Ar and Ne ions [2]; I will describe in particular the evolution of the surface upon thermal treatment. Ar atoms remain trapped under graphene, where they form clusters reaching lateral size up to tens of nanometers and height of several atomic layers (Figure 1b,c). Much larger structures, nearing 100 nm in diameter, are obtained for the case of Ne, owing to the faster diffusion with respect to the case of Ar. XAS-PEEM measurements demonstrate that Ne is not solid, pointing to the occurrence of a solid-liquid transition in the bubbles [3].



Figure 1: (a) Two contiguous unit cells of buckled graphene on Ir(001), as determined by ab initio calculations. (b) LEEM image of graphene/Ir(001) after Ar ion irradiation and subsequent annealing to 1050°C; the black dots correspond to Ar nanobubbles under graphene. (c) XAS-PEEM image of the same region. The intensity of the resulting image is proportional to the Ar concentration, with the bright regions corresponding to Ar clusters.

[1] A. Locatelli *et al.*, ACS Nano **7**, 6955 (2013).

[2] G. Zambrolini *et al.*, Nano Lett. **15**, 6162 (2015).

[3] These authors, in preparation.

Imaging strain waves in a PhotoEmission Electron Microscope: Magnetism goes surfing

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Surface Acoustic Waves (SAWs) are propagating Raleigh waves in the upper micrometric layer of a crystal. which propagate large distances and can be generated in piezoelectric materials by applying RF electric fields to transducer electrodes on the surface. We have shown that it is possible to image such waves in LiNbO3 by Xray PhotoEmission Electron Microscopy (XPEEM), since it is sensitive to the piezoelectric part of the SAW. Thus, the effect of fast strain changes on structures grown on LiNbO3 can be studied with temporal resolution below 100 ps and up to 50 nm spatial resolution, offering a novel approach for studies of dynamic strain in a wide range of research fields (crystallography, nanoparticle manipulation, chemical reactions, magnetism...) The application to the study of dynamic magneto-elastic effects in Ni microstructures will be presented. The magneto-elastic effect or inverse magnetostriction (i.e., the change of magnetic properties caused by an elastic deformation) has attracted much interest due to its potential to write small magnetic elements by an electric voltage rather than current, avoiding energy losses. However, so far practical demonstrations were realized on timescales far too slow for most applications. Combining XPEEM with XMCD magnetic contrast we have imaged the Ni magnetic states at the different phases of the SAW, demonstrating that the strain-driven magnetic anisotropy changes on the sub-nanosecond timescale are as efficient as for the static strain case. Different delays (100-300 ps) of the magnetic response to the strain wave were measured, depending on the magnetic configuration. The delays are related to the intrinsic magnetization dynamics of the Ni patterns. Thus it is shown that while the magneto-elastic effect itself is very fast, for the speed of a potential device the magnetization state has to be properly designed.



Figure 1: Left, top: Scheme of magnetic domains in a Ni square without net anisotropy, forming a Landau flux closure state (arrows indicate magnetic directions and gray color contrast in XMCD-PEEM). Left, bottom: domain configuration if an additional uniaxial magnetic anisotropy is induced, favoring horizontal magnetization (black and white domains). Right, top: Series of direct images taken with different respective positions of the strain wave and a Ni square (2 µm side). The square is in the maximum of the strain wave (white zone) between the images of 150° and 210° and in the minimum between 330° and 30°. Right, bottom: Corresponding images with XMCD magnetic contrast showing the magnetic domains in the Ni square.

[1] M. Foerster et al., arXiv:1611.02847.

CONTRIBUTED TALK

Magnetic domains on magnetite islands: from XMCD-PEEM to micromagnetism

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Magnetite nanostructures and thin films have been grown in spintronic devices such as spin valves in order to take advantage of the high Curie temperature, stability, and predicted half-metal character. However, thin films present magnetic properties which are rather different from the properties of bulk magnetite: high coercive fields, high saturation fields, out-of-plane magnetization, superparamagnetism in ultrathin films, or unexpected easy-axes. An explanation for these effects are growth defects, among which antiphase domain boundaries (APBs) are the best example. In the present work, we study the magnetic domains on flat single-crystal magnetize and other mixed spinels grown on Ru(0001) by molecular beam epitaxy [1,2]. As each island grows from a single nucleus, there are expected to be free of APBs. We have measured with nanometer-resolution the 3D magnetization of the islands by combining x-ray magnetic circular dichroism images acquired in a photoemission electron microscope at different azimuthal angles. The 3D magnetization maps have been used as the initial magnetization configuration for micromagnetic simulations of islands with the same lateral and vertical dimensions as the experimental ones. The Mumax3 software has been used to perform the micromagnetic simulations. By comparing the evolution of the micromagnetic simulations with the experimental behavior of the islands after annealing, we seek to validate the material parameters that define their magnetic behavior and to identify cases where defects or other effects play a role.



Figure 1: Left: experimental magnetization in a magnetite island as determine by XMCD-PEEM. Right: micromagnetic simulation using as a starting configuration the experimental one.

- [1] M. Monti *et al.*, Phys. Rev. B **85**, 020404 (2012).
- [2] L. Martín-García et al., Adv. Mat. 27, 5955 (2015).
- [3] A. Vansteenkiste et al., AIP Adv. 4, 107133 (2014).

CONTRIBUTED TALK

Ultrafast LEED: Exploring surface dynamics with short electron pulses

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Low-energy electron diffraction (LEED) is one of the prime techniques of surface science, allowing for detailed insights into a variety of phenomena such as structural phase transitions, surface reconstructions or chemical reactions [1]. Yet, many of these features exhibit highly-complex couplings and correlations between the electronic, magnetic and structural degrees of freedom, which are difficult to disentangle using steady state analyses of systems in equilibrium. While the electronic and spin systems are already extensively studied at surfaces on their intrinsic timescales, gaining experimental access to ultrafast structural evolution remains challenging. Hence, in order to reach a comprehensive and quantitative understanding of ultrafast dynamics at surfaces, a time-resolved implementation of LEED is highly desirable.

Here, we present the development of ultrafast low-energy electron diffraction (ULEED), employing low-energy electron pulses in a laser-pump/electron-probe scheme. Within this approach, a laser-triggered nanoscopic needle emitter is utilized in a miniaturized electrostatic lens geometry as a high-brightness source. The resulting electron pulses exhibit a minimal duration down to 1 ps at the sample for electron energies of 20-200 eV.

We demonstrate the potential of ULEED by investigating the optically induced transition between charge density wave (CDW) phases at a single-crystalline $1T-TaS_2$ surface [2,3]. We also apply ULEED to study the dynamics of adsorbates on metal surfaces.



Figure 1: Ultrafast LEED: a) Experimental setup; b) Diffraction images of 1T-TaS₂ taken before and shortly after optical excitation reveal the ultrafast transition between CDW phases; c) Temporal evolution of CDW spot intensities.

M.A. Van Hove, W.H. Weinberg and C.-M. Chan, *Low-Energy Electron Diffraction*, Springer Verlag, Heidelberg (1986)
S. Schweda *et al.*, International Conference on Ultrafast Phenomena, paper UTh2B.3, OSA (2016)
S. Vogelgesang *et al.*, in preparation

Steering the growth of multiple ordered heteromolecular phases by utilizing intermolecular repulsion

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The interfaces between organic semiconductors and metals have been investigated intensively in order to improve and develop future electronic devices. In this context the formation of molecular blends (i.e., heteromolecular layers containing at least two different types of molecules, usually charge donors und acceptors) on metal surfaces is of great interest. Many different techniques have been applied in the past to investigate different prototypical systems.

In this presentation, we report a novel thermodynamic phase diagram for molecular blends formed in submonolayers [1]. In a comprehensive LEEM study on PTCDA+CuPc on Ag(111) we find five crystalline phases (two homo- and three heteromolecular structures) having different stoichiometry. Large eutectic regions exist in the phase diagram, caused by the opposite intermolecular interaction of its components - repulsive for CuPc, attractive for PTCDA. We find that the repulsive species forms a two-dimensional lattice gas, the density of which determines the stability of all other crystalline phases. The existence of critical gas-phase densities is the basis for understanding the constant-volume phase diagram that perfectly describes our experimental observations. We anticipate the general validity of this type of phase diagram for binary systems containing 2D gas phases, and emphasize that the density of the gas phase allows engineering of the interface structure.In this presentation, we report a novel thermodynamic phase diagram for molecular blends formed in submonolayers [1]. In a comprehensive LEEM study on PTCDA+CuPc on Ag(111) we find five crystalline phases (two homo- and three heteromolecular structures) having different stoichiometry. Large eutectic regions exist in the phase diagram, caused by the opposite intermolecular interaction of its components - repulsive for CuPc, attractive for PTCDA. We find that the repulsive species forms a two-dimensional lattice gas, the density of which determines the stability of all other crystalline phases. The existence of critical gas-phase densities is the basis for understanding the constant-volume phase diagram that perfectly describes our experimental observations. We anticipate the general validity of this type of phase diagram for binary systems containing 2D gas phases, and emphasize that the density of the gas phase allows engineering of the interface structure.



Figure 1: (a) Bright-field LEEM images recorded during a binary deposition experiment: Initially, 0.17 ML of PTCDA form islands on the Ag(111) surface (upper left image). The following LEEM images were recorded during subsequent CuPc deposition of 0.7 ML. The PTCDA islands (marked green) are sequentially transformed into MBW (yellow), M121 (red) and MZZ islands (blue), according to the stoichiometry sequence. (b) Corresponding phase diagram for the submonolayer regime: Data points and colored areas mark the regimes of pure and eutectic phases as obtained from experiment and thermodynamic model, respectively. The path of the experiment shown in (a) is indicated by a dotted black arrow. The model is based on more than 20 LEEM experiments with different initial coverages. Abbreviations: P = PTCDA, C = CuPc; Sequence and stoichiometry of the phases: PTCDA (P) - MBW (P2C) - M121 (PC) - MZZ (PC2) - CuPc (C).

[1] C. Henneke, D. Schwarz, F.S. Tautz, C. Kumpf, Nature Materials, in press, DOI: 10.1038/NMAT4858

Curved crystal surfaces: A playground for general surface concepts and dimensionality transitions

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Crystal surfaces with a small deviation from a high symmetry plane have enormous potential for surface science research and applications. Such "vicinal" planes, characterized by arrays of atomic steps, exhibit distinct chemical and electronic properties, and are useful templates to achieve uniaxial symmetry and single azimuthal domains in epitaxial layers, or to drive self-organized nanostructure growth.

A way of systematically studying step-related phenomena is to use curved crystals. The beauty of these special substrates is that they integrate all vicinal directions, which are accessible by scanning the source beam or tip along the curvature of the crystal. In this way, the sample provides a smooth variation of the step density that is directly related to a terrace width variation from sub-micron to the nanometer range.

These samples has allowed us to revisit old and to explore new surface science problems [1-3]. I will discuss step-lattice interactions, scattering of surface states and growth. Our experiments demonstrate the immense power of the curved surface approach, which allows one to directly image fine physical-chemical properties of surface systems, such as to settle controversial issues and to unveil new phenomena.



Figure 1: (a) Example of three curved crystals: c-Au(111), c-Cu(111) and c-Ag(111). (b) Example of a 2D to 1D electronic transition taking place in Bi(111) under the presence of a high density of steps.

- [1] J.E. Ortega et al., Physical Review B 87, 115425 (2013).
- [2] A.L. Walter et al., Nature Communications 6, 8903 (2015).
- [3] L.A. Miccio et al., Nanoletters 16, 2017 (2016).

Mapping Enantioselectivity across Surface Structure Space

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Enantioselectivity can be observed on naturally chiral metal surfaces with structures that are described as having flat low Miller index terraces separated by kinked step edges, therefore lacking mirror symmetry. This work has mapped the enantiospecific decomposition kinetics of tartaric acid (TA) on ~500 different single crystal planes exposed by the surfaces of Cu(111) and Cu(100) Surface Structure Spread Single Crystal (S⁴C). S⁴Cs are single crystals polished into a spherical shape that expose continuous distributions of surface orientations vicinal to primary orientation [1]. The left hand panel of the figure shows a Cu(111). During isothermal decomposition, XPS has been used to map the temporal evolution of the coverage of TA at points across the Cu(111) and Cu(100) S⁴Cs. The center and right hand panels of the figure shows D- and L-TA coverage maps across the Cu(100) S⁴C following heating at 450 K to decompose ~70% of the initially adsorbed TA. Blue reveals regions in which the TA has been completely decomposed. Red reveals regions in which TA decomposition kinetics is revealed by the spiral nature of the two maps and their opposite sense of handedness for D- and L-TA. These data can be analyzed to yield the enantiospecific rate constants for TA decomposition as functions of surface orientation.



[1] A. de Alwis, B. Holsclaw, V.V. Pushkarev, A. Reinicker, T.J. Lawton, M.E. Blecher, E.C.H. Sykes, AJ. Gellman, Surface Science **608**, 80-87 (2013).

Benchmarking DFT calculations for metal oxides: geometric adsorption site of copper and silver adatoms on magnetite

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Single-site catalysis is a promising field for pursuing model catalytic reactions, with the objective of one day designing catalysts from the bottom up. However, in order to gain true insight into the inner workings of any system, it is necessary to be able to reliably theoretically model it. Thus to benchmark such theoretical calculations it is of the utmost importance to acquire stringent quantitative experimental constraints. In this work we utilize the quantitative geometric structure, determined by normal incidence X-ray standing wave (NIXSW), as a benchmark for density functional theory (DFT) calculations of one such promising single site catalyst: dispersed single adatoms on the (001) termination of magnetite.

The recently elucidated surface reconstruction of $Fe_3O_4(001)[1]$ patterns the formation of well separated single adatoms with a comparatively high coverage[2]. However, although the surface structure is well known [1], the geometry of the adatoms has only been probed by non-quantitative techniques such as STM and XPS, which do not provide suitable benchmarks for theoretical calculations, providing a fertile field for a NIXSW study.

We specifically probed the surface structure silver (Ag₁) and copper (Cu₁) adatoms, which are predicted to occupy the same lateral site, but dramatically different vertical heights. NIXSW triangulation measurements, utilising the (400), (440) and (311) reflection planes, identified that both adatoms do indeed occupy the same lateral site, specifically bridging two surface oxygen atoms, at an adsorption height of 0.43±0.03 Å and 0.96±0.03 Å respectively, as shown in Figure 1. Theoretical calculations, in which the lattice constant was correctly modelled, predicted that Ag₁ and Cu₁ lay 0.89 and 0.41 Å above the projected bulk termination, in good agreement with the experimental results. However, theoretical models that overestimated the lattice constant underestimated the adsorption height, exemplifying the necessity to accurately model the whole system.



Figure 1: (left) Cu 2p and Ag 3d NIXSW from the (400) reflection of $Fe_3O_4(001)$ and (right) the resulting difference in adsorption height of Cu₁ and Ag₁ with respect to the (400) spacing of the magnetite. Scanning tunneling microscopy image of the dimer of cyclized products (inset) and the associated calculations on Bader charge distribution, evidencing the strongly polarized bonds responsible for the attractive dipole-dipole interaction.

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[2] Z. Novotný, et al., Physical Review Letters 108, 216103 (2012).

Adsorbate Phases and Structural Evolution Upon Reduction of Quasi One-Dimensional CoO₂ Chains on Ir(100)

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On the Ir(100) surface one can prepare highly ordered, quasi one-dimensional, transition metal oxide chains in a (3×1) superstructure [1]. These oxide chains have an unusual MO_2 stoichiometry in which the metal atom (M = Mn, Fe, Ni, Co) is decoupled from the iridium substrate (Figure 1a). Using the example of CoO_2 chains we analyze structural changes and phases upon adsorption and reaction with reducing species like H_2 and CO in an UHV environment. Due to the long-range order of the system before and after the reactions it is possible to quantify these structural changes by means of high-precision, full-dynamical LEED analyses. Combining the detailed structural information with data obtained by HR-XPS, STM, TDS, and supporting DFT calculations we are able to follow the processes during the reactions on the atomic scale.

Oxidation of H₂ and CO and in consequence reduction of the CoO₂ chains eventually to a well-ordered (3×1) Ir₂Co surface alloy may be thermally activated near room temperature. As evidenced by HR-XPS spectra, the reaction with H₂ proceeds via the formation of an intermediate OH-species on the surface. In the case of reduction by CO the formation of CO₂ proceeds from a ordered $c(6\times2)$ -(CoO₂+CO) adsorbate phase in which CO occupies an Ir bridge site (Figure 1b). An intermediate carbonate or other species cannot be detected. In the case of CO oxidation the initially high reaction rate is reduced because the CO molecules assemble on the freshly formed Ir₂Co alloy and hence are spatially separated from the remaining intact or partially reduced cobalt oxide chains.



Figure 1: (a) (3×1)-CoO₂ chain structure on Ir(100) and (b) c(63×2) CO adsorbate phase on the CoO2 chain structure with best-fit models as determined of the LEED structural analyses. Pendry R-factors (a) $R_p = 0.10$, (b) $R_p = 0.13$.

[1] P. Ferstl et al., Phys. Rev. Lett. 117, 046101 (2016)

INVITED

Quasicrystals and approximants in two-dimensional perovskite oxides

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When approaching the two-dimensional limit, oxides are known to exhibit strong variations in their structures and properties as compared to the respective bulk materials [1]. One of the extreme examples are the twodimensional oxide quasicrystals (OQCs), which have been discovered for reduced perovskite oxides at the Pt(111) interface [2, 3]. OQCs have been reported for BaTiO₃ and more recently also for SrTiO₃. Furthermore, approximant structures have been observed, in which selected motifs of the OQC are periodically repeated. In Figure 1a an example of a simple approximant structures is given, which has been observed for BaTiO₃ [4]. The more complex approximant structure shown in Fig. 1b has been reported for SrTiO₃ [3]. The later is almost indistinguishable from the aperiodic structure in an diffraction experiment. Our studies unravel OQCs as best-controlled QC model systems for addressing the fundamental questions related to the driving forces for aperiodic structure formation.



Figure 1: Comparison of periodic approximant tilings (a, b) and the aperiodic Stampfli-Gähler tiling as observed for OQCs (c). The OQC tiling lacks translational symmetry.

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- [3] S. Schenk et al., J. Phys.: Condens. Matt. doi.org/10.1088/1361-648X/aa5bdb (2017).
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Biphase ordering at Fe oxides

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The phase diagram of oxide surfaces and ultrathin films may be different from that of their bulk counterparts, and binary Fe oxides provide very good examples. In the O-poor limit, their bulk phase diagram includes the antiferromagnetic rock-salt insulator FeO and the ferrimagnetic spinel half-metal Fe₃O₄. FeO is not stable at ambient conditions but with a significant number of Fe vacancies that resemble Fe₃O₄ inclusions [1]. However, a single FeO(111) monolayer has been stabilized on different substrates. Even a record thickness of 8 nm preserving the 1:1 stoichiometry has been achieved under ultra-high vacuum conditions, before the film evolves to Fe₃O₄ [2]. A more intriguing phenomena emerges when the two distinct phases coexist at the same termination (biphase ordering), as has been observed at the surface of Fe₃O₄ [3].

Here we will show that at the origin of this behavior lies the tendency of FeO(111) to introduce tetrahedrally coordinated Fe sites. Together with the reduced energy difference between FeO and Fe_3O_4 in the ultrathin limit, this favors the coexistence of both phases in the few monolayers regime, explaining the emergence of biphase ordering [4]. Furthermore, these findings provide interesting clues to solve the elusive Fe_3O_4 (111) surface structure.



Figure 1: Side view of the spinel-like and wurtzite terminations of FeO(111).

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Nanostructured Aluminum Oxides and Metal Electrodeposition

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Traditional surface science studies have been quite successful in determining several surface structures for alumina films, in particular those grown on NiAl, where the bulk structure consists of a combination of several building blocks but the surface Al atoms are found to occupy sites with either tetrahedral or pyramidal coordination [1]. However, the naturally forming 'native oxide' layers are found to be largely amorphous. The thickness of this layer can be increased electrochemically, i.e. the industrial process of anodization, and to some extent the degree of crystallinity found depends on the applied voltage [2]. This type of oxide layer is called an anodic barrier layer and forms in neutral type electrolytes. In acidic electrolytes a porous oxide film is found, in which case the oxide has many nanometer sized pores and forms the base of most industrial aluminum coloring processes. Furthermore, under certain conditions these pores are found to be self-ordering [3]. They form hexagonal arrays and the pore diameter can be tuned by changes in potential, making excellent nanoscale templates.

We have investigated the formation and self-ordering behavior of porous type anodic alumina films *in operando* using Grazing Transmission Small-Angle X-Ray Scattering (GTSAXS). The experimental setup and scattering geometry is illustrated in Fig 1A and Fig. 1B. We observe the that the in-plane arrangement of the nanopores is independent of substrate crystallographic orientation whereas the oxide growth rate is not. The self-ordering behavior is studied in a variety of electrolytes and at several potentials. It is also possible to follow the chemical etching of the oxide (pore widening) and subsequent metal deposition within the nanopores. The experimental approach presented can be applied to the study of a large variety of electrochemically produced materials such as magnetic nanowires, novel solar cell designs and catalysts.



Figure 1: Experimental Schematic. A) The electrochemical cell used for in operando experiments. B) scattering geometry and an example scattering pattern.

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INVITED

Can dynamic force microscopy really "see" intermolecular bonds?

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Since Gross *et al.*'s pioneering observation of the internal "architecture" of a pentacene molecule in 2009 [1], there has been a rapid growth in ultrahigh resolution imaging of single molecules using dynamic force microscopy [2]. Image interpretation is, however, always a challenge with any type of scanning probe technique as, very often, the precise role of the probe can be difficult to 'deconvolve' from the experimental data. I shall discuss a series of ultrahigh vacuum, low temperature force microscopy results (based around the qPlus sensor [3]) for a variety of molecules adsorbed on both metal and semiconductor surfaces: NTCDI [4,5] and biisonicotinic acid (which are both largely planar), and C_{60} (which is, of course, very far from planar) [6].

Although the biisonicotinic acid data (see Fig. 1) were acquired with a CO-terminated tip, as per the standard approach in the dynamic force microscopy community, high resolution imaging of both NTCDI and C_{60} involved imaging using a tip which, to the very best of our knowledge, was terminated by an NTCDI or C_{60} molecule respectively. Intramolecular resolution was possible for tips that interacted both very strongly (~ 2 nN) and very weakly (~ 50 pN) with the Si(111)-(7×7) surface, demonstrating that an inert probe is not a prerequisite for intramolecular imaging. This has important implications for the continuing development of 'internal' imaging of adsorbed molecules on semiconductors.





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Structure determination of individual non-planar molecules by means of nc-AFM with functionalized tips

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Functionalizing the tip of an AFM with a single CO molecule allows for unambiguous structure determination of individual molecules [1]. This technique was widely applied for different molecules [see e.g. 2]. However, the molecules under investigation exhibited manly planar structures, adsorbed parallel onto the sample surface and showed no internal degrees of freedom.

Here, we present experimental results obtained with a combined STM/AFM operated at low temperatures in UHV. We show two routes for structure determination of individual molecules by means of nc-AFM with CO functionalized tips for molecules that could not be identified from conventional scanning probe imaging:

In the first case, we determine the entire 3D geometry of a helically shaped diphenanthrene derivate. To do so, we record a time-demanding, full 3D dataset in a safe but sufficiently close distance regime [3]. To analyse the molecular geometry we display the AFM signal along different planar cross sections of the 3D data [4].

In the second case, we analyse subtle differences in the 3D structure of free-base and metallated porphyrin derivates adsorbed on Cu(111) [5]. Since unambiguous molecular identification is not possible in conventional imaging we record AFM data in a close but safe distance range by introducing vertical imaging - that is recording the frequency shift in a plane perpendicular to the sample surface. These images allow unambiguous molecular species identification. Moreover, mapping the minimum position of the frequency shift [6] within these vertical images, we quantify the vertical movement of the central metal atom upon tip induced conformational switching of one of the porphyrin derivates.

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CONTRIBUTED TALK

Demonstration of large converse piezoelectric effect on a single molecule

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The converse piezoelectric effect is a phenomenon, in which a mechanical strain is generated in a material due to an applied electrical field. Demonstration of the piezoelectric effect on nanoscale remains the challenge. In this work, we investigate the piezoelectric effect in single 2,17-Bis(acetylsulfanyl) heptahelicene (BA7H) molecules on Ag(111) surface, using the non-contact atomic force microscopy (AFM). The BA7H on the substrate forms circular and linear islands, which can be effectively disassembled to individual molecules by the AFM tip, to exclude collective influence on the piezoelectric measurements. We can reversibly flip the acetylsulfanyl group at the terminal of the molecule exposed to the tip between two metastable configurations via a controlled tip-molecule interaction. In addition, we characterized the bias-induced deformations of the BA7H molecules and found that the piezoelectric effect is intrinsic to the helicene core. We corroborate the experimental evidence by the total energy DFT simulations. The calculations reveal strong charge transfer between BA7H molecule and the metallic substrate, which gives rise to a vertical electric dipole. The presence of the electric dipole coupled with a soft vibrational mode steaming from a helical structure of the molecule originates the strong piezoelectric effect.



Figure 1: Sample graphics (B/W in print) Schematic view of a metallic tip approach over two different configurations of BA7H molecules. b) Bias dependent force-distance spectroscopy revealing strong variation of the tip-sample distance with applied bias, at which the molecule is contacted.

CONTRIBUTED TALK

On-surface synthesis and characterization of reactive molecules

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Non-contact atomic force microscopy (AFM) with functionalized tips allows direct imaging of the structure of molecules [1]. This method has been realized as an ideal tool to compare reactants with products of thermally activated on-surface reactions [2]. Another possibility to initiate on-surface reactions is atomic manipulation using the tip of the microscope. Recently, we have followed the latter route to investigate molecules that are too elusive to be characterized by other methods [3].

Suitable precursor molecules are required in which individual bonds act as predetermined breaking points. These weakest bonds (for example, carbon-halogen or carbon-hydrogen bonds) can then be cleaved by atomic manipulation. Applying this versatile procedure opens a multitude of possibilities. For example, reactive intermediates like arynes can be characterized in unprecedented detail [4], reversible ring-opening and - closing reactions can be initiated and studied [5], or diradicals like triangulene can be generated which might be interesting for spintronic applications because of their unpaired electrons [6].



Figure 1: Pseudo three-dimensional rendering of an AFM image of three molecules generated by atomic manipulation with several Br atoms adsorbed close by.

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Wednesday June 21

KEYNOTE

Towards electronic devices using graphene nanoribbons

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In this talk, I will present some studies of prototype electron devices made out of graphene nanoribbons that we have recently performed in our group in San Sebastián. In collaboration with our experimental colleagues, we have studied the properties of armchair GNRs (AGNRs) doped and functionalized in different ways. In particular, we have studied 7-AGNRs periodically doped with boron pairs on Au(111), and compared our findings with scanning tunneling microscopy/spectroscopy (STM/STS) and angle-resolved photoemission (ARPES) data. Furthermore, it is possible to grow structures formed by pristine segments separated by regions doped with B pairs [1]. We have studied the properties of such boron defects as scattering centers for GNR electrons, and found that they provide large effective barriers for the propagation of electrons in the valence band (VB), but are nearly transparent for the immediately lower energy band (VB-1) due to the different symmetry of both bands. As a result, the VB gives rise to quantized levels in the pristine regions that are clearly identified (see the Figure), with a remarkable agreement between theory and experiment [1].

From a purely theoretical perspective, we have explored a prototype 4-terminal semiconducting device formed by two crossed AGNRs as a function of the intersection angle, stacking, inter-GNR separation, GNR width, and voltage. [2] Interestingly, when the AGNRs intersect at θ =60° electrons injected from one terminal can be split into two outgoing waves with a tunable ratio around 50% and with almost negligible backreflection. The split electron-wave is found to propagate partly straight across the intersection region in one ribbon and partly in one direction of the other ribbon, i.e., in analogy of an optical beam splitter. We rationalize our findings with a simple model that suggests that electronic beam splitters can generally be realized with crossed GNRs.



Figure 1: (a) Calculated projected density of states in a pristine segment between two borylated units 65Å apart. (b) Dispersion of the VB and VB-1 bands and the corresponding transmission curves for a pristine 7-AGNR (red line), a 7-AGNR containing an isolated B-pair defect (green doted line), and a 7-AGNR containing two B-pairs separated by 65Å (blue line exhibiting characteristic Fabry-Perot-like resonances). (c) Scheme and real part of the transmission eigenchannels with an increasing number of nodes as we move down in energy.

The authors acknowledge financial support from FP7 FET-ICT project No. 610446 project, EU H2020 project No. 676598, MINECO (Grant No. MAT2013-46593-C6-2-P), the Basque Dep. de Educación and the UPV/EHU (Grant No. IT-756-13).

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In-situ atomic-scale investigation of CVD-grown graphene on polycrystalline nickel substrates

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The understanding of growth mechanisms, at the atomic level and on substrates suitable for scalable CVD production, is a key step for the use of graphene in industrial applications. However, most studies so far are based on the interpretation of post-growth experiments on model surfaces, which can sometimes be misleading.

By means of variable-temperature scanning tunnelling microscopy, we studied the graphene growth process in the 380-500°C temperature range with a time resolution down to 100 ms/image and on commercially available polycrystalline Ni substrates. (111) and (100) facets were identified in the examined regions of the polycrystalline sample and growth mechanisms were investigated on both flat (100) terraces and highlystepped regions. On flat terraces, graphene can grow directly on top of the metal or via in-plane carbide conversion, as already evidenced in our previous work on model (111) substrates [1]. On (100) grains, a variety of moiré superstructures are present, which can be well explained in atomistic models by the mismatch with the substrate and whose appearance in the STM images is well reproduced by density functional theory simulations. These moiré structures were found to be able to influence carbide segregation under graphene, thus providing a new route to tune its electronic properties on a nano-meter scale. Furthermore, with the aid of an add-on FAST module allowing for the acquisition of STM time-series up to video rate, novel growth mechanisms at stepped areas are unveiled, which rationalize the continuity of the graphene layer even when it lies on highly stepped polycrystalline substrates.



Figure 1: Graphene growth on (100) Ni facets. Left: selected frames of an atomically resolved Fast-STM movie during growth at 450°C; Right: atomistic model of the mechanism imaged on the left

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Accessing kinetics of structural rearrangements in graphene via direct atomic imaging

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The raise of nanoscience and nanotechnology and necessity to characterize the structure of individual objects consisting of a countable number of atoms determined the shift of structure characterization paradigm from bulk methods like X-ray diffractometry to local high resolution methods like electron microscopy. The similar shift in paradigm is urging now in chemistry - chemical processes defining structure and properties of nanoscale and low dimensional objects often constitute a negligible part of the total volume of the material, and thus their assessment by experimental bulk chemical methods if often impossible. The new concept is provided by the time resolved electron microscopy allowing for direct observation of atomic rearrangements.

We are developing the methodology to apply the formalism and approaches of the classical chemical kinetics for the quantitative description of atomistic processes observable in the microscope. We show that a proper statistical treatment of the data obtained in a range of experimental conditions allows determining the threshold energies for radiation induced reactions. But not only that: we show that true activation energies for thermally activated reaction pathways for individual defects can be estimated as well.

We apply this methodology for reactions of point defects in graphene. The cross-sections and threshold energies of irreversible (atom emission) and reversible (bond rotation, see Figure 1) processes are measured. Observation of statistically significant number of events at variable experimental conditions allows decoupling of radiation induced and thermal reaction pathways and obtaining independent estimations of cross-sections and activation energies for direct and backwards rotations. The cross-sections of direct rotation were found to be in a decent agreement with theoretical estimations. Interestingly the backwards rotation is characterized by very high cross-section exceeding theoretical values by 3-4 orders of magnitude. The values obtained rule out electron nucleus collisions as the main pathway of energy transfer from electron beam to the sample. We speculate that the energy is transferred through electron-electron interactions via strong coupling of excited electron states with the phonon modes localized around the defect.

Acknowledgements: The contribution of my co-workers from Nottingham University, KAUST, Novosibirsk Institute of Inorganic Chemistry, Vienna University and Graphenea Company is greatly appreciated. The work was partially supported by collaboration project with FEI Company and by FP7-PEOPLE-2011-IRSES N295180 (MagNonMag) project.



Figure 1: Sequence of electron microscopy images showing the bond rotation reaction in graphene. The upper row - unprocessed images of the graphene lattice separated by time slices of 1s. The lower row - the same images filtered in order to remove the pattern of the lattice.

Topological line defects in graphene nanoislands

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Understanding grain boundaries in polycrystalline graphene is crucial for the control of both their electronic and mechanical properties. Depending on their topological structure, boundaries can impede transport across grains, or host their own one dimensional metallic states [1]. Concerning mechanical stability, they can either weaken or strengthen the graphene sheet [2]. We here report experimental evidence on some predicted and other new topological defect boundary structures, as found by Scanning Tunnelling Microscopy (STM) in graphene nanoislands grown on Ni(111) by CVD. By using mild annealing temperatures, we obtain multidomain nanoislands with different types of domain boundaries. High-resolution STM images allow us to characterize both the stacking and orientation of graphene domains and the boundary atomic structure. From a statistical analysis of the rotated domains, we conclude that their abundance is closely related to the boundary energetics [3], evidencing that the selection of rotational domains is determined by boundary rather than stacking energetics. linear and ring boundaries separating 30Ű rotated domains are particularly interesting: the linear ones are predicted to be transparent to Dirac electrons [4], whereas confined resonances have already been observed in quantum dots bound by similar ring boundaries [5].



Figure 1: a) STM image of a zoomed area of a graphene nanoislands grown on Ni(111) by CVD. Different type of topological defect boundaries consisting on pentagon/heptagon units separate stripes (a) and quantum dots (b) of domains with 30° of relative rotation.

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Switching the reactivity of graphene on Ir(111) by hydrogen intercalation

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The functionalization of graphene with hydrogen enables a variety of new phenomena to appear such as e.g. band-gap opening[1], enhanced spin-orbit coupling [2] and ferromagnetic order in single sided hydrogenated graphene [3]. The appearance of these phenomena, however, strongly depends on the type of hydrogen structures, formation of which is often driven by the graphene-substrate interactions. [4,5] Moreover, the possibility for graphene to act as a hydrogen storage medium has led to several studies[6,7].

Using XPS and STM techniques we show that quasi free-standing graphene can be prepared on Ir(111) upon hydrogen intercalation. The intercalation in turn modifies how graphene reacts towards atomic hydrogen bombardment - resulting in formation of different type of hydrogen structures when compared to the nonintercalated case. In addition, I will show that while graphene on Ir(111) can be functionalized upon exposure to vibrationally excited $H_2^{\#}$, [8] its reactivity is fully suppressed in quasi free-standing state that is achieved by intercalation. Understanding the reactivity of graphene towards hydrogen and the role of underlying substrates in these reactions is important for the realization of carbon-based hydrogen storage materials.



Figure 1: Comparison of hydrogen structures formed on a) bare graphene and b) hydrogen intercalated graphene on Ir(111).

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Core hole clock characterization of intercalated and compressed argon under graphene monolayers and in blisters.

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Recently it has been shown by several groups[1-4] that argon can be stably intercalated and compressed into bubbles or blisters under graphene (Gr) monolayers on metal substrates. On the basis of our previous definition of these states by XPS, XAS, and STM [4], we now investigated the state of the argon atoms under Gr on Ni(111) by resonant core excitation and decay, the so-called core hole clock (CHC) method [5,6], using XPS as the transfer standard. For intercalated Ar monolayers the Ar $2p_{3/2} \rightarrow 4s$ resonance is not detected at all; the weak decay signal consists of Auger electrons only. Both these findings indicate that the core exciton state is quenched or possesses extremely fast decay. For compressed Ar in blisters containing more than 1 Ar layer a small resonance is found which decays into Auger states; for blisters containing several Ar monolayers (at least mono, bi and trilayers) a stronger, shifted resonance is detected which leads to only spectator decay electrons. We discuss these results in terms of distinguishable contributions from Ar atoms pressed into the Ni substrate, Ar in contact with the graphene cover, and those Ar atoms shielded from both interfaces in the interior of blisters. These results corroborate the interpretations given before from XPS, XAS, and STM results and contribute to the understanding of both the Ar blisters and the physics of excitation decay in strongly coupled systems.

Time permitting some interesting further details and extensions to other systems will be reported.



Figure 1: a) Scheme of the excitation-decay process for an intercalated Ar atom under a Gr ML, with decay after (left) and before (right) charge transfer. b) Schematics of the three different Ar states in a Gr blisters, and their contacts to metal and/or Gr enclosure, or shielded from both.

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Unexpected multi-orbital charge transfer at highly oriented organic/metal interfaces

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Supramolecular multiporphyrin arrays are considered ideal model systems for the study of energy transfer mechanisms and of natural photosynthesis [1]. A reliable and rigorous method is needed, in order to characterize the electronic and structural properties of porphyrins at the interface, where the molecule-substrate interactions play a fundamental role. We investigate the adsorption behavior of nickel tetraphenyl porphyrin (NiTPP) molecules on the Cu(100) surface by applying a comprehensive multi-technique approach, photoemission electron microscopy (PEEM), photoemission tomography (PT) and STM, complemented density functional theory (DFT) calculations.

The adsorbed NiTPP arrange in two different geometrical configurations with different orientation respect to [100] crystal direction. By combining STM with DFT calculations, we demonstrate that the contrast, in STM images, arises mainly from the phenyl peripheral groups, which are tilted upwards. This adsorption configuration prevents the macrocycle, where frontier orbitals are localized, to be resolved by the STM tip.

For this reason, STM cannot be used for mapping the charge distribution of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively). Therefore, as a complementary technique, we exploited the capability of our PEEM to directly image a wide reciprocal space in one single shoot. The angle-resolved photoemission data (ARPES) were then compared to DFT calculations, within the PT framework [2]. The molecular orbitals (MO) exhibit peculiar features which can be used to unambiguously identify them in the valence band spectra. This is particularly useful to determine the molecule-substrate interaction and the charge transfer phenomena between adsorbed molecules and metal surfaces. The comparison between experiment and theory shows that the former gas-phase LUMO+3 becomes occupied upon adsorption on the metal surface (see Fig1 c). This unexpected result suggests that a multi-technique approach is mandatory in order to obtain a consistent picture of the adsorption behavior and electronic properties of the molecular system.



a) STM image of the NiTPP/Cu(100). b) Proposed absorption model for NiTPP/Cu(100). c) top: Projected density of state of MOs for NiTPP/Cu(100). Bottom: comparison between ARPES and DFT calculations.

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On the origin of unexpected core level shifts of tetrapyrrole molecules on surfaces

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Several studies have addressed the presence of unexpected components in the molecular level X-ray Photoelectron Spectroscopy (XPS) spectra, specially in the N1s signal, when tetrapyrrole molecules are deposited on different surfaces in Ultra High Vacuum (UHV) conditions[1-3]. In this work, we employ a set of DFT-based tools to unravel the origin of an unpredicted peak in the N1s core level spectra of metal phthalocyanines (in particular, ZnPc) adsorbed on Cu(110). We analyze the different possible chemical or electronic mechanisms that might explain this experimental result. On one hand, we prove that surface effects, such as LUMO splitting and surface screening, cannot account for the huge experimental CLSs. On the other hand, we show that, when adsorbed at low temperatures, these molecules capture residual H atoms from the surface, giving rise to hydrogenated molecular species without de-metalation of the molecule and, thus, to an extra component in the molecular CLS spectra.[4] Only upon annealing, and subsequent H release, do the molecules recover their nominal structural and electronic properties. Our results thus demonstrate that residual hydrogen, which is known to be the primary residual gas in UHV systems, might have a significant effect on the measured electronic properties of molecule-surface complexes.



Figure 1: Left side: Dehydrogenation of adsorbed organic molecules upon annealing. Right side: Corresponding XPS spectra prior and after annealing.

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CONTRIBUTED TALK

1D and 2D extended materials on metal surfaces: Interface structure with NIXSW

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The structural properties of molecule/metal interfaces have been attracting attention for years due to their correlations with the electronic properties of the adsorbed organic semiconductor. In particular, the normal incidence x-ray standing wave (NIXSW) technique based on photoemission spectroscopy has been successfully applied to measure the equilibrium distance between adsorbed molecular species and the substrate - the adsorption height [1] - as well as possible deviations from initial molecular geometry, e.g. distorsions [2]. The adsorption height of a molecule can be used to judge about the nature of dominant interactions at the interface. As a rule of thumb, if the adsorption height is smaller than the sum of van der Waals radii of the atoms forming the molecular backbone and the atoms of surface, the contribution of chemical interactions is significant. Otherwise the dominant interactions are assumed to be of a dispersion type (van der Waals) [3]. The earlier case represents molecular chemisorption, while the later - molecular physisorption. It was experimentally shown that the choice of the surface can vary the type of adsorption of the same molecule as it, for example, happens to PTCDA molecule physisorbed on Au(111) [3] and chemisorbed on Ag(111) [1] and Cu(111) [4]. It is interesting to test if this tendency is also found for 1D and 2D extended materials, which recently came into the focus of interest due to their extraordinary electronic properties.

Here we report on our recent results on NIXSW measurements of adsorption height of 2D extended materials - graphene and hexagonal boron nitride (*h*BN) - and 1D extended materials - graphene nanoribbons (GNR) - above Cu(111) and Au(111) surfaces. We found out that both 2D materials used in experiments have the height over the Cu(111) surface exceeding the sum of corresponding van der Waals radii. Thus only weak interactions are expected for graphene/Cu(111) and *h*BN/Cu(111) interfaces as validated by the experiment. The behavior of graphene nanoribbons synthesized *in situ* from molecular precursors on Au(111) and Cu(111) is also interesting. On Au(111), the different types of GNRs studied in our work are found to be physisorbed, while on Cu(111) the adsorption height is noticeably reduced pointing at a significant contribution of chemisorptive interactions. On Au(111), GNRs retail their planar geometry, while on Cu(111) they are slightly distorted, especially in the case of N-substituted GNRs. Thus the adsorption behavior of GNRs is rather similar to that in the case of planar organic molecules.

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CONTRIBUTED TALK

Understanding molecular adsorption structures: scanning tunnelling microscopy and density functional theory are not enough

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The considerable success and increasing accessibility of density functional theory (DFT) calculations to describe molecular adsorption on surfaces has led to its increasing use as the only source of fully quantitative structural information for such systems. In many cases DFT is used in combination with scanning tunnelling microscopy (STM) alone, a technique that provides information on the surface ordering, but the only detailed quantitative structural information (adsorption height, molecular conformation, and often the local adsorption site, plus conclusions regarding surface reconstruction) to emerge from such a study is derived from the DFT calculations. Despite the considerable success of DFT calculations in reproducing many experimentally-determined structures, there are well-documented failures of the method and it also suffers from the same limitation as experimental trial-and-error structure determinations in that the correct structure cannot be obtained if only incorrect structural models are tested. Most simulations of STM images derived from DFT calculations are also rather insensitive to the correct structural model, and so are not a sound basis for identifying the correct model.

An investigation of an ordered commensurate phase of TCNQ (7,7,8,8-tetracyanoquinodimethane) on Ag(111) that we are currently completing provides a clear example of this issue [1]. Although as a free molecule TCNQ is rigid and planar, when adsorbed on coinage metal surfaces it becomes negatively charged (as manifest by photoelectron spectroscopy); the electrons become localized on the cyano groups, the central quinoid ring aromatises, the π -conjugation becomes disrupted and the peripheral carbon atoms become sp³ hybridised. This allows the molecule to become far more flexible. A number of DFT investigations (mostly without dispersion correction) of TCNQ on these surfaces indicate that the adsorbed molecule becomes highly bent, with the peripheral atoms much closer to the surface and the central quinoid ring higher above the surface. We have used a combination of STM, LEED, UPS and soft XPS to characterise the Ag(111)/TCNQ system but also normal incidence X-ray standing waves (NIXSW) to determine the height of the TCNQ constituent atoms above the surface. The NIXSW results not only reveal the absolute height of the molecule but also that the average height of all the constituent atoms are almost identical. However, while the measured coherent fractions for all the C atoms are high, indicating a single well-defined height, the coherent fraction for the N atoms is very much lower, clearly indicating the presence of at least two different N atom heights. A possible rationale for this could be the presence of Ag adatoms to form a metal-organic network, and DFT calculations do confirm that this is energetically-favoured. However, to achieve this agreement with the experimentallydetermined atom-specific heights, it was necessary to select a dispersion-correction scheme that gave good agreement for the overall molecular height and also to include the influence of the Ag adatoms. Without the input of both of these experimentally-identified aspects the DFT calculations revealed bent molecules at the wrong height, just as had been found in earlier studies.

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Surface dynamics at electrochemical interfaces

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Electrochemical interfaces are the key to many current and emerging technologies, for example in energy storage or micro-/nanofabrication. All of these applications involve atomic-scale processes on the electrode surface, such as the surface diffusion and mutual interactions of the atomic and molecular species, participating in the reactions. However, in contrast to adsorbate dynamics at solid surfaces under vacuum conditions, understanding of the surface dynamics at these complex interfaces is still rudimentary. Many aspects of the elementary dynamic events at electrochemical interface are unclear, for example: How is the motion of atoms across the surface affected by the presence of the electrolyte, in particular by coadsorbed species? Which role does the strong electric field at electrochemical interfaces play? What kinds of interactions between adsorbed species on the electrode surface exist, how strong are they, and what is their distance dependence? How do these effects influence electrochemical reactivity and the results of electrochemical reactions, e.g. the morphology of electrochemically deposited films?

A direct and powerful way to clarify such phenomena are direct observations of the atomic motion at the interface, provided the employed technique has a sufficient high spatial and temporal resolution for such studies. In the talk, I will discuss *in situs*tudies of surface transport at electrochemical interfaces by high-speed scanning tunneling microscopy (Video-STM), which allows direct observations of the atomic-scale dynamics. By detailed statistical analysis, quantitative data on the diffusion barriers and interaction energies is obtained from these video data, providing insight into the role of the electrode potential and coadsorbed species. As examples, I will discuss the diffusion of isolated anionic, cationic, and organic adsorbates on noble metal electrodes as well as the interactions between identical and different adsorbate species [1-6]. These studies reveal a very strong dependence of the tracer diffusion of these adsorbates on the electrode potential, leading to changes in mobility over several orders of magnitude. Furthermore, coadsorbed anions can have a huge influence, leading to fundamentally different behavior even in systems, in which the adsorbate layers have identical structure.

To demonstrate the relevance of these observations for interfaces processes under technologically relevant conditions, case studies of electrochemical Au and Cu deposition by *in situ* x-ray surface scattering will be discussed [7-9]. They reveal surprising differences between Au and Cu electrodeposition, specifically an inverse potential dependence, demonstrating the pronounced influence of surface active coadsorbates on real-life electrode reactions.

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Water interfaces: structure and vibrational spectroscopy from ab initio simulations

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At the interface, the properties of water can be rather different from those observed in the bulk. In this seminar I will present an overview of our computational approach to understand water structure and dynamics at the interface including atomistic and electronic structure details. In particular I will show how Density Functional Theory -based molecular dynamics simulations (DFT-MD) of solid/water and water/vapor interfaces can provide a microscopic interpretation of recent experimental results from surface sensitive vibrational Sum Frequency Generation spectroscopy (SFG) [1,2]. As an example, the organization of water at the fluorite/water interface over a wide pH range will be discussed. Moreover the energy relaxation in water at the interface will be also addressed, in connection to recent vibrational pump-probe experiments.

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Posters

NFFA-Europe: enhancing European competitiveness in nanoscience research and innovation

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NFFA-Europe is a European open-access resource for experimental & theoretical nanoscience that carries out comprehensive projects for multidisciplinary research at the nanoscale, ranging from synthesis to nanocharacterization, to theory and numerical simulation. Advanced infrastructures specialized on growth, nanolithography, nano-characterization, theory and simulation and fine-analysis with Synchrotron, FEL and Neutron radiation sources are integrated into a multi-site combination to develop frontier research on methods for reproducible nanoscience research thus enabling European and international researchers from diverse disciplines to carry out advanced proposals impacting on science and innovation. NFFA-Europe coordinates access to infrastructures on different aspects of nanoscience research that are not currently available at single specialized sites without duplicating specific scopes. Internationally peer-reviewed approved user projects have access to the best-suited instruments, competences and technical support for performing research, including access to analytical large-scale facilities, theory and simulation and high-performance computing facilities. Access is offered free of charge to European users. Two researchers per user group are entitled to receive partial financial contribution towards the travel and subsistence costs incurred. The user access scheme includes at least two ``installations" and is coordinated via a single entry point portal that activates an advanced user-infrastructure dialogue to build up a personalized access programme with an increasing return on science and innovation production. NFFA-Europe's own research activity addresses key bottlenecks of nanoscience research: i.e. nanostructure traceability, protocol reproducibility, in-operando nano-manipulation and analysis, open data (www.nffa.eu).





Figure 1: The www.nffa.eu home page, with the catalogue of tools offered for transnational access and the Single Entry Point for proposal preparation and submission.

POSTER

Transition from Sulfided Molybdenum Clusters to monolayer MoS₂ on Au(111)

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The transition metal dichalcogenides (TMDCs) are one of the most promising class of two dimensional (2D) materials to be included into new-generation electronic and optoelectronic devices [1] as the semiconducting analogue to graphene [2]. Molybdenum disulfide (MoS_2) is the most widely explored member of TMDCs, due to its uncommon size dependent properties. MoS_2 displays a shift from indirect to direct band gap when going from its bulk to monolayer form [3], with a more than a 104-fold enhancement of the photoluminescence quantum yield [4]. Currently, one of the greatest challenges in materials science is to grow stable 2D layers of MoS_2 via different synthetic approaches and to achieve structure-property correlations of monolayer, bilayer, and multilayer sheets [1]. Among the various approaches attempted to grow MoS_2 monolayer, the one consisting in the deposition of Mo atoms on Au(111) at room temperature, followed by annealing, both performed in H_2S atmosphere, led to the growth of high quality single layer nano-islands, allowing the measurement of the band structure of monolayer MoS_2 [5-7].

Here we present a high energy resolution X-ray photoelectron spectroscopy study (HR-XPS), carried out at the SuperESCA beamline of Elettra, the Italian synchrotron radiation facility, on the growth of MoS₂ on Au(111) performed with the aforementioned growth method. The XPS technique, used also in its fast modality to follow transient processes (Fast-XPS), allowed us to detect the different species present on the surface and to follow their evolution during annealing, at the transition from sulfided Mo clusters to MoS₂ monolayer. The HR-XPS spectra of the Au 4f core level showed the appearance of a new component upon MoS₂ growth, caused by the MoS₂-substrate interaction. This interaction is also detected in the S 2p core level region, where the component related to the bottom sulfur layer, which is in contact with gold, is shifted with respect to the top sulfur layer of the 'S-Mo-S' sandwich structure.

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A Non-Adiabatic Model for Intermode Coupling in Organic Adsorbates: Application to STM-induced Porphycene Tautomerization

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The intramolecular relocation of a H atom within an organic molecule, known as tautomerization, is sometimes associated to conductivity changes, which makes it attractive in the field molecular electronics. In a number of recent experiments, tautomerization reactions were accomplished in porphycene molecules adsorbed on copper surfaces using STM current [1,2] or laser [3] pulses. Here the transformation is the result of non-adiabatic coupling (NAC) of inelastically scattered electrons or holes and molecule vibrations. However, porphycene tautomerization cannot be modeled by the usual non-adiabatic models of the field, due to the large number of vibrational modes involved and to the non-negligible intermode coupling. These are common limitations of organic molecular adsorbate manipulation.

We have put forward a model that overcomes those limitations. First, the NAC-induced anharmonic (de)excitation rates of the individual modes are calculated. Then, intermode coupling is treated as a deformation of the adiabatic potential energy curve (PEC) associated to the reaction (N-H bond stretch). This procedure maps the high-dimensional problem effectively onto a one-dimensional one [4]. All the model quantities can be calculated from DFT. The accuracy of the results thus relies on the DFT description of the molecule-substrate interaction, often ruled by van der Waals forces.

The applicability of our methodology is illustrated in the case of the porphycene *trans* \rightarrow *cis* tautomerization on Cu(111) by STM [2], where we have explained key aspects such as the existence of a threshold bias and irreversibility at low temperature [4,5] (see figure).



Figure 1: (a-d) Deformed PECs for bias voltages U and the corresponding H probability distributions. (e,f) Time evolution of trans, cis populations under (e) and above (f) threshold U. (g) DFT-obtained LUMOs of adsorbed porphycene tautomers, which are imaged by STM experiments.

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Mechanisms of the surface-confined Ullmann-reaction on semiconducting TiO₂(110) surfaces

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We have recently demonstrated the synthesis of poly(p-phenylene) (PPP) nanowires from dibromo-pterphenyl (DBTP) precursors on the reduced $rTiO_2(110)$ surface under ultra-high vacuum (UHV) conditions[1]. Here, we address the influence of the degree of reduction of the $TiO_2(110)$ substrate on the polymerization reaction by temperature dependent XPS.

Specifically, we identified that the Ti catalyzed aryl-aryl homo-coupling reaction pathway is strongly suppressed on nearly stoichiometric surfaces. Moreover, we find evidence for a reaction pathways that either facilitate the homo-coupling *via* proton up-take [2] or lead to the formation of phenyl-ether-groups.

Finally, we present a control experiment where the homo-coupling reaction was deliberately induced by adding trace amounts of a metal catalyst at room temperature leading to substantially increased reaction yield and nanowire arrays in unprecedented quality even on (near) stoichiometric $sTiO_2(110)$ surfaces.



ARPES data showing the transition of the non-dispersing DBTP HOMO into the characteristic PPP p-band on $TiO_2(110)$ surfaces with different reduction levels as characterized by the in-gap DS state intensity.

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POSTER

Graphene nanoribbons growth on kinked Au(16 14 15)

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Graphene nanoribbons are an interesting class of carbon materials that on one side, exhibit some superlative properties of graphene, while on the other side possess high tunability of their electronic and structural properties. An important issue for their technological implementation stems on the capability to grow GNR with the same size [1]. While their width can be precisely controlled by on surface synthesis [1, 2], a homogeneous GNRs length distribution has not been achieved yet. For this purpose, exotic surfaces might be used to induce preferential growth or to steer on-surface selective reactions on special atomic sites [3].

In this work we study the growth of 7-armchair graphene nanoribbons (7-AGNR) on the kinked Au(16 14 15) surface. The clean surface is characterized by regular kinks and an average terrace size of 4.3 nm (Figure 1a). Upon 7-AGNRs growth the surface undergoes a strong kink reshaping and formation of larger terraces (Figure 1b). Interestingly, mobile Au atoms expelled from the kinks get trapped in between ribbons forming locally a regular missing row reconstruction. We find that the 7-AGNRs do not follow the expected parallel orientation to the steps with homogeneous lengths; however, they exhibit a well-defined occupied electronic band dispersing along the macroscopic terrace orientation. We observe by Angle Resolved Photoemission the presence of a graphene nanoribbon related band not only in the second Brillouin zone but also at the Gamma point. We explain this unexpected observation as due to the ribbons interaction with the reconstructed surface.



Figure 1: a) Clean Au(16 14 15) surface; b) One monolayer of 7-Armchair Graphene Nanoribbons grown on Au(16 14 15) following the recipe in ref. [2].

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Magnetic properties of transition metal atoms on a h-BN monolayer

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Transition metal atoms adsorbed on a surface constitute an excellent system to study the interplay between spin-spin interactions and the magnetic anisotropy, the property responsible of stabilizing a magnet [1]. These atomic magnets are subject to dissipation and loss of coherence due to the coupling with the surface degrees of freedom. An hexagonal boron nitride (h-BN) layer constitutes an excellent decoupling layer capable of diminishing these harmful effects. Hence, here we examine the magnetic properties of 3d transition metal atoms adsorbed on top of a h-BN layer. We use DFT calculations based on plane waves basis to determine the adsorption sites, adsorption distances and electronic configuration of the adatom. By calculating the maximally localized Wannier functions, we quantify the atomic character and the symmetries of the system. This allows us to build an effective tight binding Hamiltonian for 4s and 3d electrons of the adatom. We then perform a many body multiplet calculation which, in addition to the excitation spectra, leads to the expectation values of the local orbital and spin angular momentum. This in turn can be used to extract a simple effective spin Hamiltonian where the symmetry operations can be easily identified, which may help to design more robust nanomagnets [2].



Figure 1: (Left) h-BN with metal adatom (red). (Right) Electronic band structure with red shadowed area showing the in gap states from the metal adatom.

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Characterization of Pd Nanocrystals on Anatase TiO₂(001) Thin Films Grown on SrTiO₃(001) Substrates

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Nanostructured TiO_2 is a widely used material for catalysis applications. The anatase phase is more catalytically active under ultraviolet irradiation for photocatalytic applications than the rutile polymorph. However, anatase TiO_2 is generally only found in small crystal sizes, but is not thermodynamically stable for large crystals. To be able to study the surface of anatase an epitaxial growth method can be applied to grow anatase (001) onto the SrTiO₃(001) surface. The lattice of anatase is only 3.1% smaller than that of SrTiO₃. This method allows the production of epitaxial high quality large anatase (001) films which are stable at temperatures up to 860°C. These films can be used to study the interaction of Pd with the anatase surface.

The anatase films are grown using the following method. Following certain surface processing steps a class of TiO_x nanostructures are formed on the $SrTiO_3(001)$ surface. These nanostructures can be classified as parallel packed nanolines (dilines, metadilines, trilines and tetralines) or small dot features. Upon extensive UHV annealing leading to significant TiO_3 surface enrichment, the $TiO_2(001)$ anatase phase starts to nucleate on the nanostructured $SrTiO_3(001)$ surfaces. This occurs after several annealing cycles at temperatures around 880-900°C. The growth of anatase $TiO_2(001)$ can be further enhanced through the evaporation of Ti onto the nanostructured $SrTiO_3(001)$ surface followed by an annealing step at 750-900°C. Anatase $TiO_2(001)$ epitaxially grown on $SrTiO_3(001)$ surfaces can have large surface areas of (1×4) reconstructions (Figure 1a). These surfaces are ideally suited for the study of metal nanoparticle (e.g. Pd) growth. Pd nanocrystals grow into truncated triangular shapes on the anatase surfaces (Figure 1b). If the annealing temperature of these samples is raised above 600°C then the Pd-anatase system enters the strong metal-support interaction (SMSI) state, characterized by the encapsulation of Pd nanocrystals with a titanium oxide layer.



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Figure 1: STM image of (a) anatase TiO₂(001)-(1×4) surface (80×80 nm², $V_s = +1.61 V$, $I_t = 0.225 nA$); (b)Pd nanocrystals grown on anatase TiO₂(001) surface (100×100 nm², $V_s = +2.5 V$, $I_t = 0.8 nA$).

Structure and Growth of Monatomic TM-Oxide Chains - Copper Against All Others

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Annealing submonolayer deposits of 3d transition metals (TM) on Ir(100) in oxygen leads to a self-organised growth of TMO₂ chains with monatomic metal core [1]. We have investigated the growth, geometrical structure and energetics of these systems by scanning tunneling microscopy, quantitative LEED-IV analyses and density functional theory.

In case of TM = Mn, Fe, Co and Ni the oxide chains grow from the very beginning in islands with 3×1 periodicity, which is the closest possible mutual chain distance. Eventually, at a coverage of 1/3 monolayer a homogeneous phase develops. Therefore, this phase has to be regarded as a 2-dimensional phase despite the quasi one-dimensional appearance of single chains: The monatomic metal core of the chains is found to be shifted by half a substrate unit vector against the substrate with every transition metal atom being fourfold coordinated to oxygen. Below every oxide chain the Ir row is missing so that the oxide chains resides well above this trough avoiding any direct binding of the TM core with the substrate.

In stark contrast, CuO₂ is found to form (n×2) ordered phases with n=1/ θ_{Cu} (or c(8×2) in case of n=4), consisting of equally spaced chains according to the respective Cu coverage θ_{Cu} .

The space between the oxide chains is filled by narrow stripes of oxygen atoms with a local structure very similar to that of the (2×1) -O phase of oxygen on plain Ir(100) [2]. Additionally, the local chain structure deviates substantially from the other TM chains: Though the Cu core is also shifted against the substrate rows, every Cu atom is now only twofold coordinated to oxygen. Further, the Cu core lies deep within the troughs of the substrate missing row reconstruction forming two more bonds towards Ir atoms of the second layer.

Accompanying DFT calculations closely reproduce the LEED bestfit structural parameters as well as the STM appearance for all systems. The structure of the copper chains is only by less than 0.1 eV more favourable than the alternative structure corresponding to all other TM oxide chains. Therefore, the structural switch is induced by a cooperation of various contributions.



Figure 1: Appearance of the (3×1) -CoO₂ (upper row) and $c(8 \times 2)$ -CuO₂ (bottom row) phases in LEED and STM as well as the corresponding ball models in top and side view.

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Structural sensitivity of medium energy intensity data in a LEED analysis

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The crystallographic analysis of complex surface structures involves the quantitative determination of many structural parameters and therefore requires a large experimental data base. In low energy electron diffraction (LEED) intensities are taken as a function of energy, so called I(E)-spectra, within an energy range of typically 50-400 eV. A simple increase of the maximum energy would raise the amount of independent data quadratically.

In this study we demonstrate that such an extension of the energy range for a LEED analysis up to much higher energies (900 eV) does not necessarily lead to a loss of the surface sensitivity due to the increased penetration depth of the electrons. In contrast, the reduced relative scattering contribution of the surface layer is in most cases compensated by the increased structural resolution provided by the smaller electron wave length at higher energies. This holds for most scatterers except for light-weighted or heavily vibrating atoms. Moreover, the high energy data show as expected a much higher sensitivity to structural details within deeply buried layers.

The applicability of this approach is not only predicted by model calculations but also demonstrated experimentally for various structurally quite different systems. We compare the structural sensitivity of low and high energy data sets obtained for clean surfaces of a Rh(100) bulk crystal, a thick CoO(100) film, as well as different ordered phases of transition metal surface oxides on Ir(100). The extension of the energy range also improves the reliability of the LEED analysis and by that allows to determine structural parameters with a precision of one single picometer in favourite cases.

In turn, higher energy data are also more sensitive to the angle of incidence of the primary electron beam. This eventually demands for some corrections for the (slightly) convergent beam used in the experiment which are also introduced in this contribution.



Figure 1: R-Factor curves R_P vs parameter variation for the Ir(100)-3×1-CoO₃ phase. Green lines correspond to the LEED-fit within the full energy range 50-800 eV, red lines to the low energy (50-350 eV) and blue lines to the high energy regime (650-800Å eV). The top row compares the relative sensitivity on the vertical position of surface and buried Ir atoms; the bottom row corresponds to surface cobalt and oxygen atoms. For Ir and Co the positional sensitivity is superior in the high energy range, only for the lighter oxygen atoms the situation is reversed.

Coherent optical and acoustic phonons at buried GaP/Si interfaces

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Photoexcitation of a solid with a femtosecond laser pulse can lead to the generation of coherent phonons. Coherent optical phonons are non-propagating lattice oscillations with zero wavevectors and discrete THz frequencies, whereas coherent acoustic phonons, by contrast, are ultrasonic strain pulses that can have a broad spectrum from GHz up to a few THz frequencies and wide range of wavevectors. Here we present our combined experimental-theoretical studies on both coherent phonons generated at the lattice-matched GaP/Si interfaces, whose GaP overlayers are grown by MOVPE on n-type Si(001) substrates and characterized by STEM [1]. We perform pump-probe reflectivity measurements using laser pulses of 400-nm wavelength and 10-fs duration as a light source. On the sub-picosecond time scale, the reflectivity changes of the GaP/Si samples, shown for a 56-nm thick GaP layer on Si in Fig. 1a, are modulated at very fast (~10 THz) oscillations, which is comprised of the longitudinal optical (LO) phonons of GaP and Si. We find the amplitude of the LO phonon of GaP to depend critically on the growth condition of the GaP overlayers. Since the coherent LO phonons of polar semiconductors are predominantly generated by the sudden screening of the built-in surface field, we can estimate the band bending on both sides of the GaP/Si interfaces based on the LO phonon amplitude with help of simple theoretical modeling [2]. On the longer time scale, the reflectivity change is modified at slower (~0.1 THz) oscillations, as shown in Fig. 1b. The slow modulations are periodic for GaP and Si, and their frequencies agree with those of the "Brillouin oscillation", i.e., the interference between the reflections from the surface and a moving acoustic pulse [3]. The GaP/Si samples also show similar slow modulations, but with complicated phase jumps as well as a sharp spike (indicated by an arrow in Fig. 1b). The reflectivity spike appears at a time required for the longitudinal acoustic (LA) phonons to traverse the GaP layer, and is attributed to the acoustic pulse generated at the GaP/Si interface and detected at the GaP/air surface. The extremely narrow temporal width, ~0.5 ps, corresponds to a spatial extent of ~3 nm or 10 Ga-P bilayers. The generation of the acoustic pulse can be explained in terms of the ultrafast charge separation at the GaP/Si interface, leading to the effective deformation potential coupling constant that is different from intrinsic values in GaP and Si crystals.



Figure 1: Transient reflectivity change of a 56-nm thick GaP layer grown on Si(001), together with those of (001)-oriented GaP and Si. Panels (a) and (b) show identical data with different expansions.

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Structure Determination Considering Surface Dynamics: The O/Rh(100) System

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In this study we combine quantitative LEED-IV, STM and DFT calculations to reinvestigate the oxygen phases on Rh(100) up to a coverage of 0.67 ML. In this regime three distinct phases exist: A (2x2)-O [1], a (2x2)-2O [2] and a (3x1)-2O structure [3]. Their appearance in LEED and room temperature STM is displayed in Fig.1.

Regarding the (3×1)-2O phase our LEED analysis validates the structural model proposed by Gustafson *et al.* [3] with a Pendry R-factor $R_P = 0.096$. The resulting structural parameters coincide almost quantitatively to those obtained for the $Pt_{25}Rh_{75}(100)$ -(3×1)-2O structure [4].

For the (2×2)-O phase our LEED re-analysis ($R_P = 0.072$) corroborates the hollow site adsorption revealed by the early analysis of Oed *et al.* [1] and refines their structural model by the determination of 13 additional parameters. This finding, however, contrasts to the appearance in room temperature STM, where non-primitive (2×2), (2×1) and (1×1) areas are imaged (*cf.* Fig.1). We interpret these features as a time average over rapidly fluctuating light domain walls which is corroborated by small diffusion barriers (190 meV) as obtained by DFT.

In case of the (2×2)-2O structure our LEED analysis confirms the model of a clockwise-/ anticlockwise reconstruction of the substrate. However, contrary to the analysis of Baraldi *et al.* [2], our best-fit structure ($R_P = 0.098$) correctly accounts for all symmetry elements observed in experiment. This is achieved by introducing a 50 : 50 occupation of neighboring quasi-threefold oxygen adsorption sites. As proposed by Alfè *et al.* [4] and confirmed by our DFT calculations these sites are separated by a barrier as low as 24 meV.

Thus, every single oxygen atom fluctuates with close to phonon frequency preventing the substrate from a complete, symmetry-breaking local relaxation. Of course, STM can only see the mean positions of the hopping atoms and therefore pretends a simple $c(2 \times 2)$ configuration.



Figure 1: Overview of all investigated oxygen adsorption phases on Rh(100). Top row: LEED pictures. Bottom row: Corresponding atomically resolved room-temperature STM images.

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POSTER

Robustness of topological surface states against magnetic perturbations

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Topological insulators (TIs) have attracted a lot of interest in the last few years due to the unique properties of their surface states, which are protected by time-reversal symmetry (TRS). Electrons in these topological surface states can not be backscattered, making TIs promising candidates for their application in high performance electronics and spintronics. For potential spintronic devices, however, it is necessary to establish contacts between the TI and other magnetic materials. This could lead to a breaking of the time-reversal symmetry and, consequently, to a destruction of the topological surface state [1,2].

In this combined experimental and theoretical study we investigate the influence of magnetic adatoms, namely Co, on the structural and electronic properties as well as on the topological surface states of Bi_2Te_3 and $Bi_2(Se_6,Te_{1-6})_3$ (BST). Scanning tunneling microscope (STM) measurements indicate that, on the BST surface, the Co adatoms move away from the high symmetry points of the surface unit cell. Our density functional theory (DFT) calculations of the relaxed surface structures strongly support the results of these measurements. We also find, from our first-principles calculations, that the direction of the magnetic moment of the adatoms depends on the adsorption site and local environment. Thus, since an in-plane magnetic moment might mask TRS breaking [3], a 3 Tesla magnetic field is applied in the STM experiments. According to our DFT predicted low magnetic anisotropy energies this magnetic field guarantees a sizable out-of-plane magnetic moment. Our experiments show that, upon Co adsorption, the TRS is preserved for the BST surface while it is destroyed for the Bi_2Te_3 . The preservation of TRS in BST is attributed to a lack of hybridization between the Co states and the topological surface state, for which we found experimental evidence in the absence of Co states within the bulk bandgap [4].

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Understanding the Geometric Structure of a Superconductor with a Strain Induced High $\rm T_{\rm c}$

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Utilising high T_c superconductors technologically has been beset by a myriad of technical issues. The standard bearer of high T_c superconductors, the cuprates, do not exhibit the performance known from the bulk as the monolayer limit is approached[1]. However FeSe thin films, grown on SrTiO₃ (STO) substrates show a dramatic increase in T_c , compared to their bulk value (8 K). In fact, the highest F (over 60K) have been observed for FeSe monolayers[2]. This temperature exceeds all T_c of the known bulk iron-based superconductors, while still maintaining a comparatively simple composition. It is likely that the interaction between the STO and the FeSe is playing a significant role in this dramatic increase in T_c , thus gaining high precision geometric information of the adsorption structure of the FeSe on STO is of the utmost importance. Without such information, theoretical understanding of this phenomenon will remain elusive. To this end we have pursued a joint X-ray standing wave (XSW) and energy scanned photoelectron diffraction (PhD) study into the geometry of this system.

XSW triangulation has determined that the Fe atoms sit in a site above the bulk oxygen atoms in the Ti planes. However, due to a lack of chemical shift in the Se 3p XP spectra, it has not been possible to determine the Se absorption site of the two non-identical Se atoms, see figure 1 a). Therefore Se 1s and Fe 1s PhD measurements, see figure 1 b), were pursued in order to precisely illuminate the fine structure of the FeSe, and the interaction between the FeSe and the STO.



Figure 1:) Comparison of the Fe 3s and Se 3p XSW from FeSe on SrTiO₃. Note that the Se 3p XSW displays a significantly lower coherent fraction, FH, indicative of two distinct adsorption sites. b) Comparison of the Fe 1s and Se 1s PhD spectra indicating dramatically different periodicity, but comparable amplitude modulations.

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The structure of the SnO₂(110)-(4x1) reconstruction

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 SnO_2 is an important material for a number of applications such as gas sensors, catalysis and photo electronics [1], but a detailed understanding of some of the functions of the material is missing due to a lack of knowledge of the surface composition and the exact atomic arrangement. It is however known that a number of applications are based on the dual valency of Tin oxide, and the oxide prefers oxidation states of 2+ or 4+. The SnO_2 crystallizes in the rutile phase, and the most stable termination is the (110) phase, having a bulk terminated surface structure similar to $TiO_2(110)$ and $RuO_2(110)$ [1]. Early surface studies suggested that an oxidized (110) surface could be reduced upon heating and forming a disordered (1x1) termination, and only by sputtering the surface before annealing results in a more well-ordered (4x1) reconstruction, suggesting oxygen depletion by preferential sputtering of oxygen atoms at the surface [2,3].

The surface structure of the SnO₂(110)-(1x4) has been studied by several methods [4-7], and a model consisting of an in-plane oxygen vacancy structure [4,5] has been proposed, which was confirmed by Low Energy Electron Diffraction (LEED) [6] and Density Functional Theory (DFT) [7], the latter with slightly different relaxations compared to the former. Later, observations of 1Å deep antiphase domain boundaries by Scanning Tunneling Microscopy (STM) in the (4x1) structure could not be explained by the existing vacancy model. Instead, an overlayer was suggested, and a model based on Sn-O broken "chains" was proposed [8].

We have studied the SnO₂(110)-(4x1) reconstruction by a combination of Surface X-Ray Diffraction (SXRD), X-Ray Absorption Spectroscopy (XAS), DFT, and quantitative LEED. The SXRD measurements implies a single quasi-hexagonal Sn overlayer on the SnO₂(110) surface, and the models in ref [4-8] did not show a satisfying agreement with the experimental data. While the oxygen atoms are more difficult to observe in SXRD, XAS directly indicate the presence of 2+ Sn atoms in the structure, suggesting an oxygen depleted Sn_xO_y overlayer. Using an evolutionary algorithm (EA) [9, 10] implemented in the Atomic Simulation Environment (ASE) [11] software, global minimum structures were found for different Sn_xO_y compositions, and their stability at 1100K was investigated. A Sn₆O₆ overlayer was found to be more stable than the bulk termination and all other calculated structures. The theoretical structures were tested with the SXRD data, and the best theoretical model showed a good agreement. The model was also used to simulate existing STM images [8], displaying excellent agreement between data and theory.

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Initial stages of mixed nickel-iron oxides growth on Ru(0001)

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Transition metal oxides (TMO) are promising candidate materials for future spintronic devices. Their properties arise from the interactions between transition metal and oxygen ions in a given structure which are very sensitive to different bond length and angles, as well as to their particular cationic distribution. Among them, the spinel family comprises a large number of compounds. Spinels have an fcc anion lattice with cations occupying tetrahedral and octahedral sites. Spinels can be half-metallic (like $Fe_3O_4[1]$), ferrimagnetic insulators, superconductors (LiTi₂O₄[2]) or heavy fermion materials. However, their properties in thin film growth, as necessary for devices, are often disappointing, dictated by the defect density.

Here we demonstrate a method for preparing high quality ultrathin TMO films on a metallic substrate. Mixed nickel-iron oxides have been grown on Ru(0001) by oxygen-assisted molecular beam epitaxy at elevated temperatures (800 - 900K). The nucleation and growth process are observed in situ by means of Low Energy Electron Microscopy (LEEM). A comprehensive characterization is performed combining LEEM for structural characterization and PEEM (PhotoEmission Electron Microscopy) with synchrotron radiation for chemical and magnetic analysis via X-ray Absorption Spectroscopy and X-ray Magnetic Circular Dichroism (XAS-PEEM and XMCD-PEEM, respectively). The latter permits imaging the element specific magnetic domain structure.

We will show that the growth by oxygen-assisted molecular beam epitaxy takes place in two stages. First, monoxide islands nucleate and grow until they completely cover the substrate surface. Later threedimensional islands of spinel phase grow on top of the monoxide layer. Only the spinel islands show magnetic contrast, with the same domains being observed in the Fe and Ni XMCD images.

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POSTER

Electronic Structure Characterization of atomically-precise Chiral Graphene Nanoribbons on gold surfaces

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Graphene nanoribbons (GNRs) are narrow stripes of graphene that have attracted great attention because of their interest for both fundamental physics and promising applications. While sharing many of the appealing properties of their predecessor material graphene, such as high mobility charge-carriers and high specific surface area, they overcome some of its limitations as is the lack of a band gap. These nanostructures can display different edge orientations with respect to graphene's lattice vectors that largely determine their main properties. Therefore three types of ribbons can be synthesized: armchair, zigzag or chiral GNRs, the latter ones presenting a periodic combination of both armchair- and zigzag-like segments. A recently established bottom-up synthesis method based on the use of molecular precursors as building blocks allows for the synthesis of these three types of GNRs with atomic precision [1]. However, the limited experimental results on these structures are mostly focused on the electronic structure of armchair and, to a lesser extent, on zigzag GNRs, thus letting chiral GNRs (cGNRs) hardly explored. The growth of these ribbons on different noble metals was recently reported [2], hence we focus on the electronic structure of these nanomaterials.

Here, using the same molecular precursor-based methodology, we report on the electronic structure of (3,1)cGNRs on Au(111) by Scanning Tunneling Spectroscopy (STS). Moreover, the use of Au(322) vicinal substrate as template promotes the aligned growth of these ribbons along the terrace length thus enabling us to characterize the valence band by means of ARPES. Our results reveal a semiconducting bandgap on these chiral nanoribbons therefore confirming its potential applications for nanoelectronics.



Figure 1: (a) Synthetic scheme and topographic images of (3,1)-cGNR on (b) Au (111) and (c) Au(322) surfaces.

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Surface spectroscopy and spin filtering of DPEDA chiral molecular film

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Chiral structures, and in particular chiral molecules, are fascinating objects in many areas: in Physics the relationship between chirality and magnetism has puzzled researchers since the 19th century, and only in the 21th century we have learn to make use of this relationship, for example using the ability of chiral layers to scatter electrons differently depending on their spin [1]. From this technological point of view, chiral surfaces open the door to use in 2D devices different properties like chiral selectivity, enantiospecific chemical reactions [2] or the possibility to use these materials as, for instance, spin filters [3].

Thin films of pure enantiomeric diphenil ethane diamine (DPEDA) and diphenyl ethane diol (DPED) have been grown in UHV on Cu(001) and on Co/Cu(100) surface. We have used surface sensitive spectrocopies based on synchrotron techniques (XAS, XPS, spin polarized UPS, XPEEM) to study the influence of the chirality on the magnetism, demonstrating with X-ray circular natural dichroism (XNCD) measured at the C K-edge the preservation of the chiral character of these molecular thin films in the electronic structure. The effect of this chiral molecular film adsorbed on ferromagnetic cobalt has been measured though XMCD at the Co L-edges, showing a change in the magnetic moment in the cobalt atoms at the surface, with the implication of a charge transfer with spin polarization.

More indeed, in electron currents photoemitted from molecular films of DPED and DPEDA adsorbed on Co/Cu(100) surfaces we have observed macroscopic spin polarizations, showing that chiral molecules in a non-spiral geometry can filter spin electrons. These measurements also show that the different enantiomers of the same molecule can produce spin polarizations oriented along different directions in space [4].

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Decoding crystallographic domains of molecular systems by cantilever torsion imaging

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From the physical point of view, the tribological response, in particular frictional properties, of organic surfaces is an obvious subject of interest by itself. As a powerful tool to understand different dissipation mechanisms at surfaces, we commonly employ the scanning force microscope by measuring the lateral force perpendicular to the scan direction (also known as friction force microscopy, FFM). As for inorganic materials, FFM helps visualizing regions of different chemical nature. However, more subtle surface characteristics influence the frictional properties of molecular systems and well-designed and sensitive FFM measurements permit obtaining detailed structural details as molecular order (stick-slip) as well as molecular tilt angles and/or tilt angle azimuths. This is the case of observing friction anisotropy or friction asymmetry. The term anisotropy refers to the variation of friction with the relative orientation angle between sliding surfaces and is commonly correlated with surface crystallographic orientations, while asymmetry refers to a change in friction when the sliding direction is changed by 180°. FFM has been successfully employed in organic self-assembled monolayers (SAMs) not only to discriminate between ordered configurations presenting different friction coefficients or different packing, but also to decipher between equivalent structural domains as well as to identify highly dissipative transient molecular configurations during phase transitions. Outstandingly, crystallographic aspects including "stick-slip" can also be extracted from the torsion of the cantilever during scanning along its axis in the so-called transverse shear microscopy (TSM).



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Structure and electronic states of vicinal noble metal surfaces with densely kinked steps

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The thermal excitation of step-edge atoms into "kinks" ($e^{-\epsilon kT}$) is the essence of the step dynamics on a crystal surface. At a vicinal surface with high step densities, kinks also influence the equilibrium shape at finite temperature. At T=0, the density of kinks strongly depends on the in-plane orientation of the surface. At fcc - (111) vicinal planes close-packed step-edges (A-type and B-type) run parallel to equivalent [1-10] directions. As shown in Fig. 1a, steps oriented along the [11-2] direction exhibit a "100% kinked" step-edge (K-type), where out-protruding step-edge atoms have no direct nearest-neighbors parallel to the step. Remarkably, as sketched in the same Fig. 1a, in such K-steps thermal excitations have zero energy cost ϵ =0, allowing meandering and roughening of steps without energy penalty. Our objective is to investigate, theoretically and experimentally, the impact of this property in step dynamics, equilibrium shape, growth, and electronic states of K-stepped surfaces.

First experiments have been performed using a Ag single crystal curved around the (654) direction, which allows one to probe with STM and Angle Resolved Photoemission (ARPES) all K-type vicinal surfaces from the (111) plane up to α =18°. In Fig. 1b we show characteristic STM images and terrace-width distribution histograms for α =2.26° and α =12.03°. A remarkably neat transformation is observed from low to high step-densities, suggesting a dramatic transition in step interactions, from purely entropic, at low step-densities, to strongly elastic, at high step-densities. In Fig. 1c we show the energy shift Δ E of the Shockley band measured with Angle Resolved Photoemission across the curved sample. Large Δ E values are found compared to close-packed steps, indicating strong repulsive scattering due to a larger electric dipole at K-type steps. The connection of these STM and ARPES results with the particular step energetics and dynamics of K-type vicinal surfaces will be discussed.



Figure 1: (a) Schematic description of atomic K-steps and the thermal excitation of step-edge atoms, with zero energy cost. (b) STM images (top) and terrace width distribution analysis (bottom) of two K-stepped surfaces. Experiments are performed on a curved Ag(654) crystal. (c) Surface state shift as a function of the step density, measured by ARPES on the Ag(654) curved crystal.

POSTER

Non-Covalent Dimerization after Enediyne Cyclization on Au(111)

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We investigate the thermally-induced cyclization of 1,2-bis(2-phenylethynyl)benzene on Au(111) using scanning tunneling microscopy and computer simulations. Cyclization of sterically hindered enediynes is known to proceed via two competing mechanisms in solution: a classic $C^{1}-C^{6}$ or a $C^{1}-C^{5}$ cyclization pathway [1]. On Au(111) we find that the $C^{1}-C^{5}$ cyclization is suppressed and that the $C^{1}-C^{6}$ cyclization yields a highly strained bicyclic olefin whose surface chemistry was hitherto unknown. The $C^{1}-C^{6}$ product self-assembles into discrete non-covalently bound dimers on the surface (Fig. 1). The reaction mechanism and driving forces behind non-covalent association are discussed in light of density functional theory calculations [2].



Figure 1: Scanning tunneling microscopy image of the dimer of cyclized products (inset) and the associated calculations on Bader charge distribution, evidencing the strongly polarized bonds responsible for the attractive dipole-dipole interaction.

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Hierarchical chirality transfer during (S,S) and (R,R) DPEDA growth on Cu(100)

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Obtaining spatially uniform chiral thin films with atomic-scale control of their handedness is a powerful way for developing nano-devices with novel chiral properties. In this sense, it is known that chirality on solid surfaces may exist at different levels of molecular assembly, from individual adsorbed species to 1D molecular chains or 2D molecular clusters and supramolecular patterns [1-4]. A chiral molecule is necessarily chiral upon adsorption and generally assembles in homochiral ordered 2D structures originated from the asymmetry of the molecule. Therefore, deposition of the opposite enantiomer will generate the mirror image systems.

In order to explore the origin of chiral transfer and amplification involved in the 3D assembling process, we investigate the self-assembly of two enantiomers of the Diphenylethylenediamine (DPEDA) molecule deposited from the vapor phase on Cu(100) under ultra-high-vacuum (UHV) and room temperature conditions. DPEDA possesses two chiral centres located at the two carbon atoms of the ethylene chain and presents two chiral enantiomers which are designated according to their conformation and optical activity as (R,R)-(+) and (S,S)-(-). The structure at the molecular level has been determined for different surface coverages by in-situ STM/FM-AFM. We show that the chirality of the DPEDA enantiomers is transferred at different levels of the molecular organization. Below the monolayer completion, each enantiomer arranges in two-dimensional (2D) domains of a supramolecular square lattice aligned with the principal crystallographic directions of the substrate (A-SQ). The intrinsic chirality of the molecule is only manifested within the unit cell (lack of mirrorsymmetry). For increasing coverage, this A-SQ structure coexists with 2D domains of a square lattice (SQ) rotated \approx +11° or \approx -11° (for R,R or S,S, respectively) with respect to the principal direction of the Cu(100) substrate, as corresponds to enantiomeric mirror-like organization (Figure 1a). The 3D growth only occurs on top of the A-SQ structure and exhibits a clear chiral organization with an oblique unit cell. Interestingly, the chiral supramolecular order is unambiguously reflected in the chiral helicity observed for each enantiomer (Figure 1b and 1c).



Figure 1: (a) STM image ($30nm \times 29nm$) of (S,S)-DPEDA deposited on Cu(100) at room temperature. V = + 2V, I = 200pA. A second layer (2L) grows on top of a first layer in which domains of two square lattice structures (A-SQ and SQ) are seen. (b) and (c) magnification of the 2L structure ($7nm \times 7nm$) for (S,S)-DPEDA and (R,R)-DPEDA.

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Structure of the SnO₂ (110)-(4×1) with LEED I(E)

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Tin dioxide (SnO₂) is widely used as the active component of solid state gas sensors [1], and also has application in heterogeneous catalysis [2]. The basis for these applications is the reducibility of the oxide. The changes in conductivity of this n-type semiconductor resulting from surface processes are the basis for the material's gas-sensing characteristics. Because of this, it has long been a goal of fundamental research to characterize the structural, physical and chemical properties of SnO₂ surfaces.

This work presents a quantitative low energy electron diffraction (LEED) analysis for the (4×1) reconstruction of SnO_2 surface. A set of I(E) data for 15 inequivalent beams were collected with cumulative energy range of 1800 eV. The theoretical LEED intensities were fitted by using SATLEED program package [3]. The atomic coordinates for the Sn_6O_6 structure from a DFT calculation, scaled to the experimental lattice parameter of SnO_2 , were used as initial coordinates. The best fit structure, which differs from the DFT result by only a small (<0.1 Å) inward relaxation of the 6 Sn atoms, gives a Pendry reliability factor (R_P) [4] of 0.16, indicating that the model describes the experimental data well.



Figure 1: LEED I(V) measurements for $SnO_2(110)$ -(4×1). The cumulative R_P was 0.16.

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Interplay between metal-organic interface state and donoracceptor interface mediated charge separation on PTCDA/TiOPc/Ag(111)

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The electronic properties of organic semiconductors interfaces on adequate substrates are of major importance for devices based on molecular electronics for example in the field of organic photovoltaic cells or Organic Light Emitting Diodes (OLEDs). One of the important points to consider is the electron dynamics of the systems, especially on donor-acceptor architectures. In order to address the problem properly we use a model system formed by 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) and titanyl phthalocyanine (TiOPc) on Ag(111). This molecular layer system reveals well-ordered layers of each species and a sharp interface due to the strong dipolar behavior of the TiOPc molecules preferentially forming bilayers [1].

Charge separation of excitons in that model system PTCDA/TiOPc on Ag(111) was investigated by means of time-resolved two-photon photoemission (2PPE). An optical parametric oscillator provided pump pulses with photon energies ranging from 1.6 to 2.5 eV. This allowed for selective excitation of TiOPc or PTCDA. Between TiOPc and Ag(111) a Shockley derived interface state (IS) approximately 0.3 eV above the Fermi energy forms. We observe a strong coupling of the first molecular layers to the IS and determine transfer times into the IS ranging from approximately 20 fs out of the second to 160 fs out of the third and fourth molecular layers. Systematic thickness-dependent measurements quantify the distance dependence of this coupling. Whereas the IS dominates the dynamics in the second layer, the PTCDA/TiOPc acceptor-donor interface (D/A) competes for electrons from excitons in the third to fourth layer. In the fifth to sixth layer no significant IS assisted separation on a timescale below 12 ns can be detected any longer. Our results highlight the competition between IS and D/A mediated charge separation of excitons in few-layer organic systems on metal substrates.



Figure 1: Schematic description of the model system studied and description of the two-photon photoemission process to investigate the electron dynamics at the molecular interface.

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Click reaction on the chiral PdGa{111} surfaces

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Owing to the non-centrosymmetric nature of the P2₁3 space group PdGa exists in two enantiomeric crystal forms A and B and all surfaces of this intermetallic compound (IMC) are chiral. This fact, together with the possibility to prepare atomically flat, well-ordered surfaces in ultra-high vacuum (UHV) enables the investigation of asymmetric chemical surface reactions in this system.

The stacking sequence of PdGa in the [111]-direction exhibits four non-equivalent atomic planes, therefore the (111) and (-1-1-1) surface terminations of the same crystal form are found to be structurally different. Specifically, one is terminated by a single, isolated Pd atom, accordingly denoted as Pd₁, while the other reveals isolated Pd trimers as the top-most layer, referred to as Pd₃ [1]. The chiral selectivity of Pd₁ and Pd₃ can be probed by adsorption of the prochiral 9-Ethynylphenanthrene (9-EP) molecule. On Pd₁ a huge enantiomeric excess of 94-98% is found at room temperature (fig. 1b) [2], while for the same conditions a racemic mixture is observed on Pd3. Post-annealing to 490 K results in the dimerization of the 9-EP on Pd₁, whereas on Pd₃ 9-EP propellers with a homochirality of 99% are formed (fig. 1c).

These results pave the way towards highly enantioselective, covalent coupling reactions. In view of the d-band model proposed by Nørskov et al [3], which links the catalytic activity to the position of the d-band center of the surface projected density of states (pDOS), a copper catalyzed Azide-Alkine Huisgen Cycloaddition was chosen as model reaction. Due to the copper-like d-band structure of Pd₁ and Pd₃ [1] this particular reaction of the click chemistry is expected to perform on PdGa{111} under UHV conditions as it was demonstrated with similar molecules on Cu(111) [4].

UHV conditions as it was demonstrated with similar molecules on Cu(111) [4]. Indeed, co-adsorption of 9-EP and 3-(4-Azidophenyl)propionic acid (APA) followed by post- annealing to 440 K lead to covalently coupled reaction products, whereas no reaction is observed on Pd₃. The catalyzed reaction is regiostereoselective on Pd₁ as it is on Cu(111), but on Pd₁ one out of four enantiomeric forms of the reaction products is favored over the others.

On the other hand, on Pd₃, the d-band model fails due to the big impact of the ensemble effect [5] on the reactivity for this particular reaction.



Figure 1: a) racemic mixture of 9-EP. b) enantioselective adsorption on Pd₁. c) homochiral 9-EP propeller formation on Pd₃.

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Surface Structures of Niobium Oxide 2D Nanostructures and Ultrathin Films

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Niobium oxides have been proposed in a wide variety of applications as catalysts, materials in microelectronics and as gas sensors. When metal oxides are grown as ultrathin films, consisting of only a few atomic layers in thickness, the interaction between the film and the substrate exerts a strong influence on the film structure. This can result in novel properties, such as enhanced catalytic reactivity. Modelling the structure of niobium oxide based catalysts also provides insight into catalytic mechanisms on the atomic level.

Niobium oxide nanostructures and ultrathin films were grown on reconstructed Au(111) surfaces. Following Nb deposition onto room temperature Au substrates, the samples were oxidised at 600 °C in 10^{-6} Pa oxygen to create epitaxial NbO_x The phases obtained for the NbO_x film included the honeycomb structure, triangular islands (Figure 1a), nanoclusters (Figure 1b) and a Moiré pattern, as observed by scanning tunneling microscopy (STM). Atomic movements have been observed in the triangular islands and nanoclusters. By using an image processing software package, Smart Align [1], distortions and errors in the STM images were corrected. The STM images are strongly enhanced by the software as the information of many frames can be condensed into one image.



Figure 1: a) STM images of NbO_x triangular islands of different sizes in the range m= 3-9 (V_s = 0.06-1.00 V, I_t = 0.24-0.26 nA). m denotes the atomic number in the inner sides of the islands. b) STM images of NbO_x atomic clusters of different sizes. n denotes the atomic numbers in each cluster (V_s = 0.29-1.00 V, I_t = 0.18-0.24 nA).

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C₆₀ adsorption on a two-dimensional oxide quasicrystal

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The recent observation of a two-dimensional oxide quasicrystal (OQC) at the interface to Pt(111) demonstrates that quasicrystalline structures can emerge in the heteroepitaxial growth of conventional periodic materials [1]. Under reducing conditions, a long-range ordered dodecagonal wetting layer is derived from ultrathin films of $BaTiO_3$ at the threefold Pt(111) substrate. Atomically-resolved scanning tunneling microscopy (STM) images reveal the formation of a Niizeki-Gähler tiling as shown in Fig. 1a [2,3]. The contrast in the STM image is given by the sublattice of the Ti atoms. The atoms exhibit an arrangement of squares, triangles, and 30°C rhombs with a common edge length of 6.85 Å.

Due to the complexity of quasicrystalline materials, studies on the relation between aperiodic order and physical properties are challenging. Therefore, quasicrystal surfaces have been tested as templates for the growth of two-dimensional single element quasicrystals formed by molecular adsorbates. Recently, C₆₀ and Pentacene were reported to exhibit quasicrystalline networks on icosahedral Al-Cu-Fe and Ag-In-Yb [4]. Here we report the first adsorption studies on the BaTiO3-derived OQC using C₆₀ molecules. Their van-der-Waals diameter of 10 Å matches roughly the distance between two neighboring squares (9.35 Å, shown in Fig. 1b). Different coverages of C₆₀ have been deposited on the OQC at room temperature and characterized by low-electron energy diffraction (LEED), x-ray photoemission spectroscopy (XPS), and STM. C₆₀ molecules form hexagonal islands at the OQC surface or absorb at step edges, which indicates a weak interaction with the OQC substrate. With increasing coverages, second layer islands are formed well before the monolayer is completed. At temperatures of 510 K C₆₀ thermal desorption sets in.



Figure 1: (a) STM image of BaTiO₃-derived OQC at 77 K, 14x14 nm², 30 pA, -0.15 V; (b) dodecagonal structure consist of squares, triangles, and rhombs with an edge length of 6.85 Å.

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